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METAL-METAL BONDING IN DIRHODIUM TETRACARBOXYLATES
TRANS INFLUENCE AND DEPENDENCE OF THE RHODIUM-RHODIUM
BOND DISTANCE UPON THE NATURE OF AXIAL LIGANDS

The Ohio State University

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TRANS INFLUENCE AND DEPENDENCE OF THE RHODIUM-RHODIUM
BOND DISTANCE UPON THE NATURE OF AXIAL LIGANDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Yun Bai Koh, B.S., M.S.

* * * * *

The Ohio State University

1979

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J. Am. Chem. Soc., 101, 1422-1434(1979)
2. "Metal-Metal Bonding in Dirhodium Tetracarboxylates. Structure of the Bis(pyridine) Adduct of Tetra- μ -acetato-dirhodium(II)"
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Inorg. Chem., 17, 2590-2596(1978)
3. "Metal-Metal Bonding in Dirhodium Tetracarboxylates. Structure of the Bis(diethylamine) Adduct of Tetra- μ -acetato-dirhodium(II) and Systematics of the Bonding in Tetracarboxylate-Bridged Metal Dimers"
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I. INTRODUCTION

In recent years, binuclear inorganic complexes have been the subject of much lively interest to experimental and theoretical chemists. One of the problems that arose with the advent of a vast variety of metal dimers has been those of understanding the nature of metal-metal interactions and determining the descriptions of bond multiplicities. For complexes without bridging ligands, the description of the metal-metal bonding interaction is relatively straightforward and relies heavily on the metal-metal separations, which are taken, by and large, as a direct indicator of metal-metal bond strength. On the other hand, complexes with bridging ligands have presented serious difficulties in the assessment of the bonding implications between the metal centers due to the effect of stereochemical and electronic perturbations of the bridging ligands on the overall geometry, such as the size and geometrical preference of the bridging ligand, the extent of mixing of ligand orbitals with orbitals of the metal, and the overlap density of primarily metal-centered orbitals.¹ Thus no simple correlation in such complexes can be drawn between the degree of the interactions and the metal-metal distances.

The most thoroughly studied systems in this regard may be the weakly bonded metal dimers containing M_2X_2 -bridged cores(I), the simplest form of metal-metal cluster complexes, where X is a bridging

(I)

ligand such as NO, CO, H, PR₂, OR, SR, NR₂, or halide. The pioneering work of Dahl and coworkers²⁻⁵ have shown the complexity of the problem from the structural point of view and pointed out that there are cases where a short metal-metal distance may not in fact be evidence of a direct metal-metal interaction.³ They noted that the metal-metal distance in a M₂X₂ system is governed by the size and effective electronegativity of the bridging ligand atom and that the influence of a metal-metal interaction on molecular geometry can be detected from the extent of angular deformation of the bridged complex as revealed from sharper M-X-M angles in compounds containing stronger metal-metal interactions.⁵ Much of the theoretical work⁶⁻¹⁰ also has been directed toward the analyses of the factors influencing the geometry and electronic structures of the dimers within the framework of structural and spectroscopic data available, although the extrapolation to experimental results is yet far from being satisfactory. For instance, the theoretical consideration of systematic variation of bridging ligands (X=NH₂, NMe₂, S, SMe₂, and PH₂ for M=Fe(I))⁶ and the dependence of the metal-metal distances on the electron counts in a series of closely related and similar dimers (M=Fe(I), Co(I), and Ni(I) for X=NO or CO)⁹ were found to be contradictory with structural facts. However, the study of the effect of stepwise oxidation or

reduction has been shown to be a more dependable means of probing the bonding interactions in relation to the MO descriptions, particularly when highly antibonding orbitals are involved.^{7,11}

The carboxylate anion RCOO^- as a bridging ligand is much the same insofar as these uncertainties remain unresolved in the carboxylate bridged dimers(II) of various transition metals. The bond multiplicities

(II)

of most of the dimers have been routinely assigned based largely on the metal-metal distances, on the grounds that the tetracarboxylate encapsulation is sufficiently flexible that the metal atoms are free to move within the framework, and consequently a wide range of metal-metal distances can be accommodated.³⁸ Table 1 lists metal-metal distances in some tetracarboxylate metal dimers (in cases where tetracarboxylate bridged dimers are not known presently distances in similar structures are given) and the bond orders as assigned. Corresponding distances in nonbridged dimers are also presented for comparison. It appears that the formal bond order reaches a maximum for the d^4-d^4 complexes and

Table 1. Metal-Metal Distances in Metal Dimers

$d^n - d^n$	M	$d(M-M), \text{\AA}$ Bridged ^a	Bond Order	$d(M-M), \text{\AA}$ Non-bridged ^a	Bond Order	Single Bond Distance*
$d^2 - d^2$	Mo(IV)			2.52 ^b	2	2.78
	W(IV)	2.75-2.77 ^z	1			2.80
$d^3 - d^3$	Mo(III)	2.24 ^c	3	2.17-2.24	3	2.78
	W(III)	2.27-2.28	3	2.25-2.30	3	2.80
	V(II)	2.20 ^d	3			
$d^{3.5} - d^{3.5}$	Mo(2.5)	2.17 ^{c'}	3.5			2.78
$d^4 - d^4$	Cr(II)	2.28-2.54	4	1.85-2.21	4	2.52
	Mo(II)	2.09-2.13	4	2.13-2.15	4	2.78
	W(II)			2.26 ^e	4	2.80
	Re(III)	2.24-2.25	4	2.22-2.24	4	2.78
	Tc(III)	2.19	4			2.76
$d^{4.5} - d^{4.5}$	Tc(2.5)			2.12 ^{f, b'}	3.5	2.76
$d^5 - d^5$	Cr(I)			2.28 ^{g'}	3	2.52
	Mo(I)			2.45 ^g	3	2.78
	Re(II)			2.23 ^{a'}	3	2.78
	Fe(III)	2.61 ^{d'}	1			2.48
$d^{5.5} - d^{5.5}$	Ru(2.5)	2.28 ^h				2.74
$d^{6.5} - d^{6.5}$	Rh(2.5)	2.32 ^t	?			2.72
$d^7 - d^7$	Co(II)	2.83 ⁱ	1	2.74 ^j , 2.79 ^k	1	2.46
	Rh(II)	2.39-2.46 ^l 2.55 ^m	? ?	2.79 ⁿ , 2.94 ^o	1	2.72
	Pt(III)	2.56 ^p				2.72

Table 1. (Continued)

d^8-d^8	Ni(II)	2.49 ^q , 2.56 ^r	1		2.44
	Rh(I)			3.19 ^s	1 2.72
	Pd(II)	2.72 ^x	1	2.79 ^y	1 2.70
	Pt(II)	2.50 ^u		2.75 ^y	1 2.72
d^9-d^9	Ni(I)			2.32 ^w	2.44
	Cu(II)	2.58-2.89 ^v			
	Pd(I)			2.53 ^{e'}	2.70
	Pt(I)			2.58 ^{f'}	2.72

a. Values for d^3-d^3 and d^4-d^4 species are taken from ref. 12, unless otherwise specified.

b. $\text{Mo}_2(\text{OPr}^i)_8$; ref 13, c. Partially bridged $\text{Mo}_2(\text{O}_2\text{COBu-t})_2(\text{OBu-t})_4$; ref 15,

d. $\text{V}_2(2,6\text{-dimethoxyphenyl})_4\cdot\text{THF}$; ref 18, e. $\text{W}_2(\text{CH}_3)_{8-x}\text{Cl}_x^{+4}$; ref 12 and 14

f. $\text{Te}_2\text{Cl}_8^{-3}$; ref 16, g. $\text{Mo}_2(\text{CO})_4\text{Cp}_2$; ref 17, h. $\text{Ru}_2(\text{O}_2\text{CC}_3\text{H}_7)_4\text{Cl}$; ref 28,

i. $\text{Co}_2(\text{O}_2\text{CPh})_4(\text{quin})_2$; ref 24, j. $\text{Co}_2(\text{CNCH}_3)_{10}^{+4}$; ref 22, k. $\text{Co}_2(\text{CN})_{10}^{-6}$; ref 23,

l. Present work, m. $\text{Rh}_2(\text{SOCCH}_3)_4(\text{CH}_3\text{CSOH})_2$; ref 27,

n. $\text{Rh}_2(\text{CNC}_6\text{H}_4\text{Me})_8\text{I}_2^{+2}$; ref 20, o. $\text{Rh}_2(\text{DMG})_4(\text{PPh}_3)_2$; ref 26,

p. $\text{Pt}_2(\text{O}_2\text{CCF}_3)_2(\text{CH}_3)_4(\text{Mepy})_2$; ref 29, q. $\text{Ni}_2(\text{SOCPh})_4(\text{EtOH})_2$; ref. 19,

r. $\text{Ni}_2(\text{S}_2\text{CCH}_2\text{Ph})_4$; ref 21, s. $\text{Rh}_2(\text{CNPh})_8^{+2}$; ref 25, t. $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^{+}$;

ref 31, u. Average of four Pt-Pt bond distances in $\text{Pt}_4(\text{OAc})_8$; ref 30

v. See Table 57 on Pl81, w. $\text{Ni}_2(\text{CN})_6^{-4}$; ref 32, x. $\text{Pd}_2(\text{S}_2\text{CCH}_2\text{Ph})_4$; ref 33,

y. $\text{Pd}_2(\text{S}_2\text{C}_2\text{H}_2)_2$ and $\text{Pt}_2(\text{S}_2\text{C}_2\text{H}_2)_2$; ref 34, z. Trinuclear W(IV) cluster

$\text{W}_2\text{O}_2(\text{O}_2\text{CR})_6^{+2}$; ref 35, a'. $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$; ref 36, b'. Ref 41, c'. $\text{Mo}_2(\text{SO}_4)_4^{-3}$;

ref 46, d'. $\text{Fe}_2(\text{S}_2\text{CSR})_4(\text{SR})_2$; ref 47, e'. $\text{Pd}_2(\text{CNMe})_6^{+2}$; ref 48,

f'. $\text{Pt}_2\text{Cl}_4(\text{CO})_2^{-2}$; ref 49, g'. $\text{Cr}_2(\text{CO})_4\text{Cp}_2$; ref 54

* Single bond radii are taken from ref 37.

Fig. 1. MO diagrams of carboxylate bridged metal dimers.

- a) Crystal field formulation of M-M quadruple bond.
- b) MO diagram of the Rh(II) dimers proposed by Cotton.
- c) X α -SW energy levels for Rh(II) dimers.
- d) Extended Hückel energy levels for Rh(II) dimers.

decreases gradually as the electrons are added to or removed from a closed-shell, metal d-orbital derived configuration $(\sigma)^2(\pi)^4(\delta)^2$ (Fig. 1a). It is only for the triply and quadruply bonded dimers that the initial assignments of bond orders have received strong support from the existence of nonbridged dimers of comparable bond strengths and from subsequent theoretical studies,³⁹⁻⁴² with an exception of the Cr(II) dimers, for which an opposing view still persists.⁴³⁻⁴⁵ Such bonding arguments are not applicable to the weakly bonded dimers, in which the metal-metal distances are more ligand dependent than the complexes involving strong metal-metal bonds. This can be seen in the existence of numerous bridged and nonbridged species with no formal bonds.

In the case of the Rh(II) tetraacetate dimer, the controversy has been centered around whether the Rh-Rh bond is triple or single. The formulation of the triple bond has rested primarily upon the Rh-Rh bond length in $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$, now accurately known as 2.3855 Å.^{50a} The drastic shortening of more than 0.3 Å from what is believed to be the distance for a strictly single Rh-Rh bond, 2.7-2.8 Å, led Cotton and his collaborators⁵⁰ to propose a multiple interaction based on a MO energy level scheme for M_2X_8 species of D_{4h} symmetry (Fig. 1b). The nonbonding orbitals σ_n and σ'_n , and the antibonding δ orbital which were empty in the d^4 - d^4 dimers are now filled, giving an overall electronic configuration $(\sigma)^2(\pi)^4(\delta)^2(\sigma_n)^2(\sigma'_n)^2(\delta^*)^2$. A single bond formulation⁵¹ emerged at the same time from the analysis of the axial ligand dependence of the electronic spectra, providing extended Hückel MO levels; $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4$ (Fig. 1d). This formulation permitted a consistent

interpretation of the UV-Vis spectra of these complexes. In particular, the blue shift of the band in the visible region upon replacing water with a stronger axial ligand was attributed to the destabilization of the antibonding σ orbital utilized in the $\pi^*-\sigma^*$ transition. The single bond picture was further buttressed by recent SCF- $X\alpha$ -SW calculations reported by Norman and Kolari⁵² on dirhodium tetraformate and its water adduct. The $X\alpha$ -SW energy levels that are mainly of metal origin are essentially identical to the extended Hückel scheme or that in Fig. 1a. Therefore, successive addition of six electrons to the next three orbitals in the d^4-d^4 energy levels would yield a bond order of one. Norman and Kolari also argued that the shortening of the Rh-Rh bond in the carboxylate dimer reflects nothing but the full constraint of the carboxylate cage. An ESR study of a 1:1 adduct of dirhodium tetra(trifluoroacetate) with a spin label also recommended a single bond formulation.⁵³

In view of this, it seemed necessary to examine the structural consequences of varying the axial ligands in the dirhodium system. Fortunately, the dirhodium tetraacetate nucleus is stable and yet reactive towards axial substitution by neutral and anionic ligands of various donor or acceptor properties that desired adducts are synthetically easily accessible without altering the tetraacetate nucleus. The symmetry of the molecule further enables us to observe a doubled trans influence effect on the Rh-Rh bond and the acetates offer minimal steric hindrance to the axial ligand coordination. Complications that may arise from effects other than trans influence can thus be avoided in interpreting data.

The axial ligands studied for this purpose are pyridine, NHEt_2 , CO, PF_3 , P(OPh)_3 , and P(OMe)_3 , which span nearly the full range from very weak to strong σ donor strength and from ligands of no or weak π acceptor strength to extremely powerful π acceptors. A simple qualitative trans influence theory predicts that a Rh-Rh multiple bond will respond differently to these ligands than a single bond. If the Rh-Rh bond is single, then it is likely that a stronger σ donor ligand will weaken it more, with small contributions from the $d_{\pi}\text{-L}\pi$ interactions, while a strong π acceptor will have prominent influence on the Rh-Rh bond only if the latter involves substantial π character. The qualitative aspects of the trans influence theory will be discussed below in some detail in connection with the results of this investigation.

Included along with the data for the above ligand adducts are those for the asymmetrically functionalized $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$, which was initially thought to be a symmetric 1:2 adduct of NO ligand. The true constitution of the molecule was discovered only after the structure refinement was near completion. In addition to the structural investigations, ^{31}P nmr data for some representative phosphorus ligands, e.g., PCy_3 , PPh_3 , P(OPh)_3 , P(OMe)_3 , PCl_3 , and PF_3 , and ^{13}C nmr spectra for the enriched ^{13}CO adduct are included and the implications of the coupling constants and chemical shifts discussed.

II. CRYSTAL DATA

A. Preparation of Crystals

$\text{Rh}_2(\text{OAc})_4(\text{CH}_3\text{OH})_2$ was prepared by a known procedure⁵⁵ from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ purchased from Alfa Inorganics. The starting material, $\text{Rh}_2(\text{OAc})_4$, was prepared immediately before use by driving methanol off the methanol adduct in boiling benzene or by drying the methanol adduct in the oven at 100°C until infrared spectra showed no presence of the axial ligand. All solvents and reagents were used as received without further purification, unless otherwise noted.

1) $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

The crystals of the pyridine adduct were prepared by allowing the pyridine vapor from a 4:1 mixture of methanol and pyridine to slowly diffuse into a saturated methanol solution of $\text{Rh}_2(\text{OAc})_4$. Most of the red crystals which formed in a week's time were monoclinic needles. Diamond-shaped and plate-like crystals were also obtained in a small quantity. The adduct was stable at room temperature and insoluble in hydrocarbon solvents, except for dichloromethane, benzene, and toluene in which it was slightly soluble. A slow ligand exchange reaction was observed upon heating in oxygen bases;

where L is MeOH, acetone, or THF. All manipulations were carried out at room temperature in an open atmosphere.

2) $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

The adduct crystals were obtained by slow evaporation at room temperature of the solvent after dissolving a small amount of $\text{Rh}_2(\text{OAc})_4$ in neat NHEt_2 . The adduct forms stable, dark red needles soluble in most hydrocarbon solvents but reverts to green powder, presumably the axial ligand-free $\text{Rh}_2(\text{OAc})_4$, on evaporation of cyclohexane, benzene, or toluene solutions.

3) $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

CO was bubbled through a mixture of CH_2Cl_2 and $\text{Rh}_2(\text{OAc})_4$ (approximately 20 mg of $\text{Rh}_2(\text{OAc})_4$ in 20 ml of CH_2Cl_2) at -20°C under an elevated pressure (ca. 1.5 atm). In a few minutes, the solution turned orange-red as the reaction proceeded. Evaporation of the excess solvent to dryness over a period of a week yielded red crystals resembling hexagonal plates or truncated diamonds. The adduct is extremely unstable and reverts to $\text{Rh}_2(\text{OAc})_4$ with the loss of CO upon standing. Use of benzene, CCl_4 , or CHCl_3 as the solvents resulted in yellow powder under the similar condition. A water-ethyleneglycol bath cooled by a Freon compressor was used to maintain the low temperature.

4) $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

30 mg of $\text{Rh}_2(\text{OAc})_4$ and 15 ml of CH_2Cl_2 , which was purified by refluxing for 1 hour in the presence of P_2O_5 followed by fractional distillation, were placed in tube A (Fig. 2). After purging with N_2 for 1 hour the reaction tube A was placed in an ice-water bath and the cold trap (tube B) in a dry ice-acetone slush to induce gradual condensation of CH_2Cl_2 vapor. The system was then filled with PF_3

Fig. 2. Apparatus used to crystallize the PF_3 adduct.

(Ozark-Mahoning Chemical) at a slightly higher pressure by use of a 10 cm Hg column in order to prevent the back diffusion of air into the system. After several minutes of mild agitation, the solution turned reddish and yielded red cubic crystals in 2-3 days upon evaporation to dryness. The crystals were unstable and decomposed within a day or so.

5) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

The vapor of $\text{P}(\text{OMe})_3$ from a 10:1 mixture of THF and $\text{P}(\text{OMe})_3$ was allowed to diffuse into a nearly saturated solution of $\text{Rh}_2(\text{OAc})_4$ in THF. The crystals which formed in 3-4 days were mostly red monoclinic needles with a thickness of less than 0.1 mm. However, a few irregular plate-like crystals were also obtained. The adduct crystals are stable in the air at room temperature, although slow decomposition took place in the THF solution over a prolonged period. A glove bag purged with nitrogen was used to avoid possible air oxidation of the phosphite. $\text{P}(\text{OMe})_3$ was purchased from Aldrich Chemical Company.

6) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

A few drops of $\text{P}(\text{OPh})_3$ were added to 10 ml of toluene containing 20 mg of $\text{Rh}_2(\text{OAc})_4$. The resulting red solution was evaporated to dryness under nitrogen at room temperature to obtain red needle-shaped crystals. $\text{P}(\text{OPh})_3$ was purchased from Aldrich Chemical Company.

7) $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

Nitric oxide gas(99.0 %, Matheson), purified by means of cold trap (dry ice-acetone slush), was introduced into a $\text{Rh}_2(\text{OAc})_4\text{-CH}_2\text{Cl}_2$ mixture (ca. 30 mg and 20 ml, respectively) to obtain a brown solution. The

system had been flushed with nitrogen for 30 minutes and the CH_2Cl_2 was degassed prior to the introduction of the purified NO gas by repeated freeze-thaw cycles. The brown solution was dried with a continuous passage of NO for 10 hours. The dark brown crystals were of various morphologies, e.g., octagonal cylinders, hexagonal plates, and twinned octahedrons with opposite vertices truncated. The adduct is highly soluble in most solvents.

B. Cell Constants

General Procedure: The adduct crystals were subjected to preliminary photographic investigations on a Buerger precession camera using $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Zero layer photographs were taken at $\mu = 25^\circ$ with a screen having a radius of 15 mm placed at a distance of 32.5 mm from the crystal. For the upper layer photographs, the μ angles and screens were chosen so as to avoid collision between the camera and screen during the precession. An exposure time of 5 to 10 min was allowed for the alignment pictures and 30 min to 2 hours for the zero and upper layer photographs.

The crystals used for the photographic examination were generally discarded and fresh crystals with appropriate dimensions were selected for the subsequent data collections, except for $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$ for which single crystal was used for both photographic examination and data collection. The data crystals were evenly coated with a thin layer of epoxy resin and mounted on glass fibers. After transferring to an automated Syntex P1 four-circle diffractometer, the crystals were carefully centered optically with the goniometer arcs set to zero. X 2x and 2y film coordinates of 15 reflections randomly chosen from a rotation photograph were used to determine 2θ , ω , ϕ , and χ angles which were accurately optimized by program CENTERING. Appropriate cell constants were selected from the values generated by program AUTOINDEXING such that they agreed with those found from the film method. Based on this preliminary information, more accurate cell

constants and associated standard deviations, and an orientation matrix were calculated using a program UNIT CELL LEAST SQUARES. Systematic absences determined by precession photography were confirmed by the fast scan method in which several hundred reflections at lower Bragg angles were collected at fixed scan rates of $12\text{--}24^\circ/\text{min}$.

As a final check on the consistency in the cell constants and the space group, the densities were measured by flotation method for all but the unstable CO and PF_3 adducts, and compared with the calculated values.

Relevant crystal data obtained from the diffractometer are summarized in Table 2.

The following sections describe the details pertaining to the crystal data for the individual adducts. Crystals described below are the ones used for the data collections. The diffractometric work was done at $20 \pm 1^\circ\text{C}$, unless otherwise specified.

1) $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

A small section of a needle crystal, 0.15×0.16 mm in cross section and 0.21 mm in length, was mounted on a goniometer along the needle axis (0 0 1). The cell dimensions were determined by a least squares fit of the setting angles of 15 reflections for which $7.0^\circ < 2\theta < 27.0^\circ$; $a = 9.923(3) \text{ \AA}$, $b = 17.009(6) \text{ \AA}$, $c = 12.539(3) \text{ \AA}$, $\beta = 83.40(20)^\circ$, and $V = 2102.2(1.1) \text{ \AA}^3$. 594 fast scan data collected for $2\theta < 20.0^\circ$ at a scan rate of $12^\circ/\text{min}$ and precession photographs showed systematic absences $h+k=2n+1$ for hkl and $l=2n+1$ for $h0l$, indicating $\text{C}2/c$ or Cc as the probable space group. However, the structure was successfully

refined in C2/c. The density measured in a mixture of toluene and 1,2-dibromoethane was 1.85(1) g/cm³, in fair agreement with the calculated density of 1.896 g/cm³ for Z=4.

2) Rh₂(OAc)₄(NHEt₂)₂

A cleaved portion of a needle crystal having dimensions of approximately 0.33 x 0.24 x 0.32 mm was mounted with the c axis parallel to the goniometer ϕ axis. Preliminary precession photographs showed systematic absences consistent with an orthorhombic space group Pbcn; 0k ℓ absent for k=2n+1, h0 ℓ absent for ℓ =2n+1, and hk0 absent for h+k=2n+1. No fast scan data were collected. The cell parameters determined using the setting angles of 15 reflections in the region 7.0° < 2 θ < 23.0° are a=16.329(4) Å, b=8.011(4) Å, c=17.660(6) Å, and V=2310.3(1.4) Å³. The density could not be measured accurately due to the dissolution or decomposition of the crystals in all density standards employed. d=1.60(1) g/cm³ was obtained in a mixture of bromobenzene and iodobenzene, while the calculated density for Z=4 is 1.691 g/cm³.

3) Rh₂(OAc)₄(CO)₂

A large diamond-shaped crystal, 0.55 x 0.55 mm in the (1 0 0) face, 0.22 x 0.25 mm in the ($\bar{1}$ 0 0) face, and 0.39 mm in thickness, was doubly coated with epoxy and mounted with the a axis parallel to the goniometer axis. The space group was uniquely determined to be Pbca by the precession film method and this was confirmed by 402 fast scan data collected at -104(3)°C for 2 θ < 30.0° at a variable scan rate from 12 to 24°/min; k=2n+1 for 0k ℓ , ℓ =2n+1 for h0 ℓ , and h=2n+1 for hk0. The cell dimensions were determined to be a=14.368(3) Å, b=12.151(5) Å,

$c=8.800(3) \text{ \AA}$, and $V=1536.4(9) \text{ \AA}^3$, using 15 reflections for which $8.0^\circ < 2\theta < 24.0^\circ$. The calculated density is 2.153 g/cm^3 for four molecules in one unit cell.

4) $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

The preliminary photographic investigation could not be carried out to the full extent because of the extreme instability of the crystals. However, zero layer photographs taken on a cubic crystal of dimensions $0.30 \times 0.30 \times 0.30 \text{ mm}$ gave an indication for a body centered, cubic space group. A crystal of dimensions $0.33 \times 0.33 \times 0.25 \text{ mm}$, which could be best described as a hexagonal cylinder, was mounted in an arbitrary direction after doubly coating with epoxy for the data collection. 1061 reflections collected at $-109(3)^\circ\text{C}$ for $4.0^\circ < 2\theta < 40.0^\circ$ at $12^\circ/\text{min}$ produced no further information leading to the assignment of correct space group. 35 reflections in the region $24.0^\circ < 2\theta < 39.0^\circ$ were centered after the fast scan and the least squares analysis based on these reflections yielded $a=14.339(2) \text{ \AA}$, $b=14.343(2) \text{ \AA}$, $c=14.336(2) \text{ \AA}$, and $V=2948.3(7) \text{ \AA}^3$ with a calculated density of 2.088 g/cm^3 for $Z=6$.

5) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

A twinned plate-like crystal was cleaved along the twin axis and mounted on a goniometer along the b axis. The dimensions were $0.30 \times 0.21 \times 0.20 \text{ mm}$. The space group was unambiguously determined to be $P2_1/c$ by the precession film method; $0k0$ absent for $k=2n+1$ and $h0l$ absent for $l=2n+1$. The least squares fit of 15 reflections for which $15.0^\circ < 2\theta < 20.0^\circ$ gave $a=14.133(3) \text{ \AA}$, $b=15.799(4) \text{ \AA}$, $c=8.309(2) \text{ \AA}$, $\beta=138.65(1)^\circ$,

and $V=1225.7(5) \text{ \AA}^3$. The density was measured in a mixture of benzene and 1,2 dibromomethane; $d(\text{measured})=1.85(1) \text{ g/cm}^3$. The calculated density for $Z=2$ is 1.877 g/cm^3 .

6) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

A fragment of a needle crystal, $0.32 \times 0.38 \times 0.25 \text{ mm}$, was mounted on a goniometer with the needle axis $(0 \ 1 \ 0)$ collinear with the goniometer φ axis. The systematic absences determined from the preliminary investigation on a precession camera were; hkl absent for $h+k=2n+1$ and $h0l$ absent for $l=2n+1$, indicating $C2/c$ or Cc as the space group. Attempts to refine the structure in Cc were unsuccessful. Thus $C2/c$ was taken as the correct space group. The fast scan was carried out in two steps; 907 reflections for $4.0^\circ < 2\theta < 30.0^\circ$ were collected at variable scan rates of $12\text{--}24^\circ/\text{min}$ and 182 reflections for $50.0^\circ < 2\theta < 60.0^\circ$ at a fixed scan rate of $12^\circ/\text{min}$. The orientation matrix and the cell constants were redetermined after the fast scan utilizing 15 reflections in the region $14.0^\circ < 2\theta < 27.0^\circ$. The cell dimensions were $a=26.134(9) \text{ \AA}$, $b=9.951(2) \text{ \AA}$, $c=22.512(7) \text{ \AA}$, $\beta=61.45(2)^\circ$, and $V=5142.9(2.3) \text{ \AA}^3$. The density was measured in a mixture of n-hexane and iodobenzene to be $1.42(1) \text{ g/cm}^3$. The calculated density is 1.490 g/cm^3 , assuming four adduct molecules and four solvent molecules (toluene) in one unit cell.

7) $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

A twinned octahedral crystal was cleaved twice, once parallel and then perpendicular to the twin axis. The dimensions of this fragment were $0.23 \times 0.33 \times 0.25 \text{ mm}$. 419 fast scan data collected at

$-104(3)^{\circ}\text{C}$ in the region $4.0^{\circ} < 2\theta < 30.0^{\circ}$ and the precession photographs showed systematic absences consistent with a space group $P2_12_12_1$; $h00$ absent for $h=2n+1$, $0k0$ absent for $k=2n+1$, and $00l$ absent for $l=2n+1$. The cell dimensions calculated based on the setting angles of 15 reflections for which $8.0^{\circ} < 2\theta < 27.0^{\circ}$ were $a=7.126(3) \text{ \AA}$, $b=13.110(4) \text{ \AA}$, $c=16.132(5) \text{ \AA}$, and $V=1507.0(9) \text{ \AA}^3$. The density could not be measured due to the high solubility of the adduct crystals in hydrocarbon solvents. The density calculated for $Z=4$ is 2.283 g/cm^3 .

Table 2. Crystal Data for $\text{Rh}_2(\text{OAc})_4\text{L}_2$

L:	py	NHEt_2	CO	PF_3	P(OMe)_3	P(OPh)_3	$(\text{NO})(\text{NO}_2)$
Space Group	C2/c	Pbcn	Pbca	I23	P2 ₁ /c	C2/c	P2 ₁ 2 ₁ 2 ₁
a(Å)	9.923(3)	16.329(4)	14.368(8)	14.339(2)	14.133(3)	26.134(9)	7.126(3)
b(Å)	17.009(6)	8.011(4)	12.151(5)	14.339(2)	15.799(4)	9.951(2)	13.110(4)
c(Å)	12.540(3)	17.660(6)	8.800(3)	14.339(2)	8.309(2)	22.512(7)	16.132(5)
$\alpha(^{\circ})$	90.0	90.0	90.0	90.0	90.0	90.0	90.0
$\beta(^{\circ})$	83.43(2)	90.0	90.0	90.0	138.65(1)	61.45(2)	90.0
$\gamma(^{\circ})$	90.0	90.0	90.0	90.0	90.0	90.0	90.0
V(Å ³)	2102(1)	2310(1)	1536(1)	2948(1)	1226(1)	5143(2)	1507(1)
Z	4	4	4	6	2	4	4
Mol. Wt.	600.2	588.3	498.0	617.9	690.2	1062.6	518.0
d _{cal} (g/cm ³)	1.896	1.691	2.153	2.087	1.877	1.490	2.283
d _{meas} (g/cm ³)	1.85(1)	1.60(1)	-	-	1.85(1)	1.42(1)	-
$\mu(\text{cm}^{-1})$	15.8	14.3	21.4	18.8	15.1	7.5	22.0
T(°C)	20(1)	20(1)	-104(3)	-109(3)	20(1)	20(1)	-104(3)

III. DATA COLLECTION

General Procedure: Upon determination of orientation matrices and cell constants for the data crystals as described in the previous section, data were collected by the θ - 2θ scan technique using $\text{MoK}\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$) monochromatized with a graphite crystal. The temperature was maintained at $20(1)^\circ\text{C}$ for all compounds, except for $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$, $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$, and $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$ for which the data were collected at $-104(3)^\circ\text{C}$, $-109(3)^\circ\text{C}$, and $-104(3)^\circ\text{C}$, respectively. The scan rates were varied from $2^\circ/\text{min}$ for reflections giving less than 200 counts during a preliminary rapid intensity measurement to $24^\circ/\text{min}$ for those giving more than 2000 counts. The background was measured at the extremes of each scan for a period of half the total scan time. The background scan widths were 1.0° below $\text{K}\alpha_1$ and above $\text{K}\alpha_2$. Seven check reflections of varying intensities were remeasured after every 93 reflections in order to monitor the stability of the crystals and the machine. Intensities were measured for reflections with $4.0^\circ < 2\theta < 60.0^\circ$ for all but $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$ for which the data were collected out to $2\theta=75.0^\circ$. ψ scans were performed on reflections near $\chi=90.0^\circ$ at varying φ angles with fixed 2θ angles to detect intensity variations attributable to the absorption effects.

The scan counts were converted into integrated intensities using $I=R(C-T(B_1+B_2))$ where R is the scan rate, C scan counts, T the ratio of the scan time to the background counting time, and B_1 and B_2 background

counts. The estimated standard deviations for the integrated intensities were computed using the formula

$$\sigma^2(I) = R(C + T^2(B_1 + B_2) + (PI)^2)$$

where $P=0.02$ was chosen to account for the expected errors proportional to the diffracted intensity.⁵⁶

Details of the data collection for each compound are given below in the form of a table for clarity. The total number of data collected includes repeated measurements of check reflections and the ψ scan data. The number of independent data obtained after the data reduction process is also given for comparison (see Chapter IV). Overflowed reflections are the reflections whose scan counting rates exceeded 50,000 counts/sec during the time of data collection. These reflections were eliminated from the data to avoid any possible coincidence errors.

1) $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

No. of data collected: 3558

No. of independent data: 2987

2θ range: $4.0-60.0^\circ$

Scan rate: $2.0-12.0^\circ/\text{min}$

Check reflections: $(2\ 4\ 1)$ $(0\ 4\ 2)$ $(3\ 3\ 4)$ $(1\ 3\ \bar{2})$ $(0\ 0\ 16)$
 $(4\ 2\ 0)$ $(2\ 0\ 6)$

Overflowed reflections: $(0\ 0\ 2)$ $(1\ 1\ 0)$ $(2\ 0\ \bar{2})$ $(2\ 0\ 2)$

Temperature: $20(1)^\circ\text{C}$

2) $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

No. of data collected: 5042

No. of independent data: 3346

2 θ range: 4.0-60.0°

Scan rate: 2.0-24.0°/min

Check reflections: (1 2 3) (1 1 1) (3 1 0) (3 0 4)
(3 3 3) (0 4 1) (4 4 4)

Overflowed reflections: (1 1 0) (1 1 2) (2 0 0) (2 0 2)

Temperature: 20(1)°C

3) Rh₂(OAc)₄(CO)₂

No. of data collected: 4216

No. of independent reflections: 2252

2 θ range: 4.0-60.0°

Scan rate: 2.0-24.0°/min

Check reflections: (10 2 0) (8 1 2) (6 2 4) (5 4 1) (4 4 4)
(3 1 3) (2 5 1)

Overflowed reflections: (0 0 2) (0 2 0) (1 1 1) (2 0 0) (2 2 0)
(2 3 0) (2 4 0) (2 5 0) (3 0 2) (3 2 2)
(4 1 3) (4 5 0)

Temperature: -104(3)°C

4) Rh₂(OAc)₄(PF₃)₂

No. of data collected: 1605

No. of independent data: 681

2 θ range: 4.0-75.0°

Scan rate: 2.0-12.0°/min

Check reflections: (0 2 2) (1 3 6) (1 6 9) (0 2 10) (0 3 9)
(4 6 8) (3 5 8)

Overflowed reflections: (0 0 2)

Temperature: -109(3)°C

5) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

Data were collected based on a space group $P2_1$ with cell dimensions $a=8.309(2) \text{ \AA}$, $b=15.799(4) \text{ \AA}$, $c=14.133(3) \text{ \AA}$, $\beta=138.65(1)^\circ$, and $V=1225.7(5) \text{ \AA}^3$. The indices h and l were interchanged in the data reduction such that the systematic absences were consistent with $P2_1/c$. The cell axes a and c were accordingly interchanged.

No. of data collected: 5355

No. of independent reflections: 3357

2θ range: 4.0 - 60.0°

Scan rate: 2.0 - $12.0^\circ/\text{min}$

Check reflections: $(0\ 4\ \bar{1})$ $(2\ 5\ \bar{5})$ $(2\ 0\ \bar{3})$ $(3\ 4\ \bar{2})$ $(4\ 5\ 6)$ $(5\ 1\ 2)$
 $(1\ 6\ 2)$ as obtained before the interchange of
 cell constants.

Temperature: $20(1)^\circ\text{C}$

6) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

The first set of data were collected for $4.0^\circ < 2\theta < 50.0^\circ$ at a minimum scan rate of $2.0^\circ/\text{min}$ for counts less than 200 and additional data were collected for $50.0^\circ < 2\theta < 60.0^\circ$ at a minimum scan rate of $1.0^\circ/\text{min}$ for counts less than 100. The maximum scan rate was $24.0^\circ/\text{min}$ for counts more than 2000 in both cases.

No. of data collected: 9796

No. of independent reflections: 7073

2θ range: 4.0 - 60.0°

Scan rate: 1.0 - 24.0°

Check reflections: $(0\ 2\ 2)$ $(1\ 1\ \bar{1})$ $(2\ 0\ \bar{4})$ $(3\ 1\ 3)$ $(3\ 5\ 1)$
 $(4\ 2\ \bar{13})$ $(4\ 4\ 7)$

Overflowed reflections: $(0\ 0\ \bar{2})$ $(0\ 0\ 2)$

Temperature: $20(1)^{\circ}\text{C}$

7) $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

No. of data collected: 3203

No. of independent reflections: 2517

2θ range: 4.0 - 60.0°

Scan rate: 2.0 - 24.0°

Check reflections: $(5\ 0\ 2)$ $(4\ 1\ 2)$ $(3\ 3\ 3)$ $(4\ 4\ 0)$ $(2\ 1\ 5)$
 $(0\ 10\ 10)$ $(4\ 5\ 6)$

Overflowed reflections: $(0\ 1\ 2)$ $(0\ 2\ 0)$ $(1\ 1\ 1)$ $(4\ 3\ 6)$

Temperature: $-104(3)^{\circ}\text{C}$

IV. DATA REDUCTION

A. Initial Data Reduction

Lorentz and polarization corrections were applied to the raw intensity data. The Lorentz factor arises from the fact that the integrated intensity is proportional to the elapsed time required to traverse the reflection. This time depends on the position of the point in the reciprocal space and the direction of approach to the sphere of reflection. For diffractometer data obtained by the θ - 2θ scan technique, the intensity is increased by the factor

$$L = \frac{1}{\sin 2\theta}$$

The polarization factor is introduced simply to compensate for the fact that the component of the electromagnetic wave whose vibration is parallel to the plane of reflection experiences no reduction in intensity, while the intensity of the other component varies with the Bragg angle. The latter component vanishes as 2θ approaches 90° . Since the x-ray beam is polarized both by the graphite monochromator and sample crystal, the following equation is used for the correction;

$$P = \frac{1}{2}(\cos^2 2\theta_m + \cos^2 2\theta_c) / (1 + \cos^2 2\theta_m) \\ + \frac{1}{2}(\cos 2\theta_m + \cos^2 2\theta_c) / (1 + \cos 2\theta_m)$$

where $2\theta_m$ is the 2θ angle for the monochromator and $2\theta_c$ the 2θ angle for the sample crystal. The relative structure factor modulus can be related to the observed intensity by $F_{hkl} = (k \times I_{hkl} / L \times P)^{1/2}$

where k is an arbitrary scale factor. Since the precise magnitude of F_{hkl} is not required at this stage, k is set to unity.

In addition to the correction for Lorentz and polarization effects, the weight of each F_{hkl} is calculated according to

$$W_{hkl} = (1/LP)(1/\sigma'_{hkl})$$

and

$$\sigma'_{hkl} = (\sigma_{hkl}^2 + (0.02I_{hkl})^2)^{\frac{1}{2}}$$

The factor 0.02 is introduced to allow for machine fluctuations and other errors not accounted for by counting statistics which would be expected to be proportional to I_{obs} . σ_{hkl} is the standard deviation for I_{hkl} based on counting statistics.

Multiply measured reflections were averaged and systematically absent and overflowed reflections were deleted from the data. The distribution of reflection intensities over various integer multiples of sigma is given in Table 3.

Table 3. Distribution of Reflections above N Sigma

<u>N</u>	<u>py</u>	<u>NHEt₂</u>	<u>CO</u>	<u>PF₃</u>	<u>P(OMe)₃</u>	<u>P(OPh)₃</u>	<u>(NO)(NO₂)</u>
0	2770	2989	2209	649	3405	6224	2492
1	2531	2628	2105	610	3201	5315	2442
2	2316	2297	2001	564	2995	4552	2385
3	2183	2081	1923	536	2828	4028	2342
4	2098	1925	1858	512	2703	3609	2285
5	2020	1823	1802	489	2610	3287	2238
6	1960	1722	1745	473	2499	3005	2190
7	1920	1636	1704	448	2404	2753	2146
8	1858	1552	1661	432	2316	2533	2093
9	1817	1464	1628	415	2234	2345	2047
10	1781	1393	1594	402	2169	2175	1999

Reflections with negative intensities

217	357	43	32	48	849	25
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Total number of independent data

2987	3346	2252	681	3357	7073	2517
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B. Absorption Correction

The necessity of absorption corrections was judged based on the intensity variation of the ψ scan data and the transmission coefficient defined as

$$T = I/I_0 = \exp(-\mu r)$$

where I and I_0 are the transmitted and incident beam intensities, r the path length of the beam, and μ the linear absorption coefficient given by

$$\mu = \rho \sum_n (P_n/100) (\mu/\rho)_{\lambda, E_n}$$

where ρ is the calculated density and P_n the % composition of element n . The mass absorption coefficients, (μ/ρ) , were taken from International Tables for X-ray Crystallography, Vol. III.^{57a}

The differences between the estimated maximum and minimum transmission coefficients were not in general serious and the ψ scan data gave agreement in the observed structure factors within 5 %, except for the CO adduct for which the intensities were severely dependent on the crystal orientation. However, the absorption corrections were applied to the pyridine, NHEt₂, and PF₃ adducts in addition to the CO adduct. Others were not corrected for the absorption effects due in part to small dependency of intensities on the crystal orientation (e.g., the P(OPh)₃ adduct) and in part to the lack of sufficient ψ scan data that were required to obtain a reasonable least-squares fit (e.g., the P(OMe)₃ and (NO)(NO₂) adducts).

In the case of the pyridine adduct, the absorption correction was made by the method of Gaussian quadrature over a grid of 8 x 8 x 8 points utilizing the reflection angles, χ and φ , of the crystal faces

(1 1 0), (1 $\bar{1}$ 0), ($\bar{1}$ 1 0), ($\bar{1}$ $\bar{1}$ 0), (0 0 1), and (0 0 $\bar{1}$) and the crystal center-to-face distances of 0.065, 0.065, 0.065, 0.065, 0.105, and 0.105 mm, respectively. For the CO, PF₃, and NHEt₂ adducts, the absorption corrections were made using the equation

$$I_{\text{obs}} = I_{\text{corr}} \left(a_0 + \sum_{i=1}^n a_i f_i(\theta_p, \varphi_p) \right) \left(a'_0 + \sum_{i=1}^n a'_i f_i(\theta_s, \varphi_s) \right)$$

where θ_p and φ_p are the angles of the incident beam and θ_s and φ_s those of the diffracted beam relative to the crystal coordinates.⁵⁸

The coefficients were determined by an iterative non-linear least squares procedure using the ψ scan data.

The transmission coefficients were estimated from the longest and shortest data crystal dimensions described in Section B. Crystal Data. These are given below along with the maximum % deviation from the average F_{obs} of each reflection measured in the ψ scan mode. Corresponding values before the absorption corrections are included in the parentheses for comparison. The five strongest reflections are listed in cases where more than five reflections were measured in the ψ scan examinations.

1) Rh₂(OAc)₄(py)₂

$$\mu = 15.8 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.79$$

$$T_{\text{min}} = 0.72$$

ψ scan:

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(0 0 4)	294.5(266.0)	302.8(279.0)	286.1(254.1)	2.8(4.9)
(0 2 5)	101.3(92.1)	103.0(94.9)	99.3(88.5)	2.0(3.9)
(0 0 8)	476.8(432.3)	489.2(451.0)	463.1(409.5)	2.9(5.3)

2) $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

$$\mu = 14.3 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.71$$

$$T_{\text{min}} = 0.62$$

ψ scan: 457 data were collected for 13 independent reflections.

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(4 0 2)	180.5(179.0)	182.4(183.7)	176.4(171.4)	2.3(4.2)
(5 1 0)	215.8(213.6)	219.5(223.8)	212.5(206.5)	1.7(4.8)
(9 0 2)	212.2(210.5)	215.5(215.9)	208.0(204.4)	2.0(2.9)
(11 1 2)	188.4(188.5)	192.2(193.2)	185.5(183.5)	2.0(2.7)
(13 1 0)	194.0(195.8)	198.0(200.2)	192.1(188.3)	2.1(3.8)

3) $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

$$\mu = 21.4 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.43$$

$$T_{\text{min}} = 0.31$$

ψ scan: 889 data were collected for 34 independent reflections.

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(6 0 0)	446.7(438.4)	449.8(481.0)	439.3(404.5)	1.7(9.7)
(8 2 0)	546.7(539.6)	549.5(590.0)	543.3(500.2)	0.6(9.3)
(7 1 1)	488.8(481.6)	493.3(518.5)	484.5(445.3)	0.9(7.7)
(9 1 1)	414.1(412.9)	417.9(443.1)	411.4(377.9)	0.9(8.5)
(11 0 2)	396.4(388.7)	404.6(428.1)	391.2(365.4)	2.2(10.1)

4) $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

$$\mu = 18.8 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.63$$

$$T_{\text{min}} = 0.54$$

ψ scan: 593 data were collected for 10 independent reflections.

Of these, 26 reflections were judged to be in error

because of extremely low intensities and deleted prior

to the absorption correction.

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(0 2 2)	236.0(239.5)	240.1(244.6)	234.8(233.8)	1.7(2.4)
(0 3 5)	393.9(395.8)	396.8(403.6)	391.1(383.1)	0.7(3.2)
(1 1 2)	282.0(274.1)	283.4(291.0)	278.5(273.7)	0.9(6.2)
(1 2 3)	248.2(247.8)	250.7(256.0)	245.7(240.8)	1.0(3.3)
(1 3 4)	195.9(196.1)	198.6(201.4)	193.0(190.4)	1.5(2.9)

5) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{O}(\text{Me})_3)_2$

$$\mu = 15.1^{-1}$$

$$T_{\text{max}} = 0.74$$

$$T_{\text{min}} = 0.64$$

ψ scan:

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(0 6 0)	178.4	182.8	170.8	4.3
(1 4 0)	289.3	306.5	281.9	5.9
(1 6 0)	111.7	117.0	107.9	4.7
(1 10 0)	260.4	271.6	254.1	4.3
(1 12 1)	64.4	67.3	61.5	4.5

$$\mu = 7.5 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.83$$

$$T_{\text{min}} = 0.75$$

 ψ scan:

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(6 0 0)	178.0	183.8	172.7	3.3
(10 0 0)	105.8	109.7	104.0	3.7
(15 1 2)	65.3	67.3	63.0	3.5
(16 0 4)	113.3	116.6	110.3	2.9
(18 0 4)	146.7	149.5	142.5	2.9

$$\mu = 22.0 \text{ cm}^{-1}$$

$$T_{\text{max}} = 0.60$$

$$T_{\text{min}} = 0.48$$

 ψ scan:

<u>(h k l)</u>	<u>F(ave)</u>	<u>F(max)</u>	<u>F(min)</u>	<u>Max. % Dev.</u>
(2 5 1)	194.5	200.7	180.9	3.9
(2 6 1)	202.0	209.9	195.9	3.9
(3 10 2)	92.3	95.6	88.7	3.9
(3 10 1)	102.4	105.5	97.8	4.4
(3 12 2)	117.9	121.8	111.6	5.3

C. Correction for Crystal Decay

Although no appreciable changes in the intensities of the check reflections were observed, decay corrections were made for all compounds. The correction factor k determined from the least squares analysis of the standard reflections were applied to the following equation

$$F_{hkl}(\text{new}) = F_{hkl}(\text{old}) / (1.0 + kT)$$

where T is the exposure time in hours. The weight of each F_{hk} was similarly rescaled by

$$W_{hkl}(\text{new}) = W_{hkl}(\text{old}) (1.0 + kT)^2$$

Decay constants for the data crystals were;

$\text{Rh}_2(\text{OAc})_4(\text{py})_2$	0.000165 hr^{-1}
$\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$	0.000009 hr^{-1}
$\text{Rh}_2(\text{OAc})_4(\text{CO})_2$	$-0.000001 \text{ hr}^{-1}$
$\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$	0.000009 hr^{-1}
$\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$	$-0.000006 \text{ hr}^{-1}$
$\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$	0.000000 hr^{-1}
$\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$	0.000000 hr^{-1}

D. Initial Data Processing

The scattering factor of a point atom is equal to its number of electrons and is independent of the incident angle and the wavelength. However, the finite size of the electron cloud around the nucleus and thermal motion about the equilibrium position cause the scattering power to decrease with $\sin\theta/\lambda$. The scattering power of an atom is related to these factors by

$$f = f_0 \exp(-B(\sin\theta/\lambda)^2)$$

where f_0 is the scattering power of a point atom and B the mean atomic vibration given by $8\pi^2 U^2$. The theoretical average intensity for a unit cell containing N atoms is given by

$$\bar{I}_{\text{abs}} = \sum_i^N f_{0i}^2 \exp(-2B \sin^2 \theta / \lambda^2)$$

If the reciprocal space is divided into concentric shells, then the variation of $\bar{I}_{\text{abs}}$ with $\sin\theta/\lambda$ can be ignored. The average relative intensity of the reflections, $\bar{I}_{\text{rel}}$, within each shell is related to $\bar{I}_{\text{abs}}$ by

$$C = \bar{I}_{\text{rel}} / \bar{I}_{\text{abs}}$$

The scale constant C can be determined by a method known as the Wilson plot,^{59a} which is based on the functional form;

$$\ln(\bar{I}_{\text{rel}} / \sum_i^N f_{0i}^2) = \ln C - 2B(\sin\theta/\lambda)^2$$

The constant C and the temperature parameter B are evaluated from a plot of $\ln(\bar{I}_{\text{rel}} / \sum_i^N f_{0i}^2)$ vs. $(\sin\theta/\lambda)^2$. The extrapolated intercept and the slope of the best least squares line give $\ln C$ and $-2B$, respectively. After initial values of $k(=1/C^{\frac{1}{2}})$ and B are estimated from the classical

Wilson plot, they are further refined by means of a non-linear least squares procedure. Values of $\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{oi}^2)$ and $(\sin\theta/\lambda)^2$ are tabulated in Tables 4-10. Final k and $2B$ are also included along with their standard deviations. N represents the number of reflections within a shell of $\sin\theta/\lambda$.

The relative structure factors, F_{rel} 's, were put on an absolute scale using the final k value,

$$F_{\text{abs}} = 1/C^{\frac{1}{2}} F_{\text{rel}} = k F_{\text{rel}}$$

The atomic scattering factors for C, N, O, and P were taken from International Tables for X-ray Crystallography, Vol. III^{57a} and that for Rh from Vol. IV.^{57b} The form factor of H was that of Stewart, Davidson, and Simpson.⁶⁰ The scattering factor of Rh was corrected for the real and imaginary components of anomalous dispersion using the values given in International Tables for X-ray Crystallography, Vol. IV,^{57b}

$$f_o^{\text{anom}} = f_o + \Delta f' + i\Delta f'' = f' + i\Delta f''$$

Table 4. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
96	0.03084	0.280	0.797
174	0.07568	0.660	0.646
235	0.12447	0.407	0.482
267	0.17372	0.265	0.316
308	0.22272	0.185	0.151
346	0.27231	0.109	-0.016
373	0.32237	-0.181	-0.184
390	0.37152	-0.322	-0.350
396	0.42088	-0.538	-0.516
386	0.46963	-0.737	-0.680

$$2B = 3.12$$

$$\sigma(2B) = 0.18$$

$$k = 0.68$$

$$\sigma(k) = 0.02$$

Table 5. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
100	0.03072	0.147	0.716
195	0.07517	0.524	0.459
252	0.12435	0.183	0.154
301	0.17348	-0.265	-0.152
335	0.22286	-0.470	-0.458
378	0.27205	-0.685	-0.764
412	0.32215	-1.100	- .075
420	0.37146	-1.512	-1.381
460	0.42062	-1.650	-1.687
473	0.47067	-1.927	-1.998

$$2B = 5.95$$

$$\sigma(2B) = 0.19$$

$$k = 0.658$$

$$\sigma(k) = 0.020$$

Table 6. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
60	0.03159	1.410	2.062
130	0.07585	1.897	1.907
167	0.12482	1.776	1.735
196	0.17365	1.460	1.564
226	0.22287	1.399	1.391
256	0.27292	1.364	1.216
272	0.32331	0.995	1.039
284	0.37182	0.851	0.869
307	0.42066	0.651	0.697
336	0.47073	0.547	0.522

$$2B = 3.46$$

$$\sigma(2B) = 0.23$$

$$k = 0.341$$

$$\sigma(k) = 0.013$$

Table 7. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
36	0.0405	-0.001	0.408
54	0.1111	0.307	0.109
64	0.1846	-0.410	-0.203
70	0.2565	-0.592	-0.507
81	0.3291	-0.781	-0.815
90	0.4039	-1.127	-1.132
92	0.4781	-1.371	-1.446
96	0.5500	-1.769	-1.751
98	0.6199	-2.049	-2.047

$$2B = 4.07$$

$$\sigma(2B) = 0.28$$

$$k = 0.782$$

$$\sigma(k) = 0.046$$

Table 8. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
106	0.03026	1.139	1.488
206	0.07502	1.363	1.334
274	0.12464	1.132	1.162
315	0.17403	0.987	0.992
360	0.22357	0.889	0.821
392	0.27236	0.643	0.653
431	0.32146	0.405	0.483
471	0.37144	0.289	0.311
487	0.42042	0.180	0.142
498	0.47001	-0.012	-0.030

$$2B = 3.24$$

$$\sigma(2B) = 0.16$$

$$k = 0.468$$

$$\sigma(k) = 0.012$$

Table 9. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
233	0.02998	-1.114	-1.031
435	0.07549	-1.194	-1.289
564	0.12451	-1.580	-1.567
670	0.17411	-1.880	-1.847
745	0.22319	-2.127	-2.125
792	0.27241	-2.404	-2.404
763	0.32182	-2.818	-2.684
916	0.37230	-3.044	-2.970
967	0.42084	-3.162	-3.245
945	0.46969	-3.445	-3.522
$2B = 5.55$		$\sigma(2B) = 0.12$	
$k = 1.568$		$\sigma(k) = 0.030$	

Table 10. Wilson Plot for $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

N	$\sin^2\theta/\lambda^2$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{obs}}$	$\ln(\bar{I}_{\text{rel}}/\sum_i^N f_{\text{oi}}^2)_{\text{cal}}$
92	0.02918	0.541	0.966
163	0.07543	0.873	0.863
193	0.12486	0.815	0.753
231	0.17449	0.549	0.642
245	0.22339	0.472	0.533
280	0.27233	0.559	0.424
297	0.32223	0.219	0.313
322	0.37187	0.253	0.202
334	0.42152	0.078	0.091
346	0.47062	-0.015	-0.018

$$2B = 2.06$$

$$\sigma(2B) = 0.15$$

$$k = 0.615$$

$$\sigma(k) = 0.015$$

V. STRUCTURE DETERMINATION AND REFINEMENT

A. Methods in General

Heavy atom Patterson methods were employed to solve the structures of the complexes. The coordinates of rhodium atoms were determined from the three dimensional Patterson map constructed using the function

$$P_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl}^2 \cos(2\pi(hx+ky+lz))$$

where x, y, and z are the fractional coordinates of each grid point. The phases of the F_{hkl} were approximated with heavy atom coordinates, ignoring the contribution from light atoms, as

$$\alpha_{hkl} = \tan^{-1} \frac{\sum_i f_i \sin(2\pi(hx_i+ky_i+lz_i))}{\sum_i f_i \cos(2\pi(hx_i+ky_i+lz_i))}$$

and

$$F_{hkl} = |F_{hkl}| \exp(i\alpha_{hkl})$$

The positions of some of the remaining atoms were found from the Fourier map calculated based on the initially calculated phases, and these in turn were used to obtain an improved model. The electron density maps were successively calculated as the model was improved, until most or all of nonhydrogen atoms were located. The function used for the electron density map is

$$\rho_{(x,y,z)} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \exp(i\alpha_{hkl}) \exp(-2\pi i(hx+ky+lz))$$

Difference Fourier maps were calculated in the final stage of the structure determination to locate new atoms and correct the

positions of the atoms already found;

$$\rho_o - \rho_c = \frac{1}{V} \sum_h \sum_k \sum_l (|F_o| - |F_c|) \exp(i\alpha_{hkl}) \exp(-2\pi i(hx + ky + lz))$$

Structure factor calculations were carried out whenever new atoms were located from the maps described above. This gave some summary information on the agreement between the calculated and the observed structure factors. Most frequently used were the discrepancy factor R defined as

$$R = \frac{\sum |F_o|}{\sum |F_c|} = \frac{\sum ||kF_o| - |F_c||}{\sum |kF_o|} ,$$

and the weighted residual index

$$R_w = \left[\frac{\sum w^2 (k^2 F_o^2 - F_c^2)^2}{\sum w^2 k^4 F_o^4} \right]^{1/2} ,$$

and the goodness of fit

$$GOF = \left[\frac{\sum w (F_o^2 - F_c^2)^2}{n_o - n_p} \right]^{1/2} ,$$

where n_o is the number of observations and n_p the number of parameters refined.

When all of the nonhydrogen atoms were located, atomic parameters were refined isotropically by a full-matrix least squares procedure, minimizing the function

$$w (k^2 |F_o|^2 - |F_c|^2)^2$$

Hydrogen atoms were located from the difference maps calculated after the least squares refinement reached convergence. After addition of the hydrogen coordinates to the structure model, all but the hydrogen

atoms were eventually allowed to anisotropically refine. For structures in which the hydrogen atoms were not found from the difference Fourier maps, calculated positions were entered before the anisotropic refinement of the atoms to which hydrogen atoms were attached.

Corrections for the secondary extinction effect were made at the final stage of the least squares refinement if the intense low angle observed structure factors were systematically less than the calculated values;

$$F_o^2(\text{corrected}) = F_o^2(1 + 2gF_c^2)$$

where g is the secondary extinction parameter^{59b} varied in the least squares refinement.

B. Solution and Refinement

1) $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

The positions of rhodium atoms were determined from the Harker line $(0, v, 0.5)$ of a Patterson synthesis. The rhodium atoms were independently assigned to the special positions along the crystallographic two-fold axis $(0, y, 0.25)$ on the assumption that the correct space group was $\text{C}2/c$. A subsequent Fourier map revealed the locations of all of the non-hydrogen atoms. Half of the dimer molecule was related to the other half by a C_2 axis passing through both rhodium atoms. Four cycles of structure factor-least squares refinement of the coordinates and isotropic thermal parameters of the non-hydrogen atoms resulted in the agreement factors $R=0.066$ and $R_w=0.138$. A population factor of 0.5 was assigned to the atoms on the C_2 axis and their x and z coordinates were not refined. At this stage an attempt was made to locate hydrogen atoms, but it failed. The hydrogen atoms in the pyridine rings were fixed at the best theoretical positions in trigonal planar environments at a distance of $0.95 \overset{\text{O}}{\text{\AA}}$ from the carbon atoms to which they were attached. With the hydrogen atoms in the methyl groups held fixed with a random orientation, the refinement was continued anisotropically until a convergence was obtained at $R=0.033$. Inspection of the low angle reflections gave evidence for a secondary extinction effect and a parameter to account for this was accordingly included in the refinement. An examination of the general planes of a difference Fourier normal to the $\text{C}-\text{CH}_3$ axis now gave clues to the positions of the methyl hydrogen atoms. In the final cycles of

Table 11. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. 2Rh, Iso B=4.0		48.2			1.0
S.F. All Non-hydrogen Atoms Iso B=4.0		42.0			1.0
L.S. Full Matrix, Shift=0.8 All but Aromatic Carbon Atoms, Iso B=4.0	26	31.1	56.6	15.2	0.7613
L.S. All Coordinates Iso B=4.0	42	27.3	50.3	13.8	0.7351
L.S. All Coordinates and B's Refined	60	6.6	13.8	3.80	1.0063
L.S. Anisotropic Refinement for All Non-hydrogen Atoms	138	3.5	6.1	1.64	1.0146
L.S. Hydrogen Atoms Refined Secondary Extinction	182	3.1	4.80	1.30	0.9840

Secondary Extinction Coefficient = $0.594(21) \times 10^{-6}$

refinement the parameters of all hydrogen atoms were allowed to vary. The refinement was considered complete when the positional and thermal parameters showed virtually no shifts for the non-hydrogen atoms and shifts less than 1/10 of the estimated standard deviations for the hydrogen atoms. The C(7)-H(7) distance 0.67 Å as obtained in the last least squares cycle was considered unrealistic and consequently H(7) was assigned to a theoretical position so as to give a C-H distance of 0.95 Å. In the final difference map the maximum peak contained 0.83 e/Å³ and the minimum -0.82 e/Å³. These peaks were not associated with any particular features in the structure. The general noise level was ±0.30 e/Å³. The final agreement factors were R=0.031, R_w=0.048, and GOF=1.30 for n_o=2987 and n_p=183. The secondary extinction coefficient was 0.594(21) × 10⁻⁶.

The summary of solution and refinement is given in Table 11.

2) Rh₂(OAc)₄(NHEt₂)₂

The peaks at (u, 0, w) and (0, v, 0.5) in a three-dimensional Patterson map were assigned to the Rh-Rh vectors, (2x, 0, 0.5+2z) and (0, 2y, 0.5), respectively. Remaining non-hydrogen atoms were found from a Fourier calculation and a subsequent difference Fourier. Four cycles of isotropic refinement by full-matrix least squares gave R=0.11 and R_w=0.20. The refinement was continued with anisotropic thermal parameters for atoms having no hydrogen atoms. A difference synthesis showed residual peaks with intensities of as high as 0.90 e/Å³ around C(5), C(6), C(7), and C(8). Some were chosen as probable hydrogen atoms but none of them refined to convergence. Attempts to locate hydrogen atoms on C(2) and C(4) were also unsuccessful. The

Table 12. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. Rh Iso B=3.0		30.6			1.0
S.F. Rh, 20's, 6C's, N Iso B=3.0		27.8			1.0
S.F. All Non-hydrogen Atoms Iso B=3.0		23.6			1.0
L.S. All Coordinates and B's Refined	57	11.0	20.0	3.98	0.9545
L.S.* All Coordinates Anisotropic Refinement Hydrogens Refined	195	6.1	8.9	1.82	0.9351
L.S. Anisotropic Refinement Hydrogens Fixed with B=6.0	127	6.3	9.4	1.98	0.9452

* The refinement of hydrogen atoms yielded better agreement factors. However, their coordinates were unreasonable and thermal parameters were as high as $B=20.0 \text{ \AA}^2$ for some.

Fig. 3. Probable disorder of NHEt_2 in $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$
(viewd down the Rh-N axis).

hydrogen atoms were assigned to most probable positions in tetrahedral environments at C-H distances of 0.95 Å and a thermal parameter $B=6.0 \text{ Å}^2$ was given to each atom. Several cycles of anisotropic least squares refinement gave convergence at $R=0.063$ and $R_w=0.094$. Final shifts were less than 1/5 of the estimated standard deviations at the conclusion of refinement. The goodness of fit was 1.98 for $n_o=3346$ data and $n_p=126$ variables. The maximum and minimum peaks in the final difference map contained 1.75 e/Å^3 and -1.26 e/Å^3 , associated with C(5) and C(8), respectively. The general noise level was $\pm 0.40 \text{ e/Å}^3$.

Inspection of the final atomic parameters and the thermal ellipsoids of the carbon atoms of NHET_2 group gave evidence for an end group disorder. The N-C and C-C distances were shorter by 0.05-0.18 Å than the expected values for the corresponding single bonds and the vibrational amplitudes for C(5), C(6), C(7), and C(8) were unreasonably large. A difference map calculated without the disordered carbon atoms showed severe dispersion of electron density, especially for C(5) and C(7) in the direction perpendicular to the Rh-N axis. The disorder was judged to be a mixture of two or more orientations of ethyl groups, as shown in Fig. 3. Attempts were made to resolve the disorder by creating two half-weighted carbon atoms near the end of the major ellipsoid axis of each carbon atom. In two cycles of isotropic refinement, these half-weighted carbon atoms diverged, and no additional efforts were made for the disorder problem.

The summary of solution and refinement is given in Table 12.

3) $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

The rhodium atom position was determined from a Harker plane ($u, v, 0.5$) and a Harker line ($0.5, 0, w$), which were respectively assigned to the Rh-Rh vectors ($0.5+2x, 2y, 0.5$) and ($0.5, 0, 0.5-2z$). A subsequent Fourier map revealed the locations of the carbonyl group and two carbon and all oxygen atoms of the acetate bridges. The remaining non-hydrogen atoms were found from a second Fourier map. Four cycles of isotropic refinement yielded $R=0.10$ and $R_w=0.23$. Two additional cycles of anisotropic refinement, except for the methyl carbon atoms, gave convergence at $R=0.048$. The hydrogen atoms were located unambiguously from a difference synthesis constructed at this stage. In the final cycles of refinement, reflections ($4\ 6\ 3$) and ($9\ 1\ 3$) which were judged to be in error because the weighted ΔF 's were unusually large, were deleted and a correction factor for the secondary extinction effect was included. The refinement was terminated when the shifts were virtually zero for the non-hydrogen atoms and less than $1/10$ of the standard deviations for the hydrogen atoms. The final discrepancy factors were $R=0.028$, $R_w=0.058$, and $\text{GOF}=1.97$ for 2252 data and 125 parameters. The maximum and minimum peaks in the final difference map were $1.08\ \text{e}/\text{\AA}^3$ and $-0.73\ \text{e}/\text{\AA}^3$, respectively. The general noise level was $\pm 0.15\ \text{e}/\text{\AA}^3$.

The summary of solution and refinement is given in Table 13.

Table 13. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. Rh Iso B=3.0		42.0			1.0
S.F. Rh, 50's, 3C's Iso B=3.0		38.4			1.0
S.F. All Non-hydrogen Atoms		33.1			1.0
L.S. Full Matrix, Shift=0.8 All Coordinates Refined Iso B=3.0	34	21.0	44.5	13.6	0.8175
L.S. All Coordinates and B's Refined	45	10.1	22.9	7.01	0.9517
L.S. Anisotropic Refinement Except Methyl Carbons	90	4.8	11.7	3.56	0.9683
L.S. Anisotropic Refinement for All Non-hydrogen Atoms Hydrogens Refined Deletion of (4 6 3) and (9 1 3)	125	2.8	5.8	1.97	0.9338

4) $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

A three dimensional Patterson map constructed assuming a space group I23 showed that the molecules are situated at the midpoint of each cell axis with the Rh-Rh vector parallel to the axis. The rhodium atom was assigned to a position on the a axis such that the distance from (0.5, 0.0, 0.0) was half the intramolecular Rh-Rh vector. The position of P was also determined from the Patterson map. A structure factor calculation based on the Rh and P coordinates gave $R=0.336$ for 649 data having non-negative intensities. The remaining atoms were located from a difference Fourier. The difference synthesis showed severe dispersion of electron densities for fluorine atoms, the maximum intensity being no more than $3.0 \text{ e}/\text{\AA}^3$. Consequently, the fluorine atoms were assigned to the most probable positions and entered in the subsequent refinement process. Two cycles of isotropic refinement followed by three cycles of anisotropic refinement of all atoms but C(2) yielded $R=0.045$ and $R_w=0.082$ (R_w is based on all 681 independent data). Y and z coordinates of Rh and P were not refined. A population factor of 0.5 was included in the refinement for all but oxygen atoms, which assumed a population of 1.0. Examination of general planes of a difference synthesis perpendicular to the C-CH₃ axis showed six disordered hydrogen atoms having intensities of approximately $0.4 \text{ e}/\text{\AA}^3$ at distances of 0.7-1.0 Å from C(2). With the six hydrogen atoms held fixed at these positions with $B=3.0 \text{ \AA}^2$ and populations of 0.5, C(2) was allowed to vary anisotropically. The refinement converged at $R=0.034$ and $R_w=0.048$. The disorder of PF₃ was judged to be random and no attempt was made to resolve it. However, it was possible to resolve F(3) into two

Table 14. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. Rh, P Iso B=3.0		33.6			1.0
S.F. Rh, P, 20's, 2C's, 3F's Iso B=3.0		23.8			1.0
L.S. Full Matrix, Shift=1.0 All Coordinates Refined	24	15.1	31.1	4.70	0.8888
L.S. Full Matrix, Shift=1.0 Anisotropic Refinement of All Atoms But C ₂	68	4.5	8.2	2.25	0.9346
L.S. Shift=0.8 All Aniso, Hydrogens Included But Not Refined	74	3.4	4.8	1.52	0.9372
L.S. Separation of F ₃ into Two Iso F's	73	3.4	4.8	1.53	0.9372
L.S. Secondary Extinction	74	3.3	4.6	1.47	0.9483

Secondary Extinction Coefficient = $0.16(2) \times 10^{-6}$

half-weighted isotropic fluorine atoms($\text{pop}=0.25$ for both; pop of F(3) was 0.5). The refinement of this new model to convergence did not alter the agreement factors but thermal parameters of other fluorine atoms, F(1) and F(2), were significantly affected(see Table 21 and Fig. 11). Inclusion of a factor to account for the secondary extinction effect yielded the final agreement factors $R=0.033$, $R_w=0.046$, and $\text{GOF}=1.47$ for $n_p=74$ parameters and $n_o=681$ data. When the refinement was terminated, the shifts were less than $1/10$ of the standard deviations. The maximum and minimum peaks in the final difference synthesis were $0.47 \text{ e}/\text{\AA}^3$ and $-0.51 \text{ e}/\text{\AA}^3$, not associated with any particular atoms. The general noise level was $\pm 0.20 \text{ e}/\text{\AA}^3$.

The least squares refinement of the structure in other probable space groups, e.g., $I213$, $Im3$, $I432$, $I4132$, and $I43m$ did not improve the agreement factors nor did it help resolve the disorder of the PF_3 group.

The summary of solution and refinement is given in Table 14.

5) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

The position of Rh was solved by assigning two peaks at $(u, 0.5, w)$ and $(0, v, 0.5)$ on a Patterson map to $(2x, 0.5, 0.5+2z)$ and $(0, 0.5+2y, 0.5)$ vectors. The position of the phosphorus atom was also found from the Rh-P vector. All the oxygen and carbon atoms were located from two successive Fourier maps. A structure factor calculation based on these coordinates gave $R=0.34$. The refinement of coordinates and isotropic temperature factors resulted in $R=0.068$ and $R_w=0.122$ in four cycles. A difference map calculated at this point revealed the positions of at least one or more hydrogen atoms in each methyl group with intensities ranging from $0.5 \text{ e}/\text{\AA}^3$ to $0.9 \text{ e}/\text{\AA}^3$. The positions of the rest of the hydrogen atoms were theoretically calculated assuming tetrahedral environments with C-H distances of $0.95 \text{ \AA}$. With inclusion of hydrogen atoms, non-hydrogen atoms were allowed to refine anisotropically to obtain a convergence at $R=0.035$ in two cycles. Inspection of low angle data showed the secondary extinction effect and hence a correction factor was introduced. The refinement was continued until there were no changes in the agreement factors. When the refinement was terminated, no shifts were observed for the non-hydrogen atoms and shifts less than $1/20$ of the standard deviations for the hydrogen atoms. The final agreement factors were $R=0.035$, $R_w=0.052$, and $\text{GOF}=1.46$ for $n_o=3357$ data and $n_p=206$ variables. The final difference synthesis showed a maximum of $0.88 \text{ e}/\text{\AA}^3$ and a minimum of $-0.80 \text{ e}/\text{\AA}^3$, not associated with any particular features of the structure. The noise level was on the average $\pm 0.30 \text{ e}/\text{\AA}^3$.

The summary of solution and refinement is given in Table 15.

Table 15. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. Rh, P Iso B=3.0		42.0			1.0
S.F. Rh, P, 70's, C Iso B=3.0		37.1			1.0
S.F. All Non-hydrogen Atoms Iso B=3.0		34.4			1.0
L.S. Full Matrix, Shift=0.8 All Coordinates Iso B=3.0	49	19.9	34.6	9.51	0.8082
L.S. All Coordinates and B's Refined	65	6.8	12.2	3.36	0.9556
L.S. Anisotropic Refinement Hydrogens Refined	205	3.5	5.3	1.49	0.9656
L.S. Secondary Extinction	206	3.5	5.2	1.46	0.9546

Secondary Extinction Coefficient = $0.848(60) \times 10^{-6}$

6) $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

The peaks on a Harker plane ($u, 0, w$) and a Harker line ($0, v, 0.5$) were assigned to the Rh-Rh vectors ($2x, 0, 0.5+2z$) and ($0, 2y, 0.5$), respectively, from which the coordinates of Rh were unambiguously obtained and confirmed by the presence of a strong intramolecular Rh-Rh vector at ($2x, 2y, 2z$). The position of P was also calculated from an intramolecular Rh-P vector. A Fourier map computed based on this initial phasing model yielded the structure of the rhodium tetraacetate nucleus and fragments of the phenoxy groups. An additional Fourier calculation produced the final solution of the structure. The structure refined isotropically in four cycles to convergence at $R=0.18$ and $R_w=0.34$. A difference synthesis, constructed after the anisotropic refinement of atoms with no hydrogen atoms reached convergence at $R=0.12$, showed the presence of solvent molecules (toluene) with a two-fold rotational disorder about the y axis. The electron density was so severely dispersed that the maximum peak contained only $3.5 \text{ e}/\text{\AA}^3$. An attempt was made to separate two orientations (Fig. 4) by creating half-weighted atoms for each of C(42) and C(43), but it failed.

Examination of general planes of a difference synthesis perpendicular to the C-CH₃ axes yielded the positions of all hydrogen atoms on C(2) and two on C(4). The missing hydrogen atom on C(4) was assigned to a theoretical position. The positions of aromatic hydrogen atoms were calculated assuming a trigonal planar geometry at C-H distances of $0.95 \overset{\text{O}}{\text{\AA}}$. In the final cycles of the refinement C(41), C(44), and C(45) were given a population factor of 0.5 and

Fig. 4. Disorder of Solvent Molecule (viewed down the b axis). The molecule is approximately coplanar with the ac plane.

Table 16. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

<u>Model</u>	<u>No. of Variables</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. Rh, P Iso B=3.0		41.6			1.0
S.F. Rh, P, 4O's, 11C's Iso B=3		36.4			1.0
S.F. All Non-hydrogen Atoms Iso B=3.0		33.5			1.0
L.S. Full Matrix, Shift=0.8 All Coordinates Refined Iso B=3.0	109	26.7	48.2	7.86	1.0615
L.S. All Coordinates and B's Refined	145	18.2	34.2	5.63	1.0372
L.S. Aniso for Atoms with No Hydrogen Atoms	240	12.0	26.7	4.41	1.0100
L.S. Anisotropic Refinement for All Atoms Hydrogens Refined Solvent Molecule Included	409	6.8	7.5	1.25	0.9207
L.S. 4029 Data with F's > 3σ's	409	3.6	6.3	1.43	0.9214

hydrogen atoms were allowed to vary. The refinement was considered complete when there were no changes in the agreement factors. Shifts for the non-hydrogen atoms were less than 1/10 and those for hydrogen atoms less than 1/5 of the standard deviations. At the conclusion of the refinement R was 0.068, R_w 0.075, and GOF 1.25 for $n_o=7073$ data and $n_p=409$ parameters. The maximum peak in the final difference map was $0.96 \text{ e}/\text{\AA}^3$ in the proximity of C(4) and the minimum was $-0.80 \text{ e}/\text{\AA}^3$, not associated with any particular atom. The average noise level was $\pm 0.30 \text{ e}/\text{\AA}^3$.

Elimination of reflections having intensities less than 3σ substantially improved the agreement factors to $R=0.036$ and $R_w=0.063$, although GOF increased slightly to 1.43 for 4029 data and 409 parameters. However, the results given in the ensuing sections are those from the refinement with 7073 data.

The summary of solution and refinement is given in Table 16.

7) $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

A Patterson map constructed for an octant of a unit cell showed six major peaks with similar intensities on Harker planes; two peaks on each of $(u, 0.5, w)$, $(0.5, v, w)$, and $(u, v, 0.5)$ planes. These were assigned to appropriate Rh-Rh vectors, e.g., $(2x, 0.5, 0.5+2z)$ or $(2\bar{x}, 0.5, 0.5+2z)$, $(0.5, 0.5+2y, 2z)$ or $(0.5, 0.5-2y, 2z)$, and $(0.5+2x, 2y, 0.5)$ or $(0.5+2x, 2\bar{y}, 0.5)$, from which four sets of coordinates for each of the two independent rhodium atoms were determined as the probable positions. Correct locations were selected by inspection such that the Rh-Rh vector within the molecule gave a

reasonable distance from the origin. A Fourier map was calculated to locate all oxygen atoms in the acetate bridges. The remaining non-hydrogen atoms were found from a difference synthesis. Four cycles of anisotropic refinement for all but the methyl carbon atoms resulted in $R=0.062$ and $R_w=0.159$. All hydrogen atoms were located from a difference synthesis computed at this stage. With inclusion of hydrogen atoms, the methyl carbon atoms were refined anisotropically. A correction factor for the secondary extinction effect was introduced. Although the refinement of hydrogen atoms to convergence gave lower agreement factors $R=0.023$, $R_w=0.046$, and $GOF=1.40$, some of final parameters were unreasonable; some of the C-H distances were as short as $0.5\text{--}0.7\text{ \AA}$ and the H-C-H angles showed a large variation from 90° to 130° . Consequently, the hydrogen atoms were fixed at best theoretical positions calculated by a least squares fit of the refined positions with C-H distances of $0.95\text{ \AA}$. The refinement was continued until a convergence was attained at $R=0.025$, $R_w=0.052$, $GOF=1.58$ with near zero shifts for most of the parameters. The hydrogen atom positions were recalculated after each cycle of final refinement such that a tetrahedral geometry was maintained for each methyl group.

In order to determine the absolute configuration of the molecule, the signs of all z coordinates were changed. The new configuration converged in four cycles to $R=0.023$, $R_w=0.050$, and $GOF=1.53$. This new configuration was considered to be the correct configuration not only because the final discrepancy factors were lower but also because the Hamilton's R-factor ratio test⁶¹ indicated that we can reject at

Table 17. Summary of Solution and Refinement for $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

<u>Model</u>	<u>No. of Variable</u>	<u>R(%)</u>	<u>R_w(%)</u>	<u>GOF</u>	<u>Scale Factor</u>
S.F. 2Rh's Iso B=3.0		44.1			1.0
S.F. 2Rh's, 80's Iso B=3.0		41.9			1.0
S.F. All Non-hydrogen Atoms Iso B=3.0		38.8			1.0
L.S. All Coordinates Refined Iso B=3.0	80	25.0	46.7	14.1	1.0092
L.S. All Coordinates Anisotropic Refinement	208	6.2	15.9	4.78	1.0114
L.S. Hydrogen Atoms Refined Secondary Extinction	257	2.3	4.6	1.40	0.9808
L.S. Hydrogen Atoms Fixed at Calculated Positions with B=6.0	209	2.5	5.2	1.58	0.9807
L.S. All z's → -z's	209	2.4	5.0	1.53	0.9804

Secondary Extinction Coefficient = $0.487(10) \times 10^{-6}$

99.5 % confidence level the old configuration;

$$\mathcal{R} = \frac{R_w(\text{old})}{R_w(\text{new})} = \frac{0.0522}{0.0504} = 1.036$$

and

$$\begin{aligned} \mathcal{R} > \mathcal{R}_{b,n,\alpha} &= \mathcal{R}_{1,2308,0.005} = 1 + \frac{120}{2308} (\mathcal{R}_{1,120,0.005} - 1) \\ &= 1 + \frac{120}{2308} (1.036 - 1) = 1.002 \end{aligned}$$

where b is the dimension of the hypothesis, N the number of observation minus the number of variables, α the significance level. The final difference map based on this new configuration contained a maximum of $0.69 \text{ e/\AA}^3$ and a minimum of $-0.66 \text{ e/\AA}^3$. The noise was $\pm 0.25 \text{ e/\AA}^3$ on the average.

The summary of solution and refinement is given in Table 17.

C. Results

The final coordinates and thermal parameters with estimated standard deviations as determined from the inverse matrix of the final least squares cycles are listed in Tables 18-24. The distances and angles are set out in Tables 25-52, along with the least squares planes and close intermolecular distances. The perspective views of the molecules with the numbering conventions and packing diagrams are drawn in Figures 5-18 at 50 % and 25 % probability levels, respectively, with an exception of the $P(OPh)_3$ adduct for which the perspective view is drawn at 25 % probability level because of large thermal motions of individual atoms.

The standard deviations for the distances were estimated by

$$\sigma_{A-B} \cong [\bar{\sigma}_A^2 + \bar{\sigma}_B^2]^{\frac{1}{2}}$$

where

$$\bar{\sigma}_A = \frac{a\sigma_A(x) + b\sigma_A(y) + c\sigma_A(z)}{3}$$

$$\bar{\sigma}_B = \frac{a\sigma_B(x) + b\sigma_B(y) + c\sigma_B(z)}{3}$$

$\sigma_A(x) \cdots \sigma_B(z)$ are the standard deviations for the positional parameters for the specified axes and a, b, and c represent the unit cell distances. The estimated errors in the angles were computed using the mean positional standard deviations, $\bar{\sigma}$. For an angle A-C-B,

$$\sigma_{\theta(A,B)} = \arctan \frac{\bar{\sigma}_A}{D_{A-C}}$$

and the error is

$$\sigma_{\theta} \cong \sigma_{\theta(A)} + \sigma_{\theta(B)}$$

Anisotropic temperature factors listed in Tables 18-24 are in the form

$$\exp(-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$$

and their isotropic equivalents are also given for comparison.

Table 18. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh(1)	0(0)	5574(1)	25000(0)	221(1)	138(1)	202(1)	0(0)	-33(1)	0(0)	1.47
Rh(2)	0(0)	19663(1)	25000(0)	212(1)	139(1)	186(1)	0(0)	-33(1)	0(0)	1.41
O(1)	14048(16)	6000(8)	35590(12)	317(8)	223(8)	300(8)	19(6)	-104(7)	13(6)	2.17
O(2)	15068(16)	5965(8)	12513(12)	299(8)	224(8)	255(7)	28(6)	26(6)	0(5)	2.08
O(3)	13561(17)	19234(8)	36067(12)	348(9)	223(8)	286(8)	-12(6)	-132(7)	-2(6)	2.20
O(4)	15670(16)	19208(8)	12967(12)	316(8)	217(7)	287(8)	-9(6)	41(7)	28(6)	2.21
C(1)	17755(19)	12607(14)	38851(14)	258(9)	294(9)	231(8)	-15(9)	-51(7)	22(9)	2.05
C(2)	28094(28)	12503(19)	46668(21)	416(13)	409(13)	399(12)	11(13)	-207(11)	-6(13)	3.12
C(3)	19832(19)	12572(13)	9326(14)	265(9)	279(9)	220(8)	25(9)	-25(7)	13(9)	2.01
C(4)	31520(26)	12513(19)	605(20)	392(12)	401(13)	371(11)	34(13)	123(10)	4(13)	3.16
C(5)	1780(27)	88451(14)	33891(21)	475(14)	278(12)	422(12)	3(11)	-42(11)	76(10)	3.10
C(6)	1911(40)	80364(16)	34193(30)	779(23)	303(15)	650(20)	40(14)	-50(18)	167(13)	4.58
C(7)	0(0)	76355(25)	25000(0)	1027(44)	134(21)	889(39)	0(0)	30(33)	0(0)	5.48
C(8)	10787(21)	36774(13)	27472(15)	275(9)	274(10)	268(9)	-4(9)	-43(7)	-6(8)	2.14
C(9)	11181(29)	44875(14)	27553(20)	458(14)	279(11)	362(12)	-140(10)	-52(11)	-23(9)	2.89
C(10)	0(0)	48941(20)	25000(0)	657(26)	164(17)	377(18)	0(0)	-26(18)	0(0)	3.17
N(1)	0(0)	92459(15)	25000(0)	311(15)	178(13)	346(15)	0(0)	-28(12)	0(0)	2.20

Table 18. (Continued)

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
N(2)	0(0)	32733(14)	25000(0)	267(13)	179(12)	198(11)	0(0)	-16(10)	0(0)	1.70

Fractional Coordinates($\times 10^3$) and Isotropic Thermal Parameters of Hydrogen Atoms

Atom	X	Y	Z	B
H(21)	263(3)	85(2)	520(3)	4.9(0.8)
H(22)	285(3)	173(2)	503(2)	4.4(0.8)
H(23)	356(4)	119(2)	433(3)	6.3(1.0)
H(41)	333(4)	173(2)	-23(3)	5.4(0.8)
H(42)	298(3)	87(2)	-40(3)	4.7(0.8)
H(43)	394(4)	112(2)	39(3)	5.3(0.8)
H(5)	36(3)	910(2)	403(2)	4.2(0.7)
H(6)	41(3)	780(2)	401(3)	4.6(0.7)
H(7)	0(0)	708*	250(0)	2.5(0.9)
H(8)	190(3)	339(2)	285(2)	3.5(0.6)
H(9)	187(3)	470(2)	287(2)	2.9(0.6)
H(10)	0(0)	539(3)	250(0)	7.0(1.5)

* Calculated Y coordinate based on the C-H distance of 0.95 Å.
The final least squares cycle gave 724(3).

Table 19. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh	3736(2)	6749(4)	-4993(2)	355(2)	469(2)	404(2)	-28(2)	29(2)	8(2)	3.23
N	11233(26)	18181(51)	-14733(27)	810(28)	585(26)	705(29)	-85(23)	319(27)	48(25)	5.53
O(1)	-6285(16)	21634(38)	-6637(18)	435(15)	531(17)	560(20)	8(14)	20(14)	69(16)	4.02
O(2)	13227(17)	-8906(37)	-2792(18)	413(15)	602(19)	558(19)	24(14)	32(15)	67(17)	4.14
O(3)	-1167(18)	-10197(37)	-12274(18)	545(16)	591(20)	461(18)	-67(16)	26(16)	-26(16)	4.20
O(4)	8212(17)	22855(39)	2935(17)	458(15)	571(19)	489(19)	-110(15)	14(14)	0(16)	4.00
C(1)	-12448(25)	19271(54)	-2486(27)	429(21)	507(25)	512(26)	8(21)	-23(21)	-16(23)	3.81
C(2)	-19928(25)	29991(64)	-4182(32)	459(24)	817(34)	943(43)	179(25)	-51(29)	219(35)	5.84
C(3)	6004(24)	21044(59)	9801(28)	408(21)	516(25)	529(27)	-25(20)	-23(20)	-76(24)	3.82
C(4)	9424(30)	32941(62)	15476(32)	776(34)	665(32)	645(33)	-93(28)	4(30)	-201(30)	5.49
C(5)	10132(68)	34414(98)	-16612(57)	3263(128)	777(50)	1666(89)	-96(72)	1637(96)	56(57)	15.02
C(6)	10129(43)	47507(83)	-12074(44)	1264(58)	811(45)	1109(61)	18(44)	210(53)	18(44)	8.38
C(7)	13205(44)	5969(91)	-20490(39)	1217(56)	1339(57)	930(51)	-359(50)	560(46)	-219(53)	9.18
C(8)	19298(40)	8799(97)	-26409(40)	1215(53)	1573(65)	895(51)	2(55)	317(50)	-226(56)	9.69

Table 19. (Continued) Fractional Coordinates($\times 10^3$) of Hydrogen Atoms*

<u>Atom</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>B</u>	<u>Atoms</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>B</u>
H(21)	250	150	70	6.0	H(83)	170	0	-310	6.0
H(22)	250	250	20	6.0	H(1)	170	210	-160	6.0
H(23)	310	110	30	6.0					
H(41)	60	374	200	6.0	* Not refined				
H(42)	150	260	170	6.0					
H(43)	110	430	125	6.0					
H(51)	47	345	-190	6.0					
H(52)	140	367	-205	6.0					
H(61)	50	490	-95	6.0					
H(62)	140	480	-95	6.0					
H(63)	93	600	-140	6.0					
H(71)	83	21	-225	6.0					
H(72)	152	-14	-167	6.0					
H(81)	150	170	-280	6.0					
H(82)	220	110	-230	6.0					

Table 20. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh	43767(1)	3272(1)	41941(2)	186(1)	292(1)	244(1)	29(1)	-25(1)	-8(1)	1.90
O(1)	37095(10)	8310(14)	61155(18)	265(7)	469(9)	341(9)	92(7)	11(6)	-72(8)	2.83
O(2)	38007(9)	-11931(13)	43891(17)	242(6)	345(7)	326(8)	-14(6)	-43(6)	6(7)	2.40
O(3)	51333(10)	-2003(12)	23910(16)	299(7)	393(8)	237(7)	12(6)	19(6)	-25(7)	2.45
O(4)	50536(9)	17940(13)	40880(17)	292(6)	302(7)	414(9)	-3(6)	-110(7)	14(7)	2.65
O(5)	27029(11)	12778(17)	22106(21)	469(9)	838(14)	406(10)	218(11)	-136(9)	20(10)	4.51
C(1)	40848(15)	6641(18)	73961(28)	278(9)	318(9)	345(11)	-31(8)	78(9)	-59(10)	2.48
C(2)	41931(14)	-19249(17)	51755(26)	257(8)	323(10)	314(10)	10(8)	3(8)	-20(9)	2.35
C(3)	35794(20)	10491(25)	87865(32)	474(14)	403(13)	404(13)	-64(12)	193(12)	-121(12)	3.37
C(4)	37554(20)	-30388(23)	52553(40)	416(13)	367(12)	544(16)	-71(11)	-108(13)	28(13)	3.49

Fractional Coordinates($\times 10^3$) and Isotropic Temperature Factors of Hydrogen Atoms

H(1)	379(2)	158(3)	907(3)	3.3(0.6)
H(2)	354(2)	53(2)	950(3)	4.3(0.8)
H(3)	296(2)	130(3)	843(4)	6.9(0.9)
H(4)	311(2)	-297(3)	527(4)	6.0(0.8)
H(5)	393(2)	-344(3)	608(4)	5.6(0.8)
H(6)	394(3)	-340(4)	442(5)	8.2(1.2)

Table 21. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh	41555(2)	0(0)	0(0)	200(2)	261(2)	265(2)	0(0)	0(0)	2(10)	1.91
P	25237(10)	0(0)	0(0)	196(5)	756(12)	758(14)	0(0)	0(0)	-24(84)	4.50
O(1)	42204(59)	10085(70)	10119(72)	222(32)	455(53)	369(59)	149(38)	59(29)	-75(39)	2.75
O(2)	57933(69)	9966(62)	9946(66)	459(47)	248(38)	271(45)	66(34)	4(34)	-38(30)	2.52
C(1)	50285(101)	12903(26)	12808(26)	467(27)	253(17)	263(15)	-162(48)	-165(46)	14(13)	2.59
C(2)	50433(229)	20275(27)	20193(25)	741(53)	277(16)	281(15)	26(72)	-68(80)	-68(14)	3.42
F(1)	20800(141)	7735(156)	7268(176)	546(88)	744(98)	1489(166)	330(68)	154(80)	474(96)	7.31
F(2)	20102(122)	4124(122)	-7770(124)	488(59)	2238(337)	503(70)	414(116)	-306(50)	-300(108)	8.50
				<u>B</u>						
F(31)	20628(221)	8569(213)	-6847(174)	3.23(0.45)						
F(32)	18897(86)	6599(119)	1797(119)	3.85(0.32)						
Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of Fluorine Atoms before the Separation of F(3) into F(31) and F(32)										
F(1)	20677(116)	7889(197)	7599(202)	414(56)	693(77)	891(95)	128(54)	33(56)	-498(74)	5.26
F(2)	20002(138)	4196(137)	-7629(167)	526(79)	2500(505)	448(76)	596(170)	-309(66)	-207(148)	10.42
F(3)	19885(161)	7305(202)	-3312(253)	814(123)	718(106)	3305(636)	440(97)	-1099(263)	-590(216)	12.65

Table 22. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh	10700(2)	4065(1)	17409(3)	185(1)	236(1)	189(1)	-27(1)	131(1)	-19(1)	1.69
P	32162(6)	11494(4)	53691(10)	205(2)	269(3)	229(3)	-28(2)	148(2)	-30(2)	1.98
O(1)	995(16)	6275(11)	26666(28)	279(7)	393(9)	278(8)	-41(7)	215(7)	-63(7)	2.45
O(2)	18483(16)	1342(12)	4943(30)	268(7)	458(7)	336(8)	-56(7)	239(7)	-74(8)	2.69
O(3)	478(15)	14457(10)	-4823(28)	306(8)	261(8)	276(8)	-29(6)	181(6)	22(7)	2.56
O(4)	19231(16)	92937(10)	36652(28)	275(8)	279(8)	244(8)	-12(7)	142(7)	6(7)	2.58
O(5)	35498(18)	8730(12)	75954(30)	368(9)	490(11)	275(8)	-73(8)	228(8)	-31(8)	3.11
O(6)	47469(17)	9660(13)	65196(30)	274(8)	500(11)	338(9)	50(8)	216(8)	21(8)	3.04
O(7)	32831(17)	21685(10)	54476(32)	345(8)	287(8)	444(10)	-16(7)	273(8)	-30(8)	3.05
C(1)	11177(23)	96891(15)	85998(40)	297(10)	323(12)	292(10)	52(9)	234(9)	62(10)	2.29
C(2)	17618(32)	95238(23)	77996(55)	413(14)	514(18)	417(14)	43(14)	353(13)	32(14)	3.16
C(3)	11995(23)	86234(15)	26506(41)	310(10)	304(12)	273(11)	12(9)	218(9)	8(9)	2.34
C(4)	18888(36)	78251(21)	41490(61)	482(17)	338(13)	423(16)	52(13)	263(15)	100(13)	3.97
C(5)	47576(34)	11808(27)	470(51)	433(15)	636(21)	272(13)	44(15)	220(12)	-59(14)	3.93
C(6)	49747(32)	11391(23)	51363(61)	371(14)	546(20)	530(17)	25(14)	357(14)	37(16)	3.64
C(7)	20484(36)	26212(26)	44380(75)	454(16)	494(21)	605(22)	92(15)	315(17)	-137(17)	4.84

Table 22. (Continued) Fractional Coordinates($\times 10^3$) and Isotropic Temperature Parameters of Hydrogen Atoms

Atom	X	Y	Z	B
H(1)	132(3)	-91(2)	666(6)	6.1(1.0)
H(2)	272(4)	-59(2)	922(7)	6.2(0.9)
H(3)	177(4)	-6(2)	729(6)	4.8(0.9)
H(4)	127(3)	739(2)	333(6)	5.3(0.8)
H(5)	205(5)	786(3)	542(8)	9.8(1.5)
H(6)	277(4)	777(2)	485(7)	6.4(1.0)
H(7)	450(4)	333(3)	536(8)	8.7(1.3)
H(8)	489(5)	426(3)	589(9)	8.9(1.4)
H(9)	569(5)	383(3)	570(8)	10.0(1.4)
H(10)	580(3)	87(3)	592(6)	5.7(0.9)
H(11)	503(3)	176(2)	506(6)	5.1(0.8)
H(12)	424(3)	82(3)	352(6)	5.5(0.9)
H(13)	215(5)	311(3)	436(10)	10.7(1.7)
H(14)	118(4)	244(3)	302(7)	8.0(1.1)
H(15)	196(5)	270(3)	542(8)	10.2(1.6)

Table 23. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh	22918(1)	16822(2)	-2290(1)	485(1)	301(1)	430(1)	6(1)	-285(1)	-43(1)	2.98
P	18822(3)	677(8)	-6832(4)	507(5)	341(4)	427(4)	-20(4)	-259(4)	-48(4)	3.24
O(1)	31188(8)	13133(20)	-9667(10)	507(12)	422(12)	510(13)	10(10)	-248(11)	-94(10)	3.77
O(2)	14924(9)	21789(21)	5535(10)	501(13)	488(13)	579(14)	-3(11)	-274(12)	-100(11)	4.07
O(3)	22412(9)	32130(20)	-8032(10)	706(14)	397(12)	575(13)	-1(12)	-462(12)	-7(11)	3.90
O(4)	23739(9)	2892(20)	3805(10)	658(14)	355(11)	558(13)	-32(11)	-397(12)	35(10)	3.78
O(5)	22479(9)	-6076(20)	-14138(10)	622(13)	458(12)	428(12)	-94(12)	-176(11)	-92(10)	4.21
O(6)	13290(9)	6775(21)	-7157(11)	650(14)	443(13)	808(16)	93(12)	-485(14)	-169(12)	4.55
O(7)	16659(10)	-13785(20)	-3322(10)	812(16)	377(12)	464(12)	-98(12)	-268(12)	0(10)	4.45
C(1)	35367(14)	19710(29)	-9847(15)	559(20)	425(19)	462(18)	44(15)	-240(16)	-17(14)	3.82
C(2)	41241(17)	17268(53)	-15796(24)	584(21)	861(28)	681(25)	-19(28)	-109(21)	-153(25)	6.22
C(3)	24302(13)	43617(30)	-7702(15)	549(19)	394(17)	466(18)	41(15)	-263(16)	-8(14)	3.64
C(4)	24231(22)	54219(39)	-12464(22)	1144(33)	515(21)	686(24)	-74(25)	-608(24)	156(19)	5.61
C(11)	27469(16)	12842(35)	-21378(17)	744(24)	488(19)	562(20)	-55(19)	-365(20)	-52(17)	4.56
C(12)	32311(21)	17191(43)	-27313(20)	1184(34)	611(24)	632(24)	-253(26)	-523(25)	104(21)	6.10
C(13)	36446(21)	8371(55)	-31347(21)	889(32)	1127(38)	528(24)	-330(31)	-206(25)	64(26)	6.93
C(14)	35973(20)	-4996(51)	-29686(20)	807(29)	965(33)	624(26)	108(30)	-151(25)	-117(25)	6.93
C(15)	31271(17)	-9476(39)	-23941(17)	722(24)	633(23)	482(20)	57(21)	-213(20)	-9(19)	5.07
C(16)	27115(13)	-478(32)	-19830(14)	549(20)	538(19)	383(16)	-59(17)	-254(15)	-43(15)	3.77
C(21)	6109(17)	-8130(41)	-7301(20)	588(23)	734(26)	704(26)	-23(21)	-317(20)	15(22)	5.30
C(22)	3309(16)	-13352(45)	-10698(24)	594(23)	806(29)	1012(32)	-146(23)	-436(25)	-33(25)	6.18
C(23)	4902(17)	-9431(47)	-17090(23)	701(25)	927(31)	988(32)	24(24)	-610(26)	-135(27)	6.21
C(24)	9286(20)	-673(50)	-20305(22)	921(30)	1004(34)	872(32)	-92(28)	-660(26)	173(27)	6.60

Table 23. (Continued) Fractional Coordinates ($\times 10^5$) and Anisotropic Thermal Parameters ($\times 10^4$) of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
C(25)	12156(17)	4691(40)	-17072(21)	730(25)	718(25)	852(27)	-163(22)	-525(23)	239(22)	5.57
C(26)	10522(14)	925(33)	-10568(17)	525(19)	444(18)	712(22)	51(17)	-385(18)	-83(17)	4.13
C(31)	9485(16)	-9257(38)	8193(18)	702(23)	594(22)	570(21)	162(20)	-287(20)	1(18)	4.96
C(32)	6976(18)	-13196(44)	15001(20)	792(26)	857(30)	582(23)	249(25)	-199(22)	-89(22)	6.29
C(33)	9086(20)	-24011(43)	16906(19)	1058(32)	702(26)	515(23)	-23(27)	-308(24)	100(20)	6.21
C(34)	13828(18)	-30841(34)	12131(19)	941(28)	469(22)	765(25)	62(20)	-530(24)	15(18)	5.32
C(35)	16379(15)	-27156(34)	5432(17)	594(21)	439(18)	574(21)	29(17)	-267(19)	-59(16)	4.27
C(36)	14114(13)	-16492(32)	3576(14)	545(18)	392(15)	462(17)	-53(17)	-242(15)	-22(15)	3.67
<u>Solvent Molecule</u>										
C(41)	3085(41)	48112(164)	-246(57)	627(58)	1972(144)	929(76)	-597(79)	-418(59)	896(92)	9.13
C(42)	6989(38)	49651(133)	1448(45)	1755(74)	2994(112)	1698(74)	-873(84)	-1027(68)	1330(77)	16.31
C(43)	1372(39)	39498(78)	-3203(29)	1598(63)	1843(77)	900(44)	-1020(60)	-479(47)	611(45)	11.80
C(44)	-2456(72)	39224(141)	-4141(61)	1501(127)	1317(115)	1202(103)	-754(101)	-371(97)	638(88)	11.48
C(45)	6795(56)	38447(114)	-2167(49)	1264(95)	1025(82)	769(65)	153(75)	-208(70)	329(59)	8.95

Table 23. (Continued) Fractional Coordinates($\times 10^3$) and Isotropic Temperature Factors of Hydrogen Atoms

Atom	X	Y	Z	B
H(1)	432(2)	229(5)	-170(2)	11.3(1.4)
H(2)	437(2)	121(6)	-153(3)	13.0(1.6)
H(3)	421(2)	118(6)	-201(3)	12.7(1.5)
H(4)	247(2)	512(4)	-168(2)	8.2(1.1)
H(5)	272(2)	605(5)	-140(2)	11.2(1.4)
H(6)	217(3)	589(6)	-105(3)	13.7(1.6)
H(11)	250(1)	187(3)	-188(1)	4.0(0.7)
H(12)	317(1)	260(3)	-279(1)	5.2(0.8)
H(13)	393(2)	106(4)	-356(2)	7.5(1.0)
H(14)	389(2)	-106(4)	-321(2)	8.5(1.1)
H(15)	307(1)	-183(3)	-224(2)	6.2(0.9)
H(21)	50(1)	-116(3)	-30(2)	5.4(0.8)
H(22)	6(1)	-190(3)	-83(2)	5.4(0.9)
H(23)	28(1)	-132(4)	-192(2)	7.1(1.0)
H(24)	106(2)	19(4)	-246(2)	7.6(1.0)
H(25)	157(1)	108(3)	-195(2)	6.0(0.9)
H(31)	81(1)	-22(3)	69(1)	5.0(0.8)
H(32)	38(2)	-64(4)	182(2)	9.8(1.2)
H(33)	74(1)	-263(3)	219(2)	6.5(0.9)
H(34)	157(1)	-384(3)	140(1)	5.5(0.8)
H(35)	200(1)	-320(3)	19(2)	5.8(0.9)

Table 24. Fractional Coordinates($\times 10^5$) and Anisotropic Thermal Parameters($\times 10^3$) of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23	Equiv. Iso B
Rh(1)	43814(4)	-3226(2)	-63516(2)	152(1)	110(1)	127(1)	-19(1)	-15(1)	0(1)	1.02
Rh(2)	62024(4)	10083(2)	-56471(2)	138(1)	120(1)	115(1)	-8(1)	-5(1)	-16(1)	0.98
O(1)	28027(41)	-3571(24)	-52893(18)	201(14)	255(13)	164(12)	-51(13)	9(12)	-5(13)	1.63
O(2)	60142(39)	-2086(20)	-73626(17)	225(15)	206(13)	156(12)	-41(12)	16(12)	-39(11)	1.54
O(3)	61120(42)	-13989(19)	-58891(19)	201(14)	131(11)	266(14)	18(11)	-29(13)	43(11)	1.58
O(4)	27933(41)	8196(21)	-68238(20)	184(14)	177(13)	219(14)	-6(11)	-57(12)	12(12)	1.52
O(5)	43856(43)	9231(22)	-46820(17)	217(13)	268(13)	149(12)	-15(14)	22(12)	-31(12)	1.67
O(6)	77667(38)	9668(22)	-66983(17)	182(13)	182(12)	173(12)	-40(12)	40(11)	-12(13)	1.41
O(7)	77009(42)	-1868(21)	-51783(19)	196(13)	176(14)	217(14)	25(12)	-54(12)	10(12)	1.55
O(8)	44921(43)	20405(19)	-61795(18)	220(14)	139(11)	228(14)	17(11)	-25(13)	-6(11)	1.55
O(9)	9427(48)	-12201(30)	-67971(27)	264(19)	549(23)	520(24)	-151(18)	-69(18)	-101(21)	3.51
O(10)	66618(61)	28800(26)	-78413(26)	554(26)	308(18)	555(26)	136(18)	-18(23)	204(19)	3.73
O(11)	98475(45)	17265(26)	-53812(23)	202(15)	310(16)	370(19)	-49(13)	-12(14)	-96(15)	2.32
N(1)	26227(57)	-13533(26)	-68452(24)	275(19)	216(16)	183(17)	-92(15)	-48(16)	0(14)	1.78
N(2)	82667(51)	18304(26)	-52610(24)	250(19)	179(15)	197(17)	-23(14)	-11(15)	-44(14)	1.65
C(1)	30903(55)	2633(33)	-47067(24)	156(16)	260(19)	147(16)	27(17)	-9(15)	31(17)	1.48
C(2)	17647(61)	2168(40)	-39785(27)	239(21)	484(27)	184(19)	-71(21)	50(17)	0(21)	2.39
C(3)	73857(58)	4169(29)	-73149(24)	212(18)	147(16)	155(16)	25(16)	22(15)	17(15)	1.36
C(4)	86465(66)	5078(32)	-80524(26)	255(21)	298(21)	182(18)	-13(19)	63(18)	-4(16)	1.93
C(5)	73989(56)	-11035(30)	-54080(25)	166(16)	199(17)	206(18)	6(16)	12(15)	53(16)	1.51
C(6)	87092(71)	-18900(31)	-50614(32)	272(21)	227(19)	374(25)	54(19)	-67(23)	69(19)	2.30
C(7)	31733(56)	17424(29)	-66638(26)	155(17)	164(16)	202(18)	8(15)	12(16)	26(15)	1.37
C(8)	20089(70)	25517(34)	-70624(33)	294(23)	210(19)	409(27)	10(19)	-72(23)	97(20)	2.40

Table 24. (Continued) Fractional Coordinates ($\times 10^3$) and Isothermal Temperature Factors of Hydrogen Atoms

<u>Atom</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>B</u>
H(1)	93	78	-400	6.0
H(2)	107	-40	-400	6.0
H(3)	247	24	-348	6.0
H(4)	955	-2	-804	6.0
H(5)	926	115	-804	6.0
H(6)	792	46	-854	6.0
H(7)	802	-236	-473	6.0
H(8)	963	-156	-473	6.0
H(9)	930	-224	-550	6.0
H(10)	279	297	-740	6.0
H(11)	107	224	-740	6.0
H(12)	143	295	-664	6.0

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Table 25. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Distance(Å)</u>	<u>Bond</u>	<u>Distance(Å)</u>
Rh(1)-Rh(2)	2.3963(2)	C(2)-H(21)	0.95(3)
Rh(1)-O(1)	2.035(2)	C(2)-H(22)	0.93(3)
Rh(1)-O(2)	2.038(2)	C(2)-H(23)	0.82(4)
Rh(2)-O(3)	2.042(2)	C(4)-H(41)	0.89(4)
Rh(2)-O(4)	2.040(2)	C(4)-H(42)	0.91(3)
Rh(1)-N(1)	2.231(3)	C(4)-H(43)	0.96(4)
Rh(2)-N(2)	2.223(2)	C(5)-H(5)	0.95(3)
O(1)-C(1)	1.265(3)	C(6)-H(6)	0.88(3)
O(2)-C(3)	1.266(3)	C(7)-H(7)	0.95*
O(3)-C(1)	1.265(3)	C(8)-H(8)	0.97(3)
O(4)-C(3)	1.269(3)	C(9)-H(9)	0.85(3)
C(1)-C(2)	1.498(4)	C(10)-H(10)	0.85(6)
C(3)-C(4)	1.500(3)	O(1)...O(3)	2.252(2)
C(5)-C(6)	1.376(4)	O(2)...O(4)	2.254(2)
C(6)-C(7)	1.371(4)		
C(8)-C(9)	1.379(3)		
C(9)-C(10)	1.376(3)		
N(1)-C(5)	1.336(3)		
N(2)-C(8)	1.338(3)		

Average Distances of Equivalent Bonds

Rh-O	2.039(2)
Rh-N	2.227(3)
O-C	1.266(3)
C-CH ₃	1.499(4)
C-N	1.337(3)
C-C	1.376(3)

* Theoretical Value. The least squares refinement gave 0.67(4). The coordinates of H(7) were accordingly calculated based on this distance.

Table 26. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$ with Estimated Standard Deviations

Bond	Angle($^\circ$)	Bond	Angle($^\circ$)	Bond	Angle($^\circ$)
Rh(2)-Rh(1)-O(1)	87.96(5)	N(1)-C(5)-C(6)	122.39(26)	N(1)-C(5)-H(5)	121(2)
Rh(2)-Rh(1)-O(2)	88.13(5)	C(5)-C(6)-C(7)	118.12(32)	C(6)-C(5)-H(5)	116(2)
Rh(1)-Rh(2)-O(3)	87.95(4)	C(5)-C(7)-C(6')	120.36(40)	C(5)-C(6)-H(6)	119(2)
Rh(1)-Rh(2)-O(4)	87.87(4)	N(2)-C(8)-C(9)	122.63(23)	C(7)-C(6)-H(6)	123(2)
O(1)-Rh(1)-N(1)	92.04(7)	C(8)-C(9)-C(10)	118.44(26)	C(6)-C(7)-H(7)	120(2)
O(2)-Rh(1)-N(1)	91.87(7)	C(9)-C(10)-C(9')	119.66(33)	N(2)-C(8)-H(8)	119(2)
O(3)-Rh(2)-N(2)	92.05(6)	Rh(1)-N(1)-C(5)	120.69(13)	C(9)-C(8)-H(8)	118(2)
O(4)-Rh(2)-N(2)	92.17(6)	C(5)-N(1)-C(5')	118.62(28)	C(8)-C(9)-H(9)	116(2)
O(3)-Rh(2)-O(4)	89.74(7)	Rh(2)-N(2)-C(8)	120.91(13)	C(10)-C(9)-H(9)	125(2)
Rh(1)-O(1)-C(1)	119.30(13)	C(8)-N(2)-C(8')	118.19(26)	C(9)-C(10)-H(10)	120(2)
Rh(1)-O(2)-C(3)	119.07(13)	C(1)-C(2)-H(21)	112(2)	H(21)-C(2)-H(22)	107(3)
Rh(2)-O(3)-C(1)	118.88(13)	C(1)-C(2)-H(22)	112(2)	H(22)-C(2)-H(23)	106(3)
Rh(2)-O(4)-C(3)	119.26(13)	C(1)-C(2)-H(23)	108(3)	H(23)-C(2)-H(21)	110(3)
O(1)-C(1)-C(2)	116.58(22)	C(3)-C(4)-H(41)	113(2)	H(41)-C(4)-H(42)	116(3)
O(3)-C(1)-C(2)	117.59(22)	C(3)-C(4)-H(42)	107(2)	H(42)-C(4)-H(43)	110(3)
O(2)-C(3)-C(4)	116.98(21)	C(3)-C(4)-H(43)	107(2)	H(43)-C(4)-H(41)	105(3)
O(4)-C(3)-C(4)	117.43(21)				
O(1)-C(1)-O(3)	125.83(19)				
O(2)-C(3)-O(4)	125.58(18)				

Table 27. Least Squares Planes of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

<u>Plane</u>							<u>Direction Cosines</u>		
A.	Rh(1)	Rh(2)	O(1)	O(3)	C(1)	C(2)			
	0.013	-0.023	-0.012	-0.027	0.005	-0.011	-0.6577	-0.0150	0.6725
B.	Rh(1)	Rh(2)	O(2)	O(4)	C(3)	C(4)			
	0.033	-0.011	-0.040	0.006	-0.012	0.024	0.7403	-0.0181	0.7527
C.	N(1)	C(5)	C(6)	C(7)	C(6')	C(5')			
	0.000	0.003	-0.003	0.000	0.003	-0.003	-0.9634	0.0000	0.1556
D.	N(2)	C(8)	C(9)	C(10)	C(9')	C(8')			
	0.000	0.001	-0.001	0.000	0.001	-0.001	-0.2677	0.0000	-0.9263
E.	Rh(1)*	O(1)	O(2)	O(1')	O(2')				
	-0.070	0.003	-0.003	0.003	-0.003		0.0000	1.0000	0.0000
F.	Rh(2)*	O(3)	O(4)	O(3')	O(4')				
	0.075	0.002	-0.002	0.002	-0.002		0.0000	1.0000	0.0000

Dihedral Angles(°) Between Planes

A-B	91.1(2.9)	A-D	25.6(2.9)
A-C	33.3(2.9)	B-D	63.3(2.9)
B-C	57.8(2.9)	C-D	58.9(3.5)

* The rhodium atoms are given zero weight in the plane calculations.

Table 28. Short Non-bonded Interatomic Distances of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$

<u>Atoms</u>	<u>Distances($\text{\AA}$)</u>	<u>Atoms</u>	<u>Distances($\text{\AA}$)</u>
<u>Intramolecular</u>			
Rh(1)-C(5)	3.131(2)	Rh(2)-C(8)	3.129(2)
C(1)-C(3)	3.684(3)	O(1)-O(2)	2.884(2)
O(3)-O(4)	2.889(3)	O(1)-C(5)	3.240(3)
O(2)-C(5)	3.420(3)	O(3)-C(8)	3.195(3)
O(4)-C(8)	3.502(3)	O(1)-H(5)	2.78(3)
O(1)-H(21)	2.54(3)	O(3)-H(22)	2.47(3)
O(2)-H(42)	2.44(3)	O(4)-H(41)	2.46(4)
<u>Intermolecular</u>			
O(1)-C(9) ^b	3.377(3)	O(4)-C(4) ^c	3.540(3)
O(1)-C(10) ^b	3.853(2)	O(4)-C(6) ^a	3.787(4)
O(2)-C(9) ^b	3.367(3)	N(2)-C(4) ^c	3.601(3)
C(1)-C(5) ^g	3.735(3)	C(1)-C(6) ^g	3.892(4)
C(2)-C(5) ^g	3.619(4)	C(2)-C(6) ^g	3.802(5)
C(2)-C(8) ^d	3.545(3)	C(2)-C(9) ^d	3.735(4)
C(3)-C(5) ^j	3.837(3)	C(3)-C(6) ^j	3.987(4)
C(4)-C(5) ^j	3.815(4)	C(4)-C(8) ^c	3.518(3)
C(4)-C(8) ^f	3.863(3)	C(4)-C(9) ^c	3.739(4)
C(5)-C(8) ^b	3.833(4)	C(5)-C(9) ^b	3.943(4)
C(6)-C(8) ^b	3.973(5)		

Symmetry list: a;(1/2-x,-1/2+y,1/2-z), b;(1/2-x,1/2+y,1/2-z),
c;(1/2-x,1/2-y,-z), d;(1/2-x,1/2-y,1-z),
e;(1/2+x,1/2-y,-1/2+z), f;(-1/2+x,1/2-y,1/2+z),
g;(-x, -y, 1-z), h;(-1/2+x,-1/2+y,z),
i;(1/2+x,1/2+y,z), j;(x, -y, 1/2+z)

Fig. 5. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$.

Fig. 6. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{py})_2$.

Table 29. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Distance(Å)</u>	<u>Bond</u>	<u>Distance(Å)</u>
Rh-Rh'	2.4020(7)	C(1)-C(2)	1.523(6)
Rh-O	2.046(3)	C(3)-C(4)	1.492(7)
Rh-O(2)	2.031(3)	C(5)*-C(6)*	1.320(11)
Rh-O(3)	2.034(3)	C(7)*-C(8)*	1.461(10)
Rh-O(4)	2.038(3)	N-C(5)*	1.354(9)
Rh-N	2.301(5)	N-C(7)*	1.447(9)
O(1)-C(1)	1.259(5)	<u>Average Distances of Equivalent Bonds</u>	
O(2)-C(1')	1.255(6)	Rh-O	2.038(3)
O(3)-C(3')	1.253(5)	O-C	1.260(6)
O(4)-C(3)	1.273(6)	C-CH ₃	1.508(7)

*Disordered atoms

Table 30. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Angle</u>	<u>Bond</u>	<u>Angle</u>
Rh'-Rh-N	176.6(1)	O(1)-C(1)-O(2')	127.8(3)
Rh'-Rh-O(1)	87.7(1)	O(3')-C(3)-O(4)	126.1(4)
Rh'-Rh-O(2)	88.2(1)	O(1)-C(1)-C(2)	116.2(4)
Rh'-Rh-O(3)	87.9(1)	O(2')-C(1)-C(2)	116.0(4)
Rh'-Rh-O(4)	87.9(1)	O(4)-C(3)-C(4)	117.5(4)
		O(3')-C(3)-C(4)	116.4(4)
Rh-O(1)-C(1)	118.0(3)		
Rh-O(2)-C(1')	118.3(3)	Rh-N-C(5)*	119.7(5)
Rh-O(3)-C(3')	119.4(3)	Rh-N-C(7)*	112.0(4)
Rh-O(4)-C(3)	118.7(3)	C(5)*-N-C(7)*	120.4(6)
		N-C(5)*-C(6)*	127.9(9)
O(1)-Rh-O(2)	175.9(1)	N-C(7)*-C(8)*	123.3(6)
O(3)-Rh-O(4)	175.8(1)		
O(1)-Rh-O(3)	89.1(1)	<u>Average angles of equivalent bonds</u>	
O(1)-Rh-O(4)	90.9(1)	Rh'-Rh-O	87.9(1)
O(2)-Rh-O(3)	90.5(1)	Rh-O-C	118.6(3)
O(2)-Rh-O(4)	89.2(1)	O-C-O	127.0(4)
N-Rh-O(1)	95.0(1)		
N-Rh-O(2)	89.0(1)		
N-Rh-O(3)	90.2(1)		
N-Rh-O(4)	94.1(1)		

* Disordered atoms

Table 31. Least Squares Planes of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

<u>Plane</u>						<u>Direction Cosines</u>			
A.	Rh**	O(1)	O(2)	O(3)	O(4)	0.5047	0.4533	-0.7347	
	0.074	0.001	0.001	-0.001	-0.001				
B.	Rh	Rh	O(1)	O(2')	C(1)	C(2)	0.3525	0.6705	0.6528
	-0.013	-0.016	0.020	0.025	0.017	-0.033			
C.	Rh	Rh	O(4)	O(3')	C(3)	C(4)	-0.7727	0.6145	-0.1593
	-0.001	-0.004	0.004	0.007	0.000	-0.005			
D.	N	C(5)*	C(6)*	C(7)*	C(8)*		-0.8143	0.0647	-0.5769
	-0.156	0.266	-0.128	0.105	-0.087				

Dihedral Angles(°)

A-D	92.6(6.0)	C-D	40.5(2.4)
B-D	50.9(2.6)	B-C	92.0(2.3)

*Disordered atoms

** The rhodium atom was given a zero weight in the plane calculation.

Table 32. Short Non-bonded Intermolecular Distances of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$

<u>Atoms</u>	<u>Distance(Å)</u>	<u>Atoms</u>	<u>Distance(Å)</u>
O(1)-C(8)*c	3.812(8)	C(1)-C(6)*e	3.720(9)
O(1)-C(4) ^e	3.993(6)	C(2)-C(8)*c	3.826(9)
O(2)-C(6)*a	3.891(8)	C(2)-C(4) ^e	3.967(7)
O(2)-C(2) ^d	3.801(6)	C(2)-C(6)*e	3.749(9)
O(3)-C(6)*a	3.858(7)	C(3)-C(6)*e	3.667(8)
O(3)-C(7)*c	3.848(8)	C(4)-C(8)*b	3.816(8)
O(3)-C(8)*c	3.883(8)	C(4)-C(6)*e	3.607(9)
O(4)-C(2) ^d	3.583(5)		

*Disordered atoms

Symmetry list: a;(x,l+y,z), b;(1/2-x1/2-y,-1/2+z), c;(-x,y,-1/2-z)
d;(-1/2+x,1/2-y,-z), e;(-x,l-y,-z)

Fig. 7. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$.

Fig. 8. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{NHEt}_2)_2$.

Table 33. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Distance($\text{\AA}$)</u>	<u>Bond</u>	<u>Distance($\text{\AA}$)</u>
Rh-Rh'	2.4191(3)	C(1)-C(2)	1.498(4)
Rh-O(1)	2.038(2)	C(3)-C(4)	1.494(4)
Rh-O(2)	2.032(2)		
Rh-O(3)	2.027(1)	C(2)-H(1)	0.75(3)
Rh-O(4)	2.033(2)	C(2)-H(2)	0.89(3)
Rh-C(5)	2.095(2)	C(2)-H(3)	0.99(3)
		C(4)-H(4)	0.93(3)
O(1)-C(1)	1.266(3)	C(4)-H(5)	0.91(4)
O(2)-C(3)	1.260(3)	C(4)-H(6)	0.90(4)
O(3)-C(1')	1.271(3)		
O(4)-C(3')	1.272(3)	O(1)...O(3')	2.254(2)
O(5)-C(5)	1.096(3)	O(2)...O(4')	2.245(2)

Average Distances of Equivalent Bonds

Rh-O	2.033(2)
C-O	1.267(3)
C-C	1.496(4)

Table 34. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$ with Estimated Standard Deviations

<u>Bond</u>	<u>Angle(°)</u>	<u>Bond</u>	<u>Angle(°)</u>
Rh'-Rh-C(5)	178.51(6)	O(1)-C(1)-O(3')	125.38(18)
Rh'-Rh-O(1)	87.74(4)	O(2)-C(3)-O(4')	124.92(16)
Rh'-Rh-O(2)	87.32(4)	O(1)-C(1)-C(2)	118.08(20)
Rh'-Rh-O(3)	87.59(4)	O(2)-C(3)-C(4)	118.48(20)
Rh'-Rh-O(4)	87.76(4)	O(3')-C(1)-C(2)	116.54(21)
		O(4')-C(3)-C(4)	116.60(19)
Rh-C(5)-O(5)	175.46(20)		
Rh-O(1)-C(1)	119.35(14)	C(1)-C(2)-H(1)	109.9(2.1)
Rh-O(2)-C(3)	120.39(13)	C(1)-C(2)-H(2)	112.6(2.0)
Rh-O(3)-C(1')	119.93(13)	C(1)-C(2)-H(3)	105.9(2.0)
Rh-O(4)-C(3')	119.58(13)	H(1)-C(2)-H(2)	113.8(3.0)
		H(2)-C(2)-H(3)	112.4(2.9)
O(1)-Rh-O(2)	90.65(6)	H(3)-C(2)-H(1)	101.4(2.9)
O(2)-Rh-O(3)	89.83(6)		
O(3)-Rh-O(4)	89.13(6)	C(3)-C(4)-H(4)	109.5(2.0)
O(4)-Rh-O(1)	89.99(6)	C(3)-C(4)-H(5)	113.8(2.2)
		C(3)-C(4)-H(6)	106.5(2.7)
O(1)-Rh-C(5)	90.90(7)	H(4)-C(4)-H(5)	108.6(2.9)
O(2)-Rh-C(5)	93.32(7)	H(5)-C(4)-H(6)	107.7(3.6)
O(3)-Rh-C(5)	93.76(7)	H(6)-C(4)-H(4)	110.7(3.3)
O(4)-Rh-C(5)	91.62(7)		

Average Angles of Equivalent Bonds

Rh-Rh-O	87.60(4)
Rh-O-C	119.81(13)
O-Rh-O	89.90(6)
O-C-O	125.15(17)

Table 35. Least Squares Planes of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

<u>Plane</u>						<u>Direction Cosines</u>		
A.	Rh'	. Rh	O(1)	C(1)	O(3')			
	0.006	-0.006	0.006	0.001	-0.007	0.4499	0.8910	-0.0604
B.	Rh'	Rh	O(2)	C(3)	O(4')			
	0.008	-0.006	0.003	0.007	-0.012	0.5082	-0.3077	-0.8044
C.	Rh*		O(1)	O(2)	O(3)			
			O(4)					

Dihedral Angle($^\circ$)

A-B 90.2(3.3)

* The rhodium atom is given a zero weight in the plane calculation

Table 36. Short Non-bonded Intermolecular Distances of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

<u>Atoms</u>	<u>Distance($\text{\AA}$)</u>	<u>Atoms</u>	<u>Distance($\text{\AA}$)</u>
O(5)-C(2) ^a	3.278(3)	O(2)-C(2) ^b	3.465(3)
O(5)-C(1) ^b	3.492(3)	O(2)-C(4) ^e	3.756(4)
O(5)-C(3) ^b	3.354(3)	O(4)-C(1) ^c	3.701(3)
O(5)-C(2) ^b	3.649(5)	O(4)-C(2) ^c	3.380(3)
O(5)-C(4) ^b	3.454(4)	O(3)-C(4) ^e	3.468(3)
O(5)-O(1) ^b	3.408(3)	C(5)-C(2) ^a	3.597(4)
O(5)-O(2) ^b	3.293(2)	C(5)-C(2) ^b	3.692(5)
O(5)-C(2) ^c	3.750(4)	C(5)-C(2) ^c	3.795(4)
O(5)-C(4) ^d	3.501(4)		

Symmetry List: a; (x,y,l+z), b; ($\frac{1}{2}$ -x,-y, $\frac{1}{2}$ +z), c; (x, $\frac{1}{2}$ -y, $\frac{1}{2}$ +z),
d; ($\frac{1}{2}$ -x,- $\frac{1}{2}$ +y,z), e; (x,- $\frac{1}{2}$ -y, $\frac{1}{2}$ +z)

Fig. 9. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$.

Fig. 10. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$.

Table 37. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$ with Estimated Standard Deviations

<u>Bond</u>	<u>Distance(Å)</u>	<u>Bond</u>	<u>Distance(Å)</u>
Rh-Rh'	2.4215(6)	P-F(1)	1.650(27)
Rh-O(1)	2.051(12)	P-F(2)	1.460(22)
Rh'-O(2)	2.020(12)	P-F(31)	1.706(31)
Rh-P	2.340(2)	P-F(32)	1.337(27)
O(1)-C(1)	1.286(16)		
O(2)-C(1)	1.244(17)	O(1)...O(2)	2.256(14)
C(1)-C(2)	1.496(5)		

Table 38. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$ with Estimated Standard Deviations

<u>Bond</u>	<u>Angle(°)</u>	<u>Bond</u>	<u>Angle(°)</u>
Rh'-Rh-O(1)	87.4(3)	O(1)-C(1)-O(2)	126.1(8)
Rh-Rh'-O(2)	87.9(3)	O(1)-C(1)-C(2)	116.5(1.6)
O(1)-Rh-P	92.6(3)	O(2)-C(1)-C(2)	117.4(1.6)
Rh-O(1)-C(1)	118.3(7)	F(1)-P-F(2)	90.9(1.2)
Rh'-O(2)-C(1)	120.3(8)	F(2)-P-F(31)	22.2(1.3)
Rh-P-F(1)	112.7(7)	F(2)-P-F(32)	61.2(1.7)
Rh-P-F(2)	120.3(8)	F(1)-P-F(31)	74.3(1.5)
Rh-P-F(31)	112.8(8)	F(1)-P-F(32)	30.7(1.7)
Rh-P-F(32)	132.8(1.1)	F(31)-P-F(32)	48.5(1.8)

Table 39. Least Squares Planes of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

<u>Plane</u>							<u>Direction Cosines</u>		
A.	Rh	Rh'	O(1)	O(2)	C(1)	C(2)	0.0012	-0.7054	0.7088
	-0.003	0.000	0.005	0.003	-0.005	-0.001			
B.	Rh*	O(1)	O(1) ^a	O(2) ^b	O(2) ^c		1.0	0.0	0.0
	-0.083	0.010	0.010	-0.010	-0.010				

* The rhodium atom was given a zero weight in the plane calculation

Symmetry list: a;(x,-y,-z), b;(1-x,y,-z), c;(1-x,-y,z)

Table 40. Short Non-bonded Intermolecular Distances of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$

<u>Atoms</u>	<u>Distance(Å)</u>	<u>Atoms</u>	<u>Distance(Å)</u>
F(1)-F(1) ^a	2.698(37)	F(31)-F(31) ^c	2.638(47)
F(1)-F(2) ^a	3.748(34)	F(31)-F(32) ^c	3.040(41)
F(1)-F(31) ^a	3.334(39)	F(31)-F(32) ^b	3.633(45)
F(1)-F(32) ^a	2.767(37)	F(32)-F(32) ^a	3.098(49)
F(1)-F(32) ^b	3.161(42)	F(32)-F(32) ^b	3.097(49)
F(2)-F(2) ^c	2.941(35)	F(32)-F(32) ^c	3.656(50)
F(2)-F(31) ^c	2.508(33)		
F(2)-F(32) ^c	2.649(35)		

Symmetry list: a;(z,x,y), b;(y,z,x), c;(-z,x,-y)

Fig. 11. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$ before (a) and after (b) the separation of F(3) into F(31) and F(32).

Fig. 12. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$.

Table 41. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{p}(\text{OMe})_3)_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Distance($\overset{\text{O}}{\text{\AA}}$)</u>	<u>Bond</u>	<u>Distance($\overset{\text{O}}{\text{\AA}}$)</u>
Rh-Rh	2.4556(3)	C(2)-H(1)	0.93(4)
Rh-P	2.4367(6)	C(2)-H(2)	0.93(3)
Rh-O(1)	2.044(1)	C(2)-H(3)	0.79(3)
Rh-O(2)	2.044(1)	C(4)-H(4)	0.89(3)
Rh-O(3)	2.047(2)	C(4)-H(5)	0.90(4)
Rh-O(4)	2.051(2)	C(4)-H(6)	0.89(2)
P-O(5)	1.589(2)	C(5)-H(7)	0.97(4)
P-O(6)	1.604(1)	C(5)-H(8)	0.90(5)
P-O(7)	1.611(2)	C(5)-H(9)	0.98(2)
O(5)-C(5)	1.442(3)	C(6)-H(10)	0.91(3)
O(6)-C(6)	1.434(2)	C(6)-H(11)	0.98(4)
O(7)-C(7)	1.436(3)	C(6)-H(12)	1.02(3)
O(1)-C(1')	1.265(2)	C(7)-H(13)	0.79(5)
O(2)-C(1)	1.264(3)	C(7)-H(14)	0.90(4)
O(3')-C(3)	1.264(3)	C(7)-H(15)	0.93(3)
O(4)-C(3)	1.258(3)		
C(1)-C(2)	1.499(2)	O(1)...O(2')	2.252(2)
C(3)-C(4)	1.506(4)	O(3)...O(4')	2.249(3)

Table 42. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Angle($^\circ$)</u>	<u>Bond</u>	<u>Angle($^\circ$)</u>
Rh'-Rh-P	176.28(2)	O(1')-C(1)-O(2)	125.84(12)
Rh'-Rh-O(1)	87.24(5)	O(1')-C(1)-C(2)	117.50(16)
Rh'-Rh-O(2)	87.04(5)	O(2)-C(1)-C(2)	116.66(18)
Rh'-Rh-O(3)	86.88(4)	O(3')-C(3)-O(4)	126.17(20)
Rh'-Rh-O(4)	87.33(4)	O(3')-C(3)-C(4)	116.78(22)
		O(4)-C(3)-C(4)	117.05(21)
O(1)-Rh-O(3)	89.09(5)		
O(1)-Rh-O(4)	91.20(5)	C(1)-C(2)-H(1)	114.7(1.7)
O(2)-Rh-O(3)	89.72(5)	C(1)-C(2)-H(2)	105.4(2.6)
O(2)-Rh-O(4)	89.41(5)	C(1)-C(2)-H(3)	110.9(2.8)
O(1)-Rh-P	90.91(4)	H(1)-C(2)-H(2)	111.9(3.1)
O(2)-Rh-P	94.86(5)	H(2)-C(2)-H(3)	104.1(2.6)
O(3)-Rh-P	96.31(4)	H(3)-C(2)-H(1)	109.3(3.5)
O(4)-Rh-P	89.49(5)		
		C(3)-C(4)-H(4)	110.7(2.2)
Rh-P-O(5)	108.29(7)	C(3)-C(4)-H(5)	111.3(2.8)
Rh-P-O(6)	121.31(7)	C(3)-C(4)-H(6)	109.6(2.2)
Rh-P-O(7)	120.81(7)	H(4)-C(4)-H(5)	100.0(2.9)
Rh-O(1)-C(1')	119.82(10)	H(5)-C(4)-H(6)	103.7(2.9)
Rh-O(2)-C(1)	120.05(10)	H(6)-C(4)-H(4)	120.7(2.7)
Rh-O(3)-C(3')	120.11(13)		
Rh-O(4)-C(3)	119.51(17)	O(5)-C(5)-H(7)	111.4(3.1)
		O(5)-C(5)-H(8)	100.0(2.0)
O(5)-P-O(6)	99.66(7)	O(5)-C(5)-H(9)	116.9(2.6)
O(6)-P-O(7)	105.69(9)	H(7)-C(5)-H(8)	108.1(2.9)
O(7)-P-O(6)	98.31(8)	H(8)-C(5)-H(9)	98.6(3.9)
P-O(5)-C(5)	123.63(22)	H(9)-C(5)-H(7)	118.7(4.6)
P-O(6)-C(6)	120.12(16)		
P-O(7)-C(7)	117.73(16)		

Table 42. (Continued)

<u>Bond</u>	<u>Angle(°)</u>	<u>Bond</u>	<u>Angle(°)</u>
O(6)-C(6)-H(10)	106.1(1.8)	O(7)-C(7)-H(13)	108.4(1.8)
O(6)-C(6)-H(11)	108.4(1.2)	O(7)-C(7)-H(14)	118.1(2.3)
O(6)-C(6)-H(12)	110.2(1.1)	O(7)-C(7)-H(15)	117.7(2.7)
H(10)-C(6)-H(11)	112.7(2.5)	H(13)-C(7)-H(14)	110.6(4.8)
H(11)-C(6)-H(12)	117.2(2.8)	H(14)-C(7)-H(15)	104.5(2.6)
H(12)-C(6)-H(10)	101.7(2.7)	H(15)-C(7)-H(13)	95.3(4.1)

Table 43. Least Squares Planes of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

<u>Plane</u>							<u>Direction Cosines</u>		
A.	Rh	Rh'	O(1')	O(2)	C(1)	C(2)	0.0113	-0.8287	0.3604
	0.003	-0.012	0.017	0.000	0.002	-0.009			
B.	Rh	Rh'	O(3')	O(4)	C(3)	C(4)	-0.9362	0.1798	0.9023
	0.002	-0.009	0.011	0.001	0.006	-0.009			
C.	Rh*	O(1)	O(2)	O(3)	O(4)		0.3489	0.5260	0.2506
	0.103	0.001	0.001	-0.001	-0.001				

Dihedral Angle

A-B 90.5(2.3)°

* A weight of zero was given in the plane calculation

Table 44. Short Non-bonded Intermolecular Distances of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$

<u>Atoms</u>	<u>Distance($\overset{\text{O}}{\text{\AA}})$</u>	<u>Atoms</u>	<u>Distance($\overset{\text{O}}{\text{\AA}})$</u>
O(2)-C(7) ^a	3.715(4)	O(6)-C(2) ^g	3.501(3)
O(3)-C(7) ^a	3.233(2)	O(7)-C(5) ^h	3.507(4)
O(3)-C(1) ^b	3.500(2)	O(7)-C(6) ^h	3.750(4)
O(4)-C(5) ^c	3.615(3)	C(1)-C(3) ⁱ	3.715(3)
O(4)-C(6) ^c	3.759(1)	C(1)-C(2) ⁱ	3.727(4)
O(4)-C(1) ^d	3.494(2)	C(5)-C(4) ^c	3.724(4)
O(5)-C(2) ^e	3.406(3)	C(6)-C(7) ^a	3.736(4)
O(5)-C(5) ^f	3.613(4)	C(6)-C(6) ^f	3.610(7)
O(6)-C(6) ^f	3.731(4)	C(2)-C(2) ⁱ	3.731(6)

Symmetry List: a;(x, $\frac{1}{2}$ -y, $\frac{1}{2}$ +z), b;(-x,1-y,1-z), c;(1-x,1-y,1-z),
d;(x,y,1+z), e;(x,1+y,z), f;(1-x,-y,1-z), g;(1-x,1-y,2-z),
h;(x, $\frac{1}{2}$ -y,- $\frac{1}{2}$ +z), i;(-x,2-y,1-z)

Fig. 13. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$
Hydrogen atoms are omitted for clarity.

Fig. 14. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OMe})_3)_2$.

Table 45. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$ with Estimated Standard Deviations

<u>Bond</u>	<u>Distance($\text{\AA}$)</u>	<u>Bond</u>	<u>Distance($\text{\AA}$)</u>	<u>Bond</u>	<u>Distance($\text{\AA}$)</u>
Rh-Rh'	2.4434(6)	O(6)-C(26)	1.408(6)	C(13)-H(13)	0.91(4)
Rh-P	2.412(1)	C(26)-C(21)	1.368(7)	C(14)-H(14)	0.89(5)
Rh-O(1)	2.033(3)	C(21)-C(22)	1.388(8)	C(15)-H(15)	0.93(3)
Rh-O(2)	2.048(3)	C(22)-C(23)	1.350(7)	C(21)-H(21)	0.92(3)
Rh-O(3)	2.043(2)	C(23)-C(24)	1.343(8)	C(22)-H(22)	0.87(4)
Rh-O(4)	2.033(2)	C(24)-C(25)	1.378(9)	C(23)-H(23)	0.95(5)
P-O(5)	1.603(2)	C(25)-C(26)	1.367(6)	C(24)-H(24)	0.89(4)
P-O(6)	1.602(4)			C(25)-H(25)	1.01(4)
P-O(7)	1.609(2)	O(7)-C(36)	1.393(3)	C(31)-H(31)	0.90(4)
		C(36)-C(31)	1.364(6)	C(32)-H(32)	1.05(5)
O(1)-C(1)	1.257(6)	C(31)-C(32)	1.404(5)	C(33)-H(33)	1.01(3)
O(2')-C(1)	1.264(4)	C(32)-C(33)	1.368(8)	C(34)-H(34)	1.08(4)
O(3)-C(3)	1.262(4)	C(33)-C(34)	1.371(7)	C(35)-H(35)	0.97(4)
O(4')-C(3)	1.258(5)	C(34)-C(35)	1.376(5)		
C(1)-C(2)	1.498(7)	C(35)-C(36)	1.374(6)	O(1)...O(2')	2.248(4)
C(3)-C(4)	1.511(6)			O(3)...O(4')	2.248(4)
		C(2)-H(1)	0.72(6)		
O(5)-C(16)	1.391(4)	C(2)-H(2)	0.87(8)	<u>Solvent Molecule</u>	
C(16)-C(11)	1.363(5)	C(2)-H(3)	1.04(5)	C(41)-C(42)	1.25(2)
C(11)-C(12)	1.399(6)	C(4)-H(4)	0.98(4)	C(41)-C(43)	1.29(2)
C(12)-C(13)	1.351(8)	C(4)-H(5)	0.92(6)	C(42)-C(45)	1.40(2)
C(13)-C(14)	1.371(7)	C(4)-H(6)	0.75(6)	C(43)-C(45)	1.55(2)
C(14)-C(15)	1.365(7)	C(11)-H(11)	0.86(3)	C(43)-C(44)	1.12(3)
C(15)-C(16)	1.370(6)	C(12)-H(12)	0.91(3)		

Table 46. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Angle(°)</u>	<u>Bond</u>	<u>Angle(°)</u>
Rh'-Rh-P	179.91(3)	C(12)-C(13)-C(14)	120.5(5)
Rh'-Rh-O(1)	87.20(7)	C(13)-C(14)-C(15)	119.9(5)
Rh'-Rh-O(2)	87.31(8)	C(14)-C(15)-C(16)	119.4(4)
Rh'-Rh-O(3)	86.96(8)	C(15)-C(16)-C(11)	121.9(3)
Rh'-Rh-O(4)	87.55(8)	C(16)-C(11)-C(12)	117.7(4)
O(1)-Rh-P	92.71(7)	P-O(6)-C(26)	125.4(2)
O(2)-Rh-P	92.78(8)	O(6)-C(26)-C(21)	120.0(3)
O(3)-Rh-P	93.00(8)	O(6)-C(26)-C(25)	119.5(4)
O(4)-Rh-P	92.48(8)	C(21)-C(22)-C(23)	120.2(5)
Rh-P-O(5)	123.14(12)	C(22)-C(23)-C(24)	120.7(6)
Rh-P-O(6)	111.11(9)	C(23)-C(24)-C(25)	120.4(4)
Rh-P-O(7)	120.71(11)	C(24)-C(25)-C(26)	119.3(5)
		C(25)-C(26)-C(21)	120.5(5)
O(1)-Rh-O(3)	89.02(10)	C(26)-C(21)-C(22)	118.8(4)
O(1)-Rh-O(4)	90.83(10)	P-O(7)-C(36)	126.1(2)
O(2)-Rh-O(3)	90.94(10)	O(7)-C(36)-C(31)	121.6(4)
O(2)-Rh-O(4)	88.69(10)	O(7)-C(36)-C(35)	116.3(3)
Rh-O(1)-C(1)	120.12(19)	C(31)-C(32)-C(33)	120.9(4)
Rh-O(2)-C(1')	119.01(25)	C(32)-C(33)-C(34)	119.5(4)
Rh-O(3)-C(3)	119.51(26)	C(33)-C(34)-C(35)	120.7(4)
Rh-O(4)-C(3')	119.48(19)	C(34)-C(35)-C(36)	119.1(4)
O(1)-C(1)-O(2')	126.3(5)	C(35)-C(36)-C(31)	122.0(3)
O(1)-C(1)-C(2)	116.6(3)	C(36)-C(31)-C(32)	117.8(4)
O(3)-C(3)-O(4')	126.4(3)	O(5)-P-O(6)	102.8(2)
O(3)-C(3)-C(4)	116.9(4)	O(6)-P-O(7)	104.4(2)
O(4')-C(3)-C(4)	116.7(3)	O(5)-P-O(7)	91.5(1)
P-O(5)-C(16)	127.4(2)	C(1)-C(2)-H(1)	117.4(4.5)
O(5)-C(16)-C(11)	123.2(3)	C(1)-C(2)-H(2)	119.1(3.6)
O(5)-C(16)-C(15)	114.9(3)	C(1)-C(2)-H(3)	126.0(4.4)
C(11)-C(12)-C(13)	120.6(4)		

Table 46. (Continued)

<u>Bond</u>	<u>Angle($^{\circ}$)</u>	<u>Bond</u>	<u>Angle($^{\circ}$)</u>
C(3)-C(4)-H(4)	117.1(2.4)	C(26)-C(21)-H(21)	124.3(2.9)
C(3)-C(4)-H(5)	116.5(4.1)	C(22)-C(21)-H(21)	116.7(2.8)
C(3)-C(4)-H(6)	109.1(4.2)	C(21)-C(22)-H(22)	112.9(2.7)
H(4)-C(4)-H(5)	98.9(4.3)	C(23)-C(22)-H(22)	126.8(2.8)
H(4)-C(4)-H(6)	115.5(6.6)	C(22)-C(23)-H(23)	117.0(2.1)
H(5)-C(4)-H(6)	98.0(6.6)	C(24)-C(23)-H(23)	122.3(2.1)
C(16)-C(11)-H(11)	123.3(2.0)	C(23)-C(24)-H(24)	123.5(3.4)
C(12)-C(11)-H(11)	119.0(2.0)	C(25)-C(24)-H(24)	116.1(3.4)
C(11)-C(12)-H(12)	107.7(2.3)	C(24)-C(25)-H(25)	121.6(2.2)
C(13)-C(12)-H(12)	131.3(2.1)	C(26)-C(25)-H(25)	118.9(2.3)
C(12)-C(13)-H(13)	122.0(2.7)	C(36)-C(31)-H(31)	120.2(1.8)
C(14)-C(13)-H(13)	116.6(2.5)	C(32)-C(31)-H(31)	122.1(2.0)
C(13)-C(14)-H(14)	119.8(2.6)	C(31)-C(32)-H(32)	111.5(2.3)
C(15)-C(14)-H(14)	120.0(2.5)	C(33)-C(32)-H(32)	127.4(2.4)
C(14)-C(15)-H(15)	125.1(2.3)	C(32)-C(33)-H(33)	119.3(2.4)
C(16)-C(15)-H(15)	115.4(2.4)	C(34)-C(33)-H(33)	121.0(2.5)
H(1)-C(2)-H(2)	94.1(7.7)	C(33)-C(34)-H(34)	116.6(1.6)
H(1)-C(2)-H(3)	104.7(5.2)	C(35)-C(34)-H(34)	122.4(1.7)
H(2)-C(2)-H(3)	88.1(5.6)	C(34)-C(35)-H(35)	122.9(2.0)
		C(36)-C(35)-H(35)	118.0(2.0)

Table 47. Least Squares Planes in $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$

<u>Plane</u>		<u>Direction Cosines</u>							
A.	Rh Rh'	O(1)	O(2')	C(1)	C(2)	0.4343	-0.7206	0.6823	
	-0.023 -0.026	0.044	0.039	0.019	-0.053				
B.	Rh Rh'	O(3)	O(4')	C(3)	C(4)	0.6587	-0.2452	-0.3100	
	0.020 0.022	-0.038	-0.035	-0.016	0.046				
C.	C(11) C(12)	C(13)	C(14)	C(15)	C(16)	0.8459	0.1588	0.8515	
	-0.002 -0.001	0.000	0.003	-0.006	0.006				
D.	C(21) C(22)	C(23)	C(24)	C(25)	C(26)	0.5627	-0.7522	-0.0323	
	0.001 0.005	-0.008	0.005	0.002	-0.004				
E.	C(31) C(32)	C(33)	C(34)	C(35)	C(36)	0.7778	0.6133	0.4928	
	0.003 0.008	-0.012	0.005	0.006	-0.010				
F.	Rh*	O(1)	O(2)	O(3)	O(4)	0.6487	0.6625	0.6389	
	-0.098 0.001	0.000	0.000	0.000					

Dihedral AngleA-B 93.4(1.7)^o

* A weight of zero was given in the plane calculation.

Table 48. Intermolecular Distances Less Than $3.8 \text{ \AA}$ in $\text{Rh}_2(\text{OAc})_4(\text{P(OPh)}_3)_2$

Atoms	Distance($\text{\AA}$)	Atoms	Distance($\text{\AA}$)
O(1)-C(34) ^a	3.412(4)	C(23)-C(32) ^d	3.679(9)
O(4)-C(35) ^a	3.524(5)	C(42) ^e -C(35)	3.78(1)
C(4)-O(7) ^b	3.794(5)	C(43) ^d -C(22)	3.80(1)
C(4)-C(12) ^c	3.694(9)	C(43) ^f -C(14)	3.73(1)
C(4)-C(13) ^c	3.689(11)	C(44) ^d -C(36)	3.75(2)
C(12)-C(23) ^c	3.761(9)	C(45) ^d -C(22)	3.78(1)
C(12)-C(24) ^c	3.770(8)	C(45) ^f -C(14)	3.65(1)
C(13)-C(22) ^c	3.703(8)	C(45) ^g -O(6)	3.50(1)
C(15)-C(34) ^a	3.591(8)	C(45) ^g -C(3)	3.69(2)
C(21)-C(21) ^d	3.687(9)	C(45) ^g -O(2)	3.71(2)
C(23)-C(31) ^d	3.796(8)		

Symmetry List: a; $(\frac{1}{2}-x, -\frac{1}{2}-y, -z)$, b; $(x, -1+y, z)$, c; $(\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z)$,
d; $(-x, -y, -z)$, e; $(x, 1+y, z)$, f; $(\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z)$, g; (x, y, z)

Fig. 15. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$.

Fig. 16. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{P}(\text{OPh})_3)_2$.

The solvent molecule is arbitrarily represented by isotropic spheres of $B=3.0 \text{ \AA}^2$ at 25 % probability level.

Table 49. Bond Distances of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Distance($\overset{\circ}{\text{\AA}}$)</u>	<u>Bond</u>	<u>Distance($\overset{\circ}{\text{\AA}}$)</u>
Rh(1)-Rh(2)	2.4537(4)	C(3)-O(2)	1.278(5)
Rh(1)-O(1)	2.050(3)	C(3)-O(6)	1.258(5)
Rh(1)-O(2)	2.009(3)	C(5)-O(3)	1.262(5)
Rh(1)-O(3)	2.017(3)	C(5)-O(7)	1.276(5)
Rh(1)-O(4)	2.026(3)	C(7)-O(4)	1.266(6)
Rh(2)-O(5)	2.028(3)	C(7)-O(8)	1.283(5)
Rh(2)-O(6)	2.030(3)	C(1)-C(2)	1.508(6)
Rh(2)-O(7)	2.041(3)	C(3)-C(4)	1.496(6)
Rh(2)-O(8)	2.013(3)	C(5)-C(6)	1.499(6)
		C(7)-C(8)	1.492(6)
Rh(1)-N(1)	2.008(4)	O(1)...O(5)	2.247(4)
Rh(2)-N(2)	1.927(4)	O(2)...O(6)	2.255(4)
N(1)-O(9)	1.212(5)	O(3)...O(7)	2.263(4)
N(1)-O(10)	1.235(5)	O(4)...O(8)	2.260(4)
N(2)-O(11)	1.151(5)		
C(1)-O(1)	1.260(5)		
C(1)-O(5)	1.266(5)		

Table 50. Bond Angles of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$ with
Estimated Standard Deviations

<u>Bond</u>	<u>Angle(°)</u>	<u>Bond</u>	<u>Angle(°)</u>
Rh(1)-Rh(2)-N(2)	162.03(11)	Rh(1)-O(1)-C(1)	121.34(26)
Rh(2)-Rh(1)-N(1)	172.98(11)	Rh(1)-O(2)-C(3)	116.21(24)
Rh(2)-Rh(1)-O(1)	85.34(9)	Rh(1)-O(3)-C(5)	117.19(24)
Rh(2)-Rh(1)-O(2)	90.97(8)	Rh(1)-O(4)-C(7)	120.68(27)
Rh(2)-Rh(1)-O(3)	90.16(8)	Rh(1)-N(1)-O(9)	119.60(31)
Rh(2)-Rh(1)-O(4)	86.78(8)	Rh(1)-N(1)-O(10)	116.89(28)
Rh(1)-Rh(2)-O(5)	88.79(8)	O(9)-N(1)-O(10)	123.4(5)
Rh(1)-Rh(2)-O(6)	83.36(8)	Rh(2)-O(5)-C(1)	118.63(25)
Rh(1)-Rh(2)-O(7)	84.40(8)	Rh(2)-O(6)-C(3)	123.87(26)
Rh(1)-Rh(2)-O(8)	87.74(8)	Rh(2)-O(7)-C(5)	121.81(26)
O(1)-Rh(1)-O(2)	176.27(12)	Rh(2)-O(8)-C(7)	119.89(23)
O(1)-Rh(1)-O(3)	90.62(12)	Rh(2)-N(2)-O(11)	128.78(31)
O(1)-Rh(1)-O(4)	91.38(12)	O(1)-C(1)-O(5)	125.7(4)
O(2)-Rh(1)-O(3)	89.90(12)	O(2)-C(3)-O(6)	125.5(4)
O(2)-Rh(1)-O(4)	87.89(12)	O(3)-C(5)-O(7)	126.2(4)
O(3)-Rh(1)-O(4)	176.20(12)	O(4)-C(7)-O(8)	124.9(4)
O(5)-Rh(2)-O(6)	172.05(11)	O(1)-C(1)-C(2)	116.9(4)
O(5)-Rh(2)-O(7)	90.41(12)	O(5)-C(1)-C(2)	117.4(4)
O(5)-Rh(2)-O(8)	88.75(12)	O(2)-C(3)-C(4)	117.6(3)
O(6)-Rh(2)-O(7)	90.10(12)	O(6)-C(3)-C(4)	117.0(4)
O(6)-Rh(2)-O(8)	89.66(12)	O(3)-C(5)-C(6)	118.1(4)
O(7)-Rh(2)-O(8)	172.09(11)	O(7)-C(5)-C(6)	115.8(4)
O(1)-Rh(1)-N(1)	88.52(14)	O(4)-C(7)-C(8)	118.2(4)
O(2)-Rh(1)-N(1)	95.14(14)	O(8)-C(7)-C(8)	116.9(4)
O(3)-Rh(1)-N(1)	93.30(13)		
O(4)-Rh(1)-N(1)	89.98(14)		
O(5)-Rh(2)-N(2)	105.66(14)		
O(6)-Rh(2)-N(2)	82.30(11)		
O(7)-Rh(2)-N(2)	84.85(13)		
O(8)-Rh(2)-N(2)	102.94(13)		

Table 51. Least Squares Planes in $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

<u>Plane</u>							<u>Direction Cosines</u>		
A.	Rh(1)	Rh(2)	O(1)	O(5)	C(1)	C(2)	-0.5954	0.6841	-0.4213
	0.037	-0.021	-0.046	0.018	-0.007	0.019			
B.	Rh(1)	Rh(2)	O(2)	O(6)	C(3)	C(4)	-0.5904	0.7118	-0.3805
	-0.020	0.024	0.020	-0.028	-0.002	0.005			
C.	Rh(1)	Rh(2)	O(3)	O(7)	C(5)	C(6)	0.6083	0.0942	-0.7881
	-0.017	0.041	0.012	-0.054	-0.006	0.024			
D.	Rh(1)	Rh(2)	O(4)	O(8)	C(7)	C(8)	0.6213	0.0433	-0.7824
	0.016	0.009	-0.026	-0.018	-0.007	0.026			
E.	Rh(2)	N(2)	O(11)				-0.0718	0.5708	-0.8179
	0.000	0.000	0.000						
F.	N(1)	O(9)	O(10)				0.0083	0.4526	-0.8917
	0.000	0.000	0.000						
G.	Rh(1)*	O(1)	O(2)	O(3)	O(4)		-0.5756	-0.6930	-0.4341
	0.061	-0.005	-0.005	0.005	0.005				
H.	Rh(2)*	O(5)	O(6)	O(7)	O(8)		-0.5744	-0.6918	-0.4376
	-0.140	0.000	0.000	0.000	0.000				

Dihedral Angles ($^\circ$)

A-C	92.0(2.3)	B-D	87.8(2.3)
B-C	90.4(2.3)	A-D	89.4(2.3)
A-E	141.1(9.7)	A-F	132.9(4.1)
E-F	170.8(12.8)		

* A weight of zero was given in the plane calculation.

Table 52. Short Non-bonded Intermolecular Distances of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

<u>Atoms</u>	<u>Distance($\overset{\circ}{\text{\AA}}$)</u>	<u>Atoms</u>	<u>Distance($\overset{\circ}{\text{\AA}}$)</u>
O(1)-O(7) ^a	3.647(4)	O(7)-C(4) ^e	3.586(5)
O(1)-O(11) ^a	3.452(5)	O(8)-O(11) ^a	3.575(5)
O(1)-C(6) ^a	3.561(6)	O(8)-N(2) ^f	2.890(5)
O(1)-C(6) ^b	3.710(5)	O(8)-O(11) ^f	3.003(5)
O(2)-C(2) ^c	3.274(5)	N(1)-C(2) ^c	3.776(6)
O(2)-C(8) ^d	3.386(5)	N(2)-C(7) ^g	3.626(6)
O(3)-C(6) ^b	3.212(5)	N(2)-O(11) ^f	3.254(5)
O(4)-O(6) ^a	3.593(4)	O(9)-C(3) ^a	3.425(5)
O(4)-O(11) ^a	3.352(5)	O(9)-C(4) ^a	3.451(6)
O(4)-O(4) ^a	3.581(6)	O(9)-C(5) ^a	3.380(6)
O(4)-C(2) ^c	3.746(6)	O(9)-C(6) ^a	3.338(7)
O(5)-O(11) ^a	3.583(5)	O(9)-C(8) ^h	3.225(6)
O(5)-C(4) ^e	3.521(5)	O(11)-C(1) ^g	3.194(5)
O(5)-N(2) ^f	3.053(5)	O(11)-C(2) ^g	3.302(6)
O(5)-O(11) ^f	3.101(5)	O(11)-C(7) ^g	3.146(5)
O(6)-O(9) ^g	3.656(5)	O(11)-C(8) ^g	3.301(6)
C(6)-C(8) ^g	3.715(6)	C(1)-C(4) ^e	3.681(6)
O(7)-O(9) ^g	3.741(5)	C(2)-C(4) ^e	3.718(6)
O(7)-C(2) ^g	3.523(5)	C(5)-C(6) ^b	3.795(6)

Intramolecular Distances

O(9)-O(1)	2.992(5)
O(9)-O(4)	2.982(5)
O(10)-O(2)	3.166(5)
O(10)-O(3)	2.999(5)
O(11)-O(6)	2.776(5)
O(11)-O(7)	2.956(4)

Symmetry List: a;(1+x,y,z), b;(½+x,-½-y,-1-z), c;(½-x,-y,½+z),
d;(1-x,½+y,-1½-z), e;(1½-x,-y,-½+z), f;(½+x,½-y,-1-z),
g;(-1+x,y,z), h;(-x,½+y,-1½-z)

Fig. 17. Perspective view of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$.

Fig. 18. Packing diagram of $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$.

VI. NMR STUDIES

A. Preparation of Samples

Preliminary investigation with the ligand adducts of $\text{Rh}_2(\text{OAc})_4$ yielded spectra of poor quality because of their uniformly low solubility in hydrocarbon solvents. In addition, attempts to attain spectra for the 1:1 adducts, which would provide vital information leading to unambiguous spectral assignments, were unsuccessful. Thus $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$ was chosen as a more suitable alternative to $\text{Rh}_2(\text{OAc})_4$.

1) Synthesis of $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$

$\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$ was prepared by refluxing $\text{Rh}_2(\text{OAc})_4$ in Me_3CCOOH under N_2 for 2 hours. The excess Me_3CCOOH was evaporated in vacuo over a steam bath to obtain green powder of $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$. The powder was redissolved in CH_2Cl_2 and filtered to eliminate unreacted residue of $\text{Rh}_2(\text{OAc})_4$ (this procedure is not usually necessary because 100 % conversion can be achieved by prolonged reflux). After evaporating the CH_2Cl_2 in an open atmosphere, the product was further purified by recrystallization from MeOH by addition of water until the green powder precipitated out. The powder was then immediately filtered off and rinsed with water several times in order to ensure thorough removal of excess Me_3CCOOH . The axial ligands (either MeOH or H_2O) were driven off by heating in an oven at 100°C for 24 hours. Unlike $\text{Rh}_2(\text{OAc})_4$, $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$ is very soluble in CH_2Cl_2 , toluene, MeOH, and acetone, and soluble in benzene, CHCl_3 , and CCl_4 , and slightly soluble in H_2O .

2) Preparation of Nmr Samples

The ligands used were PF_3 (Ozark-Mahoning Chemical Company), P(OPh)_3 (Aldrich Chemical Company), P(OMe)_3 (Aldrich Chemical Company), PCl_3 (Aldrich Chemical Company), PPh_3 (Matheson Coleman and Bell Chemical Company), and PCy_3 which was kindly provided by Dr. Terry Mazanec of the Ohio State University Chemistry Department. The purity of these ligands was checked prior to use by means of blank runs. Clean spectra were obtained for all but PCy_3 , which showed impurity peaks attributable to SPCy_3 and OPCy_3 . No attempt to purify PCy_3 was made because the dirhodium complex binds PCy_3 and no side reactions arising from the presence of impurities were observed during the course of experiment. All samples were prepared in situ by dissolving appropriate amount of $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$ (usually 0.01-0.05 g depending upon the solubility of the adduct at low temperature, and 0.15-0.20 g for the 1:2 adducts of P(OPh)_3 and P(OMe)_3) in 2-3 ml of CH_2Cl_2 in 10 mm nmr tubes. After degassing the solution with N_2 for several minutes, the phosphorus ligands were added as desired. In most cases, the adduct was assumed to consist of a 1:1 ratio when the color of the solution turned blue-violet and to consist of a 1:2 ratio when it was red.

B. ^{31}P Nmr Measurement

Phosphorus-31 spectra were collected on a Bruker HX-90 spectrometer operating at 36.43 MHz with a Nicolet BNC-12 data system. Deuterated acetone($(\text{CD}_3)_2\text{CO}$) was used as an internal deuterium lock and trimethylphosphate as internal reference($\delta=58.09$ Hz(1.594 ppm) with respect to 85 % H_3PO_4). A coaxial tube containing deuterated acetone and trimethylphosphate($\sim 20:1$ by volume) was inserted into the sample tube as an internal standard. The protons were broadband decoupled at 90 MHz to avoid spectral complexity and to enhance the signal to noise ratio. The desired temperature was maintained constant within $\pm 2^\circ\text{C}$ by a combination of an N_2 gas cold stream and a heater. The frequency resolution of the instrument was ± 2.0 Hz for the usual sweep width of 8000 Hz and the FID memory space of 8 K. Repeated measurements on the same sample with varying concentrations(allowing a temperature variation of $\pm 50^\circ\text{C}$) showed a reproducibility not greater than ± 2.0 ppm for the chemical shifts. The coupling constants were reproducible within ± 2.0 Hz.

Good spectra were obtained in less than 5000 scans for the 1:1 and mixed ligand adducts that gave first-order splitting patterns. Attempts to observe very weak, out-lying signals arising from the phosphorus-phosphorus spin couplings in the symmetric 1:2 adducts were unsuccessful due to the extremely low intensity ratios($\sim 300:1$ as compared to the major center peaks) and low solubilities of the adducts, except for the 1:2 adducts of $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$ which are quite soluble.

C. Analysis of Spectra

1) General Aspects

Some typical spectra are depicted in Figures 19, 20, 21, and 23, showing an equilibrium mixture of 1:1 and 1:2 adducts, the phosphorus-phosphorus spin coupling in a symmetric 1:2 adduct, a first-order splitting of a mixed ligand adduct (note the presence of the 1:2 adduct of each ligand, formed by the displacement reaction; $L-Rh-Rh + L' \rightarrow L-Rh-Rh-L' \xrightarrow{L'} L'-Rh-Rh-L' + L$), and a second-order splitting.

The 1:1 adducts are ABX spin systems. The appearance of the X part consists of a doublet of doublets with separations of $^1J(BX)$ and $^2J(AX)$ centered at the chemical shift of the X nucleus. The coupling constants and chemical shifts for the X parts as obtained from the spectra are presented in Table 53.

The symmetric 1:2 and mixed ligand adducts can be referred to as AA'XX' and ABXY systems, respectively. If the shift difference $|\delta(X) - \delta(X')|$ or $|\delta(X) - \delta(Y)|$ is much larger than coupling constants, the splitting pattern follows the rules for the first-order splitting. Spectra for $Ph_3P-Rh-Rh-L$ ($L = P(OMe)_3$, $P(OPh)_3$, and PCl_3) and $Cy_3P-Rh-Rh-P(OMe)_3$ where $|\delta(P) - \delta(P')| / ^3J(PP')$ ranges from 6 to 8 are essentially of this type. When the coupling constants are of a size comparable to or larger than their relative chemical shifts, then the spectra become complex and the rules for the first-order splitting no longer hold. The spectra of this type are those for $(MeO)_3P-Rh-Rh-P(OPh)_3$ (Fig. 23) and the symmetric 1:2 adducts (Fig. 20), the latter of which are the worst case of a second-order pattern in the series because the shift

difference is zero. The spectrum of $(\text{MeO})_3\text{P-Rh-Rh-PCl}_3$, for which $|\delta(\text{P}) - \delta(\text{P}')| / {}^3J(\text{PP}') \approx 2$, is also second-order (Fig. 25).

2) Computer Analysis

Computer simulation of the experimental spectra were performed using a program ITRCL, an adapted version of LAOCOON III¹¹⁷ by Nicolet Instrument Corporation. Shifts and coupling constants, guessed or estimated from the experimental spectra, were entered in the least squares iteration when the calculated transitions agreed with experimental transitions within ± 2.0 Hz.

The unobserved splittings such as ${}^1J(\text{RhRh})$ and ${}^2J(\text{RhPPh}_3)$ in the $\text{Ph}_3\text{P-Rh-Rh-L}$ systems were assumed to be 5.0 and 0.0, respectively, in the least squares analyses and were not refined. These values were arbitrarily chosen for convenience assuming that ${}^1J(\text{RhRh})$'s in the $\text{Ph}_3\text{P-Rh-Rh-L}$ systems do not differ appreciably from those determined for the 1:2 P(OMe)_3 and P(OPh)_3 adducts (vide infra) and that splittings that are smaller than 2.0 Hz in magnitude would be identical to zero within the limit of frequency resolution (vide supra). The spectrum of $(\text{MeO})_3\text{P-Rh-Rh-P(OPh)}_3$ was analyzed in a similar manner but the ${}^2J(\text{RhP})$'s were allowed to vary. The computer simulated spectra are shown in Fig. 22 and 24 for $\text{Ph}_3\text{P-Rh-Rh-P(OPh)}_3$ and $(\text{MeO})_3\text{P-Rh-Rh-P(OPh)}_3$ complexes.

The transitions of the 1:2 adducts of P(OMe)_3 and P(OPh)_3 were not entered in the least squares program but calculated by a trial and method until the calculated spectra matched with observed spectra within ± 1.5 Hz. Noticeably poorer fits were obtained when any one

Fig.19. ^{31}P nmr spectrum of an equilibrium mixture of 1:1 and 1:2 P(OPh)_3 adducts. The weak signals arising from the P-P spin splitting are marked with arrows(see Fig. 20).

Fig. 20. ^{31}P nmr spectrum of the 1:2 $\text{P}(\text{OPh})_3$ adduct, showing the P-P spin coupling (concentration ≈ 0.2 M, number of scans ≈ 30000).

Fig. 21. The first-order splitting of a mixed ligand adduct. Note that the intensity of the PPh_3 part of the spectrum is approximately twice that of the P(OPh)_3 part, an indication of a near zero $\text{Rh}-\text{Rh}-\text{PPh}_3$ coupling.

Fig. 22. Computer simulated spectrum of a mixed ligand adduct $(\text{PhO})_3\text{P-Rh-Rh-PPh}_3$. Coupling constants and shifts are taken from Table 54. The experimental spectrum is shown in Fig. 21.

Fig. 23. The second-order splitting of a mixed ligand adduct.

Fig. 24. The computer simulated spectrum of a mixed ligand $(\text{MeO})_3\text{P-Rh-Rh-P(OPh)}_3$. In order to simulate the experimental spectrum (Fig. 23), line width=8 Hz was used. The horizontal scale is expanded for clarity.

Fig. 25. The spectrum of a mixed ligand adduct, PCl₃ and P(OMe)₃.

coupling constant was varied by 1.0 Hz from the values listed in Table 54. Although $^1J(\text{RhP})$ and $^2J(\text{RhP})$ could be simultaneously varied by more than 1.0 Hz without altering the spectra significantly, the resultant values were identical with those given in Table 54 within the limit of reproducibility.

The separation of the very weak out-lying signals (Fig. 20) is most sensitive to $^1J(\text{RhRh})$, which is approximately half of the separation in the spectra of 1:2 adducts of P(OPh)_3 and P(OMe)_3 .

The simulation of 1:2 adduct spectra of PCy_3 and PPh_3 was performed also by a trial and error method on the major center peaks with $^1J(\text{RhRh})$'s and $^2J(\text{RhP})$'s held constant at 5.0 and 2.0 Hz, respectively. The calculated positions of the major peaks were relatively insensitive to the magnitude of $^3J(\text{PP})$. However, the deviation from the observed transitions was appreciable when $^3J(\text{PP})$ was changed by 30 Hz from 370 Hz for PPh_3 and 300 Hz for PCy_3 . It was not possible to obtain reasonable coupling constants for the 1:2 adduct of PCl_3 , due to the fact that the PCl_3 resonance appeared as a triplet with an intensity ratio of 1:2:1.

The final chemical shifts and coupling constants as determined from the computer analyses are summarized in Table 54.

Table 53. ^{31}P Nmr Data for 1:1 and 1:2 AdductsCoupling Constants^a for 1:1 Adducts

<u>L</u>	$\frac{{}^1J(\text{RhL})}{\text{Hz}}$	$\frac{{}^2J(\text{RhRhL})}{\text{Hz}}$	$\frac{\delta(\text{L})}{\text{ppm}}$	$\frac{T}{^\circ\text{K}}$
PF_3	163.8	77.4	-3.2	185
PCl_3	125.5	104.9	63.9	193
P(OPh)_3	147.7	59.1	18.2	243
P(OMe)_3	147.7	45.3	40.8	243
PPh_3	97.1	32.4	-37.6	283
PCy_3	94.9	33.1	-34.3	273
$^{13}\text{CO}^*$	41.2	10.3	152.1	193

Chemical Shifts^b for 1:1 and 1:2 Adducts

<u>L</u>	$\frac{\delta(1:1)}{\text{ppm}}$	$\frac{\delta(1:2)}{\text{ppm}}$	$\frac{\delta(\text{free L})}{\text{ppm}}$	$\frac{\Delta\delta(1:1)^c}{\text{ppm}}$	$\frac{\Delta\delta(1:2)^c}{\text{ppm}}$
PF_3	-3.2(185)	$\sim 60(200)^d$	97.0 ^e	100.2	37.0
PCl_3	63.9(193)	147.8(193)	217.8(233)	153.9	70.0
P(OPh)_3	18.2(243)	78.9(243)	125.1(233)	106.9	46.2
P(OMe)_3	40.8(243)	100.0(243)	140.4(233)	99.6	40.4
PPh_3	-37.6(283)	-19.0(223)	-6.0(283)	31.6	13.0
PCy_3	-34.3(273)	-14.2(273)	8.7(273)	43.0	22.9
$^{13}\text{CO}^*$	152.1(193)	169.4(193)	184.9(193)	32.8	15.5

* ^{13}C nmr data are presented for comparison. Shifts are relative to TMS.

a. Errors in coupling constants are ± 2.0 Hz.

b. Shifts are relative to 85 % H_3PO_4 , except for ^{13}CO .

Errors in shifts are ± 2.0 ppm, allowing for the temperature dependence. Temperatures at which shifts were measured are given in parentheses.

c. Upfield shifts from free ligands.

d. The shift for the 1:2 adduct could not be measured accurately due to the low solubility.

e. Literature value; reference 106.

Table 54. ^{31}P Nmr Data for $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4\text{LL}'^{\text{a}}$

L	L'	$^1\text{J}(\text{RhL})$ Hz	$^2\text{J}(\text{RhRhL})$ Hz	$\delta(\text{L})$ ppm	$^1\text{J}(\text{RhL}')$ Hz	$^2\text{J}(\text{RhRhL}')$ Hz	$\delta(\text{L}')$ ppm	$^3\text{J}(\text{LL}')$ Hz	$^1\text{J}(\text{RhRh})$ Hz	T °K
PPh_3	P(OMe)_3	84.0	$<2^{\text{b}}$	-16.0	138.7	3.9	94.7	526.1	5.0^{c}	243
PPh_3	P(OPh)_3	87.2	$<2^{\text{b}}$	-15.9	128.7	14.3	79.6	542.7	5.0^{c}	223
PPh_3	PCl_3	94.4	$<2^{\text{b}}$	-10.0	96.9	34.9	152.2	807.5	5.0^{c}	180
PPh_3^{d}	PPh_3^{d}	88.0	2.0^{c}	-19.0	88.0	2.0^{c}	-19.0	$370(30)^{\text{e}}$	5.0^{c}	223
P(OMe)_3	PCy_3	136.5	$<2^{\text{b}}$	93.6	86.5	$<2^{\text{b}}$	-9.8	542.0	5.0^{c}	180
$\text{P(OMe)}_3^{\text{d}}$	$\text{P(OMe)}_3^{\text{d}}$	134.0	4.0^{g}	100.0	134.0	4.0	100.0	832.0	7.5	243
P(OMe)_3	P(OPh)_3	140.8	5.9^{g}	90.9	130.5	4.4	83.2	860.2	5.0^{c}	180
$\text{P(OMe)}_3^{\text{f}}$	PCl_3^{f}	124(20)	5.0^{c}	78.6	70(20)	30.0^{c}	144.9	1100(20)	5.0^{c}	180
$\text{P(OPh)}_3^{\text{d}}$	$\text{P(OPh)}_3^{\text{d}}$	130.0	4.0	78.9	130.0	4.0	78.9	890.0	6.0	243
PCy_3^{d}	PCy_3^{d}	85.0	2.0^{c}	-14.2	85.0	2.0^{c}	-14.2	$300(30)^{\text{e}}$	5.0^{c}	273
$^{13}\text{CO}^{\text{h}}$	$^{13}\text{CO}^{\text{h}}$	32.5(4.0)	7.2(3.0)	169.4	32.5(4.0)	7.2(3.0)	169.4	0.0^{c}	11.8(4.0)	193

- a. Shifts are relative to 85 % H_3PO_4 , except for ^{13}CO . Errors in coupling constants are ± 2.0 Hz, unless otherwise specified. Errors in chemical shifts are ± 2.0 ppm, allowing for the temperature dependence.
- b. Splittings that are smaller than 2.0 Hz were not observed and consequently $J=0.0$ was used in the analysis.
- c. These are the assumed values and were not varied.
- d. Values for the symmetric 1:2 adducts were obtained by a trial and error method.
- e. $^3\text{J}(\text{PP})$'s were not observed but estimated from the computer simulations on the major peaks.
- f. Coupling constants were estimated by a trial and error method. Errors in J's are large due to the poor resolution of the spectrum(see Fig. 25).
- g. The simulation gave -4.0 and -5.9 Hz.
- h. Coupling constants were estimated by a trial and error analysis of the positions and intensities of the observed peaks and refined by the least squares iteration, assuming that $^3\text{J}(\text{CC})=0.0$. See the text for the evaluation of the errors. The ^{13}C shift is relative to TMS.

D. ^{13}C Nmr Spectra of the CO Adducts

1) Preparation of the Sample

$\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4$ (~ 0.05 g, $\sim 8 \times 10^{-5}$ moles) was dissolved in 3 ml of deuterated acetone in a 10 mm nmr tube with a rubber septum cap. The solution was purged with N_2 gas and cooled to dry ice-acetone slush bath temperature. N_2 gas was then withdrawn out of the tube with a syringe and the tube was charged with an excess amount of 90 % enriched CO gas ($\sim 9 \times 10^{-4}$ moles). Several drops of TMS (internal standard) were added to the solution.

CD_2Cl_2 could not be used as the solvent because of the low solubility of the adducts at low temperature.

2) ^{13}C Nmr Measurement

^{13}C spectra were collected on a Bruker HX-90 spectrometer operating at 22.625 MHz with a Nicolet BNC-12 data system. Other features of the instrumentation are the same as those described for ^{31}P nmr.

3) Analysis of Spectra

The temperature dependent spectra are shown in Fig. 26. At room temperature (Fig. 26a), the ^{13}C CO resonance appears as a singlet as a result of a rapid equilibrium between free CO, mono- and bisadducts;

As the temperature is lowered to -80°C (Fig. 26b), the singlet is split into a sharp doublet of doublets at 152.1 ppm for the monoadduct (the solvent molecule is coordinated to the vacant site) and a single peak for free CO at 184.9 ppm. The bisadduct resonance occurs at 169.4 ppm

Fig. 26. ^{13}C nmr spectrum of mono and bisadducts of CO.

between free CO and the monoadduct. The monoadduct was unambiguously identified by the appearance of four peaks (two doublets) with equal intensities, as is expected for a first-order splitting of the Rh-Rh-CO system. Even if one assumes that the peaks centered at 169.4 ppm have equal intensities and consist of two doublets, the observed separation of these doublets is smaller than that of those centered at 152.1 ppm (29 vs. 41 Hz). Therefore, by analogy with the trend in the ^{31}P nmr spectra that the monoadducts appear at higher fields with larger doublet separations (larger $^1\text{J}(\text{RhP})$'s) than those at lower fields (see Fig. 19, for example), the peaks at 152.1 ppm can by no means be assigned to the bisadduct.

The coupling constants for the monoadduct were readily determined from the spectrum and are included in Table 53. The computer analysis of the bisadduct spectrum was performed in similar manner described for ^{31}P spectra. Assuming that $^3\text{J}(\text{CC})$ is zero, other coupling constants $^1\text{J}(\text{RhC})$, $^2\text{J}(\text{RhC})$, and $^1\text{J}(\text{RhRh})$ were estimated by a trial and error method and entered in the least squares iteration when the calculated transitions agreed with the observed ones within ± 1.0 Hz. The least squares refinement converged in four cycles. Since the shifts and the relative intensities of the peaks are equally sensitive to the magnitudes of coupling constants, the errors were estimated by varying one coupling constant with others held constant until the calculated spectrum consisted of six or more lines with separations of approximately 2.0 Hz, the instrumental resolution. The reason for this is because it is quite possible that two closely spaced lines at this resolution may be observed as a single peak with an intensity

that is the sum of individual intensities, giving rise to four lines with a relative intensity ratio of about 2:1:1:2, as shown in Fig. 26b.

The final values from the least squares cycles are included in Table 54, along with the estimated errors.

VII. DISCUSSION

A. Description of Structures

General: The structural parameters for the five-membered rings $\overline{\text{Rh-Rh-O-C-O}}$ are summarized in Table 55. The Rh-Rh distance ranges from 2.3863 Å for L=py to 2.4556 Å for L=P(OMe)₃. The average Rh-O and C-O bond lengths are constant to within ± 0.01 Å. The variation in the Rh-Rh distance is accompanied by the proper adjustments of internal angles, in particular the Rh-Rh-O angle which decreases with increasing Rh-Rh distance. The Rh-O₄ plane distance shows a gradual increase with increasing Rh-Rh distance, as would be expected from the trend in the Rh-Rh-O angle. There are no observable trends in the variations in the Rh-O-C and O-C-O angles. However, examination of a wide variety of tetracarboxylate bridged metal dimers shows that these angles do vary systematically in response to the changes in the metal-metal distances. This is discussed in full in section C.

In all structures, the acetate frameworks are essentially planar with deviations of individual atoms being no more than 0.05 Å from the planes. D_{4h} symmetry is maintained for the tetraacetate nuclei, although the overall molecular point symmetry is lower. The crystal packings are strictly dictated by the van der Waals contacts, except for the CO adduct in which there are contacts slightly shorter than the sum of normal van der Waals radii. Non-bonded intermolecular distances are shown in appropriate packing diagrams and tables.

Table 55. Structural Parameters for Rh₂(OAc)₄L₂

L	d(Rh-Rh)	d(Rh-O)	d(Rh-O _L)*	d(C-O)	∠RhRhO	∠RhOC	∠OCO	d(Rh-L)	d(Rh(I)-L)	d(Rh(III)-L)
H ₂ O ^a	2.3855(5)	2.039(8)	0.071	1.269(4)	88.01(3)	119.5(3)	124.8(3)	2.310(3)		2.03(1) ^b
py	2.3963(2)	2.039(2)	0.073	1.266(3)	88.0(1)	119.1(1)	125.7(2)	2.227(3)	2.107(8) ^c	2.06(1) ^d
NHEt ₂	2.4020(7)	2.038(3)	0.074	1.260(6)	87.9(1)	118.6(3)	127.0(4)	2.301(5)		2.07(1) ^e
CO	2.4191(3)	2.033(2)		1.267(3)	87.6(1)	119.8(1)	125.2(2)	2.095(2)	1.82(2) ^f	1.89(1) ^g
PF ₃	2.4215(6)	2.035(1)	0.083	1.265(2)	87.7(3)	119.3(8)	126.1(8)	2.340(2)	2.16(1) ^h	
P(OPh) ₃	2.4434(6)	2.039(3)	0.098	1.260(5)	87.3(1)	119.5(3)	126.4(4)	2.412(1)	2.142(3) ⁱ	
P(OMe) ₃	2.4556(3)	2.047(2)	0.103	1.263(3)	87.1(1)	119.9(1)	126.0(2)	2.437(1)		2.199(5) ^j
PPh ₃ ^t	2.449(2)	2.044(4)	0.100	1.259(7)	87.1(1)	119.7(4)	126.2(5)	2.479(3)	2.290(4) ^k	2.338(4) ^l
(NO)(NO ₂)	2.4537(4)	2.027(3)	0.061 ^m 0.140 ⁿ	1.269(5)	88.3(1) ^o 86.1(1) ^p	118.9(3) ^o 121.1(3) ^p	125.6(4)	2.008(4) ^q 1.927(4) ^r		1.912(10) ^s

a. Ref 50a, b. trans-RhCl₄(H₂O)₂⁻;ref 118, c. Rh(C₅HF₆O₂)(py)(C₇H₆(CO₂CH₃)₂);ref 79, d. Rh(Salbn)(py)Cl;
ref 80, e. Rh(Et)(NH₃)₅⁺²;ref 81, f. Rh₂(CO)₂(-Cl)₂(N₂Ph₂)₂;ref 82, g. I₃(OC)RhCPh(NMe)CPhNMe;ref 83,
h. RhH(PF₃)(PPh₃)₃;ref 84, i. Rh₂(-Cl)₂(C₈H₁₂)(P(OPh)₃)₂;ref 85, j. RhCl₃(n-Bu₃P)₂(P(OMe)₃);ref 86,
k. trans-Rh(PPh₃)₂(C(NMe₃CH₂)₂)(NC(CF₃)₂);ref 119, l. RhHCl(SiCl₃)(PPh₃)₂;ref 120, m. Distance to Rh bonded
to NO₂, n. Distance to Rh bonded to NO, o. Average Angle involving acetate oxygen atoms facing NO₂,
p. Average angle involving acetate oxygen atoms facing NO, q. L=NO₂, r. L=NO, s. Rh(II)-NO distance in
RhCl₂(PPh₃)₂(NO);ref 87, t. Ref 75

* Distance from the plane defined by four equatorial oxygen atoms.

The Rh-L distances are 0.1-0.2 Å longer than the corresponding values in monomeric species of Rh(I) or Rh(III). Some Rh(I)-L and Rh(III)-L distances are listed in Table 53 for comparison. It is known that strongly bonded metal dimers have little tendency to bind donor ligands on the coaxial positions.⁶² When a ligand is coordinated to the axial site the metal-ligand bond is extremely weak and unstable, as evidenced in a quadruply bonded molybdenum dimer $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$ in which the metal-ligand bond is nearly 0.4 Å longer than that expected for a normal Mo-N bond.⁶³ This was attributed to the strong metal-metal trans influence that roughly correlates with the strength of the metal-metal bond. In Fig. 27, the M-N(pyridine) (M=Mo, Cr, Rh, and Cu) distances are plotted against the metal-metal bond strengths as measured by the effective shrinkage or expansion from the normal metal-metal single bond distances, which are estimated from the metal-oxygen (equatorial) distances within the molecular structures for consistency; $d(\text{M-M}) - 2(d(\text{M-O}) - \text{covalent radius of oxygen}(0.66))$. Likewise, the lengthening of the M-N bonds is corrected for the differences in the covalent radii of the metals. An inverse correlation is seen in the series Mo, Cr, and Cu. Although the effective Rh-Rh bond strength derived in this manner is comparable with that of the chromium dimer, the degree of weakening of the metal-ligand bond is much smaller and in fact similar to that in the dicopper systems where the metal-metal interaction is believed to be extremely weak. The deviation of the point for the dirhodium seems to suggest some unusual metal-ligand interactions that are independent of the metal-metal bond strength.

Fig. 27. Dependence of metal-ligand distances on effective metal-metal bond strengths.

1; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$ 2; $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{py})_2$ 3; $\text{Rh}_2(\text{OAc})_4(\text{py})_2$
 4; $\text{Cu}_2(\text{O}_2\text{CET})_4(3\text{-Mepy})_2$ 5; $\text{Cu}_2(\text{O}_2\text{CET})_4(\text{py})_2$
 6; $\text{Cu}_2(\text{O}_2\text{CCH}_2\text{Cl})_4(2\text{-Mepy})_2$ 7; $\text{Cu}_2(\text{O}_2\text{CCF}_3)_4(\text{quin})_2$
 Appropriate bond distances are tabulated in Table 57.

We will next consider some aspects inherent to each of the dirhodium complexes. For convenience, the seven structures will be divided into groups of closely related adducts, e.g., 1) pyridine and NHET_2 adducts, 2) phosphorus ligand adducts, 3) CO adduct, and 4) $(\text{NO})(\text{NO}_2)$ adduct.

1) $\text{Rh}_2(\text{OAc})_4(\text{py})_2$ and $\text{Rh}_2(\text{OAc})_4(\text{NHET}_2)_2$

The Rh-Rh distance is $2.4020(7) \text{ \AA}$ in the amine adduct, which is $0.01 \text{ \AA}$ greater than $2.3963(2) \text{ \AA}$ in the pyridine adduct in accordance with the increased σ -donor strength for NHET_2 . In both structures the rhodium atoms are $0.07 \text{ \AA}$ displaced out of the plane of equatorial oxygen atoms toward the axial ligands. The Rh-Rh-N linkage is not quite linear in the amine adduct, while in the pyridine adduct it is exactly linear because of the imposition of crystallographic constraints, the atoms of interest being positioned on the C_2 axis.

The amine group is far from being planar, as is shown by the substantial deviations of the atoms from the least-squares plane based on the positions averaged by the disorder. This suggests that the orientations of NHET_2 shown in Fig. 3 are of unequal population. Although the large thermal motions preclude assessment of intermolecular interactions, $\text{C}(4) \cdots \text{C}(6)$ seems to constitute the shortest contact of about $3.4 \text{ \AA}$ when the amine group is properly oriented toward the acetate bridge containing $\text{C}(4)$. The major contacts in the pyridine adduct are between the acetate oxygen atoms and the aromatic ring parallel to the $(1\ 0\ 0)$ plane (Fig. 6).

The overall geometry of the pyridine ring does not differ significantly from that of free pyridine.⁶⁴ The internal angles range from 118.1° to 124.4° . The planarity is excellently maintained in both rings, the deviations of individual atoms from the mean plane being no more than $0.003 \text{ \AA}$ in one and $0.001 \text{ \AA}$ in the other (Table 27). The dihedral angle between the aromatic rings is 58.9° , which is identical within the error limit to that determined for monoclinic $\text{Cu}_2(\text{OAc})_4(\text{py})_2(60^\circ)$.⁶⁵ In contrast, the pyridine rings in the structures of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$ ⁶³ and orthorhombic $\text{Cu}_2(\text{OAc})_4(\text{py})_2$ ⁶⁶ are contained in the same plane. The lack of preferred orientation of the pyridine rings, despite the absence of close intermolecular contacts that may induce steric crowding (aromatic hydrogen-equatorial oxygen distances are longer than the sum of van der Waals radii for any assumed orientations of the pyridine molecule) suggests that the Rh-py π interactions, if any, are not important and easily overcome by the packing forces. The essential linearity of the plot of Rh-Rh distances against the lone-pair ionization potentials of the σ -donor ligands (Fig. 38), H_2O , py, and NHET_2 , supports this.

There is, however, thermodynamic evidence for Rh-L π interactions for pyridine and imidazole as the axial ligands. Kitchens and Bear have measured ΔH for the thermal decomposition reaction

by differential scanning calorimetry.⁶⁷ ΔH values are given in Table 56 and a plot of ΔH 's against pK_b 's is shown in Fig. 28. With an exception of Et_2NH , potential π -acceptors such as pyridine, imidazole,

Table 56. ΔH data for the Thermal Decomposition
 $\text{Rh}_2(\text{OAc})_4\text{L}_2(\text{s}) \rightarrow \text{Rh}_2(\text{OAc})_4(\text{s}) + 2\text{L}(\text{g})$

<u>L</u>	<u>ΔH^a(Kcal/mole)</u>	<u>pK_b^b</u>	<u>L</u>	<u>ΔH^a(Kcal/mole)</u>	<u>pK_b^b</u>
NEt_3	27.2	2.98	imidazole	33.6 ^c	7.05
NHMe_2	26.5	3.27	pyridine	36.7	8.80
NHEt_2	33.1	3.51	DMSO	29.1	15.54 ^d
NMe_3	24.7	4.19	H_2O	23.2	15.70 ^e
NH_3	23.8	4.75	SEt_2	27.4	20.99 ^d

a. Data are taken from reference 67.

b. "Handbook of Chemistry and Physics", R. C. West, 53rd ed.,
 Chemical Rubber Publishing Co., Cleveland, Ohio, 1973.

c. Estimated from data given in reference 68.

d. Calculated from data given in reference 70.

e. Reference 71.

Fig. 28. Plot of ΔH 's vs. pK_b 's.

Values are taken from Table 56.

DMSO, and diethyl sulfide lie substantially above the line connecting the σ -donor ligands. ΔH for imidazole was estimated from the ligand displacement reaction⁶⁸

combined with ΔH for $\text{L}=\text{H}_2\text{O}$ in the decomposition reaction.

Since the observed ΔH 's are the sum of two factors, the bond dissociation energy and the lattice energy as the structure is disrupted by the departing ligand, the scatter of points may reflect the uncertain and structure dependent values of the latter contributor. Thus it is difficult to gauge from ΔH 's alone the degree of involvement of Rh-L π interactions. Measurements of ΔH 's similar to the ligand displacement reaction in solution for a series of ligands would at least remove the question of lattice energy contributions and provide more reliable data. Until more extensive and dependable data become available, the question of Rh-py π interaction should remain unresolved.

Upon completion of the structure determination it was discovered that the structure of the pyridine adduct is isostructural with that of monoclinic form of $\text{Cu}_2(\text{OAc})_4(\text{py})_2$. These two molecules have not only an identical space group but also identical cell constants; for $\text{Rh}_2(\text{OAc})_4(\text{py})_2$ and $\text{Cu}_2(\text{OAc})_4(\text{py})_2$, respectively; $a=9.923(3)$ and $9.955(5) \text{ \AA}$, $b=17.009(6)$ and $17.314(10) \text{ \AA}$, $c=12.539(3)$ and $12.542(10) \text{ \AA}$, $\beta=96.60(2)$ and $96.72(10)^\circ$, and $Z=4$ and space group= $C2/c$ for both. Only the b axis, which is parallel to the M-M axis, differs substantially between the two members. Interestingly, structures of $\text{M}_2(\text{OAc})_4(\text{H}_2\text{O})_2$

for $M=\text{Rh(II)}$, Cr(II) , and Cu(II) are also isostructural. It may be possible to induce $\text{Rh}_2(\text{OAc})_4(\text{py})_2$ and $\text{Cu}_2(\text{OAc})_4(\text{py})_2$ to co-crystallize and form a continuous series of solid solutions.⁶⁹ Such mixed crystals may be useful for the study of the antiferromagnetic dicopper systems since the dirhodium complex is diamagnetic and could thus serve as an inert host matrix.

2) $\text{Rh}_2(\text{OAc})_4\text{L}_2$, $\text{L}=\text{P(OMe)}_3$, P(OPh)_3 , and PF_3

The Rh-Rh distance increases with increasing basicity of the ligand, e.g., $\text{PF}_3 < \text{P(OPh)}_3 < \text{P(OMe)}_3$. The rhodium atoms are 0.1 Å out of the plane of basal oxygen atoms, towards the axial ligands, in the P(OMe)_3 and P(OPh)_3 adducts. The Rh-Rh-P linkage is linear in the P(OPh)_3 adduct but it slightly deviates from the linear axis in the P(OMe)_3 adduct (179.9° and 176.3° , respectively). A linear Rh-Rh-P linkage is required in the structure of the PF_3 adduct by crystallographic symmetry.

The C-C(OP)-C angles in the phenyl rings are 1° larger on the average than the neighboring C-C-C angles, indicating that the non-bonding electrons of phenoxy oxygen is partially delocalized throughout the aromatic ring. The effect of delocalization is also seen in the angles involving the ortho-carbon atoms, which are evidently smaller than the remaining C-C-C angles, presumably due to the ortho-carbon atoms being in a relatively electron-rich state as a result of delocalization. Angle distortions around phosphorus are severe, the O-P-O angles ranging from 91.5° to 104.4° . The average Rh-P-O and O-P-O angles in P(OMe)_3 are $116.8(1)^\circ$ and $101.2(1)^\circ$, which can be

compared with $118.3(1)^\circ$ and $99.6(2)^\circ$ in $\text{P}(\text{OPh})_3$. Since steric interactions between the substituents are not important in these ligands the large Rh-P-O angle in $\text{P}(\text{OPh})_3$ may be ascribed to the increase in the s-character in the bonding orbital of phosphorus as the methoxy groups are replaced with more electronegative phenoxy groups.⁷²

Unlike the Rh-Rh bond, the Rh-P bond shows a remarkable variation in length from $2.340(2) \text{ \AA}$ in the PF_3 adduct to $2.437(1) \text{ \AA}$ in the $\text{P}(\text{OMe})_3$ adduct. This is to be expected if one accepts the view that a phosphorus ligand with more electronegative groups attached to it is capable of forming a stronger M-P bond because of enhanced $d_{\pi}\text{-P}\pi$ interactions. The underlying assumption is of course that the concurrent weakening due to the decrease in basicity is insignificant in comparison. Alternatively, it can also be rationalized in terms of the effective covalent radius of phosphorus. For example, in $\text{H}_3\text{B-PR}_3$ the B-P bond is longer when $\text{R}=\text{CH}_3$ than when $\text{R}=\text{F}$.^{73,77,78} Since π type interactions are deficient in this system the shortening of the B-P bond for $\text{R}=\text{F}$ can be attributed to the decrease in the covalent radius of phosphorus arising from net withdrawal of charge into fluorine. Consideration of σ -donor strengths alone would lead to an opposite trend, namely, a longer B-P bond distance for PF_3 than for $\text{P}(\text{CH}_3)_3$. Additional support for this argument is provided by the electron diffraction study of $\text{t-Bu}_n\text{PF}_{3-n}$ systems,⁷⁴ where the P-F and P-C bond lengths increase almost linearly with increasing number of t-Bu groups. The C-P-F and C-P-C angles, on the other hand, decrease as fluorine atoms are substituted with the t-Bu groups, suggesting the lack of steric strain. This implies that the lengthening of the P-F and P-C

bonds is of inductive origin.

Although which of these effects is the major contributor to the trend in this study is not obvious, the experimental data appear to be more consistent with the concept of π -bonding. The P-O distances in the P(OMe)_3 and P(OPh)_3 adducts are identical, despite the slight difference in the electronegativities of the P substituents. The Rh-P bond, however, is shorter by $0.025 \text{ \AA}$ in the P(OPh)_3 adduct than in the P(OMe)_3 adduct, as would be expected if P(OPh)_3 is viewed as a stronger π -acceptor. Since the identical P-O distances are indicative of identical covalent radius of P in both ligands, one would then anticipate somewhat different results in the absence of such d_π - $\text{P}\pi$ interactions, possibly a change in the opposite direction.

The Rh-P bond distance in $\text{Rh}_2(\text{OAc})_4(\text{PPh}_3)_2$ ⁷⁵ was found to be $2.479(3) \text{ \AA}$, $0.067 \text{ \AA}$ longer than that in the P(OPh)_3 adduct, once again in concert with the predictable trend in the π -acceptor series. A similar trend is seen in the Cr(0) complexes,¹¹⁵ $\text{Cr(CO)}_5(\text{PPh})$ and $\text{Cr(CO)}_5(\text{P(OPh)}_3)$; the variation in the Cr-P distance in going from P(OPh)_3 to PPh_3 is as large as $0.113 \text{ \AA}$. This can be accounted for by the differing degree of participation of metal d_π electrons, due in part to the difference in the oxidation states of metal centers and the neighboring ligand groups, particularly the ones in trans relation to the phosphorus ligands.

Surprisingly, a plot of the Rh-P distances against the lone-pair ionization potentials of free ligands gave an excellent linear fit as depicted in Fig. 29. This correlation is understandable in the sense that the removal of electron density from phosphorus would lower the

Fig. 29. Plot of $d(\text{Rh-P})$'s vs. IP 's.

IP 's are taken from Table 58 and distances from Table 55.

energy of the acceptor orbital as well as that of the donor orbital and hence the energy match becomes more favorable for the π -interaction with the metal center. However, this should not be misconstrued as suggesting that $d_{\pi-P\pi}$ bonding is the sole determiner of the relative Rh-P bond strength in the series, for the PF_3 adduct is presumably the least stable species. Once prepared in crystalline form, it reverts at room temperature to the green starting material within a day or so, while the PPh_3 adduct is stable (at least for two years). In this respect, the simultaneous weakening of the Rh-P σ -bond as P becomes more electronegative appears to be important, although the bond length data imply the strength order $Rh-PF_3 > Rh-PPh_3$.

The next interesting feature is the correlation between the Rh-P and Rh-Rh bond lengths (Fig. 30). The points for PF_3 , $P(OPh)_3$, and $P(OMe)_3$ yield a good straight line. The anomaly in that the point for PPh_3 does not fall on the line may be of steric origin; cone angles are 145° , 104° , 107° , and 118° for PPh_3 , PF_3 , $P(OMe)_3$, and $P(OPh)_3$, respectively.⁷⁶ Such steric strain is likely to produce an angular distortion, as well as an elongation of the Rh-P bond to accommodate the steric demands. In this case, the Rh-P bond would be a little longer than it should be and subsequently the Rh-Rh bond would be shorter than expected if it were under the full influence of the axial ligands at a closer distance. Examination of the linear plots of the Rh-P and Rh-Rh distances against the IP's for PF_3 , $P(OMe)_3$, and $P(OPh)_3$ suggests that the Rh-P and Rh-Rh bond lengths may be altered from "strain free" values by 0.01-0.02 Å. This is not a unreasonable magnitude in view of the structural deformations observed in systems

Fig. 30. Plot of $d(\text{Rh-P})$'s vs. $d(\text{Rh-Rh})$'s.
Values are taken from Table 55.

where relatively less rigid and flexible equatorial ligand groups release the strain by appropriate geometric adjustments. For example, in the structures of $\text{Rh}_2(\text{DMG})_4(\text{PPh}_3)_2$ ²⁶ and $\text{Rh}(\text{DMG})_2(\text{PPh}_3)\text{Cl}$,³⁸ the DMG planes are bent away from the phenyl groups, causing the rhodium atom to be displaced toward PPh_3 by 0.126 Å in the latter and by an average of 0.025 Å in the former. In $\text{Rh}_2(\text{OAc})_4(\text{PPh}_3)_2$, the O_4 units encounter strong opposition from each other through the O-C-O linkages. Thus the strain can be more effectively released via elongation of the Rh-P bond than via angular deflection of the O_4 units from the axial ligands. The correlation between the Rh-Rh and Rh-P bond distances contrasts with the inverse correlations depicted in Fig. 27 or in Cr(II) carboxylate complexes¹⁷³ where the $\text{Md}\pi\text{-L}\pi$ interactions are of little importance.

3) $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$

The Rh-C-O bond is bent, $175.5(3)^\circ$, due to the close contacts of the carbonyl oxygen atom with the methyl groups in neighboring molecules (Table 36 and Fig 10). The shortest contact is 3.28 Å, slightly smaller than a normal value of 3.4 Å.

The C-O bond length is 1.096 Å, shorter by 0.03 Å than the value for free CO. This is somewhat unusual in view of the fact that the C-O bond is in general weakened upon coordination. From an energetic point of view, it is expected for a coordinated carbonyl group that donation of σ -electrons from the antibonding $5\sigma(\text{CO})$ orbital to the metal will lead to a stronger C-O bonding interaction and hence a shorter C-O distance, while an increase in the overall $\pi^*(\text{CO})$ orbital population through π -backbonding will give rise to an opposite effect.

Fig. 31. Plot of Rh-CO vs. C-O distances in Rh-CO complexes
The error bars represent one standard deviation from the points.

1. $\text{Rh}_2(\text{OAc})_4(\text{CO})_2$; this work, 2. $\text{Rh}(\text{Cp})(\text{CO})\text{I}(\text{C}_2\text{F}_5)$; ref 156,
3. $(\text{Cp})_2\text{Rh}_2(\text{CO})_3$; ref 157, 4. $\text{Rh}(\text{CO})_2(\text{N}(\text{n-Pr})_4)\text{I}_4$; ref 158,
- 5-8. $\text{Rh}_4(\text{CO})_{12}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$; ref 159, 9. $\text{Rh}_2\text{I}_6(\text{MeCO})_2(\text{CO})_2^{-2}$; ref 160,
10. $\text{RhCl}(\text{CO})(\text{t-Bu}_3\text{P})_2$; ref 161, 11, 12. $\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{CCCF}_3)(\text{Cp})_2$; ref 162
13. $\text{RhH}(\text{CO})(\text{PPh}_3)_3$; ref 163, 14. $\text{Rh}(\text{CO})_2(\text{s-t-Bu-N}, \text{N}'\text{-dimesitylsulfur-diimine})$; ref 164,
15. $\text{Rh}(\mu\text{-SPh})_2(\text{CO})_2(\text{PMe}_3)_2$; ref 165, 16. $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)_2$; ref 166,
17. $\text{Rh}(\text{CO})(\text{Ph}_2\text{PC}_2\text{OC}_2\text{PPh}_2)$; ref 167,
- 18, 19. $\text{RhCl}_2(\text{CO})_2^{-}$; ref 168, 20. $\text{Rh}(\text{CO})((\text{Ph}_2\text{PC}_2)_2\text{O}(\text{C}_2\text{O})_2)$; ref 167,
- 21, 22. $\text{Rh}(\text{CO})(\text{MeCOCHCOME})$; ref 169, 23, 24. $\text{Rh}(\text{CO})_2\text{Cl}(\text{OPCy}_3)$; ref 170,
25. $\text{Rh}(\text{n-Bu}_4\text{N})\text{Cl}_2(\text{CO})_2$; ref 171

The π backbonding is presumed to be much sensitive to the M-C bond length, declining sharply with increasing M-CO distance, in contrast with the relatively invariant σ -bonding.⁸⁸ Fig. 31 is a plot of Rh-CO vs. C-O distances in some Rh(0), Rh(I), and Rh(III)-CO complexes (there are no other known structures of Rh(II)-CO complexes). A rough inverse correlation is seen between the two variables. The Rh-CO bond length found in our structure is too long for an effective π -overlap, as indicated by a small decrease in the CO stretching frequency from the value for free CO ($\nu(\text{CO})=2104 \text{ cm}^{-1}$ both in CH_2Cl_2 and Nujol as compared to 2143 cm^{-1} for free CO). The shortening of the C-O bond is however inconsistent with the apparent decrease in the CO stretching frequency.

The disparity between the C-O bond length and stretching frequency may be rationalized in terms of the effective covalent radius of the carbonyl carbon atom. Since at an extremely long M-CO distance the M-CO σ -overlap is more effective than the M-CO π back-bonding there is a net withdrawal of charge from CO into the metal center. In other words, the carbon atom becomes more electropositive due to the loss of charge. This will lead to a reduction of the covalent radius of carbon which will give rise to a shorter, but weaker, C-O bond in agreement with the structural data and CO stretching frequency. Although the ^{13}C nmr shifts cannot be explained by the screening effect alone, the upfield shift of the bisadduct of CO relative to free CO does not appear to support the above argument (see section B. Nmr Studies in this chapter).

4) $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$

There are some features in the acetate framework that are not seen in other dirhodium complexes. First, the variation in the Rh-O(acetate) distance is large, ranging from 2.009(3) Å to 2.050(3) Å with an average of 2.027(3) Å which is somewhat shorter than the values found other adducts. Second, the average Rh-Rh-O and Rh-O-C angles on the NO side (86.1° and 121.1°) differ significantly from those on the NO₂ side of the molecule (88.3° and 118.9°). Third, the displacement of Rh from the O₄ unit is 0.08 Å larger toward NO than toward NO₂ (0.14 Å vs. 0.06 Å).

All the above anomalies arise entirely from steric interaction between the acetate oxygen and axial ligand oxygen atoms. Appropriate intramolecular distances are included in Table 52. Both NO and NO₂ ligands are positioned so as to minimize intramolecular non-bonded contacts. The RhNO and ONO planes are approximately coplanar and bisect two acetate planes (C_s closely approximates the molecular point symmetry). The NO moiety is tilted toward halfway between O(6) and O(7) but with O(11) pointing more toward O(6); the O(11)···O(6) and O(11)···O(7) distances are 2.78 Å and 2.96 Å, respectively. Thus O(6) and O(7) are pushed away from NO, the former more so, as can be seen in the Rh-Rh-O angles of 83.4° and 84.4° for O(6) and O(7), whereas those for O(5) and O(8) are 88.8° and 87.7°. The impact of these interactions is also apparent in the Rh-O-C angles. The Rh(2)-C(6)-C(3) angle is 2° greater than the Rh(2)-O(7)-C(5) angle and the average is 122.8° as compared to 119.3° for the average of Rh(2)-O(5)-C(1) and Rh(2)-O(8)-C(7) angles. Even the angle O(6)-Rh(2)-O(7)

Fig. 32. Steric distortion of acetate frameworks in $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$.

is slightly wider than the angle O(5)-Rh(2)-O(8) (90.1° for the former and 88.8° for the latter). Furthermore, the Rh-O distances appear to be slightly elongated for O(6) and O(7) in order to release the strain. Expectations are then that within the five membered ring $\overline{\text{Rh-Rh-O-C-O}}$ the closing and opening of Rh-Rh-O and Rh-O-C angles on one side would be properly balanced by the opening and closing of the corresponding angles on the other side if the O-C-O linkage is rigid. This is indeed what is observed on the NO₂ side of the molecule. The Rh(1)-O(2)-C(3) and Rh(1)-O(3)-C(5) angles are much smaller than the Rh(2)-O(6)-C(3) and Rh(2)-O(7)-C(5) angles. Also, the Rh-Rh-O angles for O(2) and O(3) are altered as anticipated. The steric pushing effect is propagated throughout the molecular skeleton so that the NO₂ moiety is bent away from the acetate planes involving C(3) and C(5), causing acetate planes involving C(1) and C(7) to distort toward NO. The distortion of the molecule is illustrated in an exaggerated manner in Fig. 32. It is seen that the acetate frameworks are skewed from the normal geometry and the axial ligands are deflected from the Rh-Rh axis in the direction to minimize the repulsive interactions with the acetates. That the rhodium atom is more displaced from the plane of equatorial oxygen atoms at the NO end is due to the shorter Rh-NO distance and the larger deflection angle which would certainly otherwise yield even greater strain.

The most important aspect of such structural deformations is that the Rh-O(acetate) distances are always shorter for the oxygen atoms that are less influenced by the repulsive forces. A beautiful example is the case of O(2) for which the intramolecular contact is

the longest. Consequently, the Rh-O distance is the shortest, 2.009(3) Å. Moreover, the average of the Rh(1)-O(2) and O(3) distances is only 2.013 Å, while that for O(1) and O(4) is 2.038(3) Å.

Undoubtedly, the tendency for the Rh-O bond to shorten is due to the unusual properties of the axial ligands. The N-O distance and O-N-O angle for the NO₂ ligand are 1.224(5) Å and 123.4(5)°, intermediate between the corresponding values in the anionic NO₂⁻ in the crystal structure of NaNO₂^{89a} and in the neutral NO₂ determined by microwave spectroscopy^{89b}; 1.240 Å and 114.9° in NaNO₂ and 1.197 Å and 134.2° in gaseous NO₂. Similar intermediate values were also found in other M-NO₂ complexes such as Cr(Me₆(14)₄,11-dieneN₄)(NO)(NO₂)(PF₆)(d(N-O) = 1.236(4) Å and ∠ONO = 118.2(3)°)^{125a} and cis-Co(NO₂)₂(N₂C₄H₁₂)₂(d(N-O) = 1.21(1) Å(ave) and ∠ONO = 118.6(7)°(ave))^{125b}. The Rh-N-O(nitrosyl) angle 128.8(3)° is normal for a bent M-N-O structure and may be compared to 125(2)° determined for the five coordinate Rh(II)-NO complex, RhCl₂(NO)(PPh₃)₂⁸⁷. It may be worth noting that the Rh-N-O angle could be even smaller than is observed in the absence of repulsive interactions.

It is well known that the O-N-O angle is dependent on the effective charge of the moiety and expected to decrease with increasing negative charge. In the series NO₂⁺, NO₂, and NO₂⁻, the O-N-O angles and N-O distances, in the order given, are 180° and 1.15 Å, 134° and 1.20 Å, and 115° and 1.24 Å.⁹⁰ The same basic argument holds even when one oxygen atom is replaced by a metal atom. For a six-coordinate nitrosyl complex, addition of one or two electrons to the 3π(π*(NO), d_{xz}, d_{yz}) orbitals of a linear MNO system leads to a bent MNO system.^{90a} In the

case of one electron addition, the bending is intermediate as is observed in $\text{FeBr}(\text{NO})(\text{diarsine})^+(\angle \text{FeNO}=148^\circ)^{90a}$. Formal addition of two electrons causes the M-N-O bond to bend further to about 120° . As a result a pair of electrons are localized on the central atom $\text{N}(\text{sp}^2)$ and the initially d^n metal atom can be described as having a d^{n-1} configuration after the formal transfer of electron density to NO. Within this formalism, the dirhodium complex can be described as $\text{ON}^--\text{Rh}(\text{III})-\text{Rh}(\text{III})-\text{NO}_2^-$, or, at very least, $\text{ON}^{\delta-}-\text{Rh}(\text{II})^{\delta+}-\text{Rh}(\text{II})^{\delta+}-\text{NO}_2^{\delta-}$. The reduction in the Rh-O distance can then be interpreted as due to the contraction of metal centers after the charge transfer. A similar reduction in Rh-O distances is also observed in the structure of $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^+$ species.³¹

It is interesting to note that although one expects similar metal contractions upon partial oxidation and observes this in the Rh-O distances, the Rh-Rh distance decreases in one case but increases in the other, if comparison is made with $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^{50a}$. This paradox can of course be resolved by considering the trans influence of the axial ligands. In going from the neutral to the cationic water adduct, one only sees the contraction effect. In $\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$, however, the contraction effect is overshadowed by the trans influence. Some important data are given below:

Complex	$d(\text{Rh}-\text{O}), \text{\AA}$	$\Delta d(\text{Rh}-\text{O}), \text{\AA}$	$d(\text{Rh}-\text{Rh}), \text{\AA}$	$\Delta d(\text{Rh}-\text{Rh}), \text{\AA}$
$\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2^+$	2.014(10)	-0.025	2.318(2)	-0.068
$\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$	2.039(8)	0.000	2.3855(5)	0.000
$\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$	2.027(3) 2.017(3)	-0.012 -0.022	2.4537(4)	+0.068

The question is, which of the two dissimilar axial ligands contributes more to the weakening of the Rh-Rh bond? Although the scarcity of available experimental data for nitro complexes prevents definitive conclusions, the NO_2 contribution appears to be minor. The relative magnitude of the trans influence is dramatically illustrated in the series of $\text{Co}(\text{NH}_3)_5\text{L}^{+n}$ where $\text{L}=\text{NH}_3$,⁹¹ NO ,⁹² and NO_2 ,⁹³ and $n=2$ or 3 :

Complex	$\text{d}(\text{Co}-\text{NH}_3)$, cis Å	$\text{d}(\text{Co}-\text{NH}_3)$, trans Å
I	1.968(5)	1.968(5)
II	1.981(6)	2.220(4)
III	1.98(2)	1.98(2)
$\text{Co}(\text{NH}_3)_5\text{Cl}^+$	2.01(2)	1.97(2)

Comparing the structures of I, II, and III, one finds that the $\text{Co}-\text{NH}_3$ (cis) bonds in all three are similar in length, in spite of the differences in the oxidation states of the metal. In addition all these $\text{Co}-\text{NH}_3$ distances are substantially shorter than the value in a strictly $\text{Co}(\text{II})$ complex $\text{Co}(\text{NH}_3)_5\text{Cl}^+$,⁹⁴ a fact that supports the foregoing argument. The $\text{Co}-\text{NH}_3$ bond trans to NO_2 shows no induced changes, but a drastic lengthening is seen in the $\text{Co}-\text{NH}_3$ bond trans to NO .

Such strong trans influence of the NO^- ligand has been observed in a Co(III) complex.⁹⁵ It is expected that NO and NO_2 with sp^2 hybridized N atoms (under NO^- and NO_2^- formalism) would have similar metal-ligand distances. The remarkably shorter M-NO distance in the dirhodium complex, as well as in the Co complexes, gives evidence of a stronger metal-ligand interaction for NO than for NO_2 .

Minor points of interest are the direction of bending of NO and vibrational stretching frequencies of the ligand. Hoffmann, et al.,⁹⁶ predicted that NO in a five-coordinate complex would be bent in such a way to maximize the $d_{z^2}-\pi^*(\text{NO})$ overlap. The observed crystal structures of some hexa- and pentacoordinate nitrosyl complexes are in accord with the theoretical inferences.^{92,95,96} The NO ligand in the dirhodium complex however is bent in the opposite direction to the prediction. The infrared spectrum of the material shows three bands in the $\nu(\text{NO})$ region, 1695, 1720, and 1811 cm^{-1} (KBr disk), indicating the presence of other species than the ON-Rh-Rh-NO_2 complex. Johnson, et. al.,⁹⁷ observed two bands at 1800 and 1710 cm^{-1} for the symmetric ON-Rh-Rh-NO complex. If their assignment is correct, the band at 1695 cm^{-1} may be assigned to the NO stretching in the asymmetric ON-Rh-Rh-NO_2 complex and the other two bands can be regarded as arising from the 1:2 NO adduct that was simultaneously formed. Only two bands attributable to NO_2 are observed, at 1298 and 811 cm^{-1} .

The origin of NO_2 is uncertain. Although the possibility of NO_2 being present as an impurity in the reaction medium cannot be excluded, it is likely that the nitric oxide disproportionation reaction may have been induced by the metal center⁹⁸; $3\text{NO} \xrightarrow{\text{Rh}_2(\text{OAc})_4} \text{NO}_2 + \text{N}_2\text{O}$.

B. Nmr Studies

The ^{31}P nmr data for 1:1 and 1:2 adducts and mixed ligand adducts of the form $\text{R}_3\text{P}-\text{Rh}-\text{Rh}-\text{PR}'_3$ are assembled in Tables 53 and 54. The one bond coupling constants are in the normal range for rhodium-phosphorus bonds but the long-range couplings between phosphorus nuclei are extremely large. The coordination chemical shifts $\Delta\delta$, defined as $\delta(\text{L})-\delta(\text{complex})$, are very unusual in that they are positive (upfield) for all compounds. Of particular interest is that the resonances of 1:1 adducts appear at even higher fields than those of 1:2 adducts with ratios $\Delta\delta(1:1)/\Delta\delta(1:2) \sim 2.3$.

We first consider the chemical shifts of phosphorus resonances. Factors influencing the chemical shifts in phosphine complexes can be summarized by three major contributing terms¹⁰⁶

$$\delta = \delta_d + \delta_p + \delta_a$$

where δ_d represents the diamagnetic shielding effect which depends on the electron density around phosphorus and δ_a is the contribution of neighboring atoms in the molecule. The neighbor anisotropy term δ_a is proportional to a quantity $\Delta\chi R^{-3}$ where R is the distance from the phosphorus nucleus and $\Delta\chi$ the anisotropy in the magnetic susceptibility tensor. The paramagnetic term δ_p arises from the mixing of excited states with ground states induced by the magnetic field applied to the molecule. A detailed theoretical study¹³⁰ of the paramagnetic term shows that the shift is related to both p and d orbital occupations of phosphorus in the following manner

$$\delta = -\frac{k}{\Delta E} (\langle r^{-3} \rangle_p \uparrow_1 + \langle r^{-3} \rangle_d \uparrow_2)$$

where k is a positive constant involving the gyromagnetic ratio, ΔE the average excitation energy, and r the average radii of the phosphorus atomic orbitals specified by the subscripts. The coefficients ξ_1 and ξ_2 in this expression take into account the population of phosphorus p and d orbitals, which are respectively involved in σ and π bonding.

Assuming that the transitions in the visible spectra of the adducts correspond to the orbital levels involved in the M-L bonding, such that the energy separations ΔE are the same as those in the above equation, we now consider the effect of changes in excitation energy in the dirhodium complexes. Although accurate transition energies were not measured, it can be readily inferred from the colors of compounds that the 1:1 adducts(violet-blue) have lower excitation energies in the visible region than the 1:2 adducts(red), e.g., $\Delta E_{1:1} < \Delta E_{1:2}$. If δ is largely dependent on ΔE , the absolute magnitude of shift surely parallels ΔE^{-1} , a larger shift for the monoadduct than bisadduct, in agreement with the theoretical prediction. For any given ligand, the shift for the monoadduct would have to be downfield relative to the bisadduct(in the above equation an increase in the negative number corresponds to a downfield shift;the ^{31}P measurements in this study were based on an opposite sign convention), as opposed to the trend observed. Therefore, ΔE cannot be a dominating factor that determines $\Delta\delta$ in these complexes.

If a M-P bond consists essentially of M-P σ type interaction with no substantial π backbonding, the term ξ_1 will decrease. The

contraction of the p orbital will result in a decrease in r and, hence, it is quite possible that the entire term $\langle r^{-3} \rangle_p \xi_1$ is dominated by the increase in $\langle r^{-3} \rangle_p$. In this case, the shift would be expected to be to lower field from the free ligand. If, instead, the orbital contraction exerts no significant influence on r , the term $\langle r^{-3} \rangle_p \xi_1$ may decrease and an upfield shift would be observed upon complexation. Similar arguments should hold for the d orbital occupation. An increase in ξ_2 due to the M-P π bonding must accompany the expansion of the d orbitals. As the d orbitals are more exposed to external fields than p orbitals, $\langle r^{-3} \rangle_d$ should have a larger dependence on the charge residing in the phosphorus atomic orbitals. The term $\langle r^{-3} \rangle_d \xi_2$ can become either smaller or larger, depending upon whether $\langle r^{-3} \rangle_d$ or ξ_2 dominates. In any case, when the sum of the two factors, $\langle r^{-3} \rangle_p \xi_1 + \langle r^{-3} \rangle_d \xi_2$, is smaller in the complex than in the free ligand, the resonance would appear at a higher field.

Application of the above relations to the dirhodium complexes would be rather difficult without the knowledge of relative importance of the contributing terms. A qualitative analysis based on one factor isolated from the others would not allow reasonable rationalizations of the upfield shifts in dirhodium compounds. For a ligand PR_3 , consideration of ξ_1 alone predicts that the bisadduct should appear at a higher field than the monoadduct because the loss of p orbital electrons (through Rh-P σ interaction) in the monoadduct would be smaller than in the bisadduct owing to the weaker trans influence of the Rh-Rh bond on Rh-P bond in the latter. The dependence of ξ_1 on the rehybridization effect caused by the R-P-R angle variation is not at all important in

this consideration, for it can be safely assumed that the geometry of PR_3 is the same for both mono- and bisadduct. This is in particular true for the PPh_3 adduct where the C-P-C angle is not altered appreciably upon coordination (103.0° ⁷⁵ vs. 103.4° in free PPh_3 ¹⁴²). An increase in the d orbital population due to Rh-P π backbonding may lead to a upfield shift, only if the subsequent expansion of r perturbs the term $\langle r^{-3} \rangle_{d_{\frac{5}{2}}}$ more than $\frac{5}{2}$ itself does. As regards the possibility that the Rh-P bond shortens in going from the monoadduct to bisadduct, which will strengthen the Rh-P π interaction, despite the expected reduction by sharing the Rh-Rh $d\pi$ density, it is difficult to predict from the bonding argument alone whether the mono or bisadduct will have a larger upfield shift.

The effect of neighbor anisotropy should be minor as the neighboring atoms are similar for both mono- and bisadducts of a particular ligand. Thus this does not appear to be a dominant contributor to such a large separation of the resonances between mono- and bisadducts.

A simpler interpretation based on local diamagnetic shielding may account for the relative positions of resonances. It is conceivable that the Rh-P π backbonding is stronger when only one axial ligand is coordinated to the dirhodium than when two identical ligands are sharing the same Rh-Rh $d\pi$ electrons; there is more charge concentrated on phosphorus in the monoadduct, resulting in a larger upfield shift. The upfield shift of the bisadduct from the free ligand can be explained in a similar fashion. The underlying assumption required by this mechanism is that the loss of charge through the Rh-P σ bonding interaction is small, if not negligible, in comparison, a fact that is not

supported by the structural results nor by the stability argument (see the Description of Structures). The infrared stretching frequency of CO in the CO adduct also indicates that such is not the case. In addition, the above argument does not agree with the generally accepted view that the ^{31}P resonances of strongly π interacting phosphorus ligands occur at lower fields because of the dominance of the paramagnetic term. Nevertheless, the trend observed for the dirhodium complexes seems to argue for the increased diamagnetic shielding. In Figure 33, the coordination shifts $\Delta\delta$ are plotted against the ionization potentials of free ligands which correlate with π acceptor strengths (IP of PCl_3 is unknown and consequently it is excluded from consideration). An excellent linear correlation is seen among PPh_3 , P(OMe)_3 , P(OPh)_3 , and PCl_3 . $\Delta\delta$ is also proportional to $\delta(\text{L})$ (vide infra). The substituent atoms directly bonded to phosphorus have either π electrons (phenyl groups) or lone pair electrons (O, Cl, and F) that can form partial double bonds¹³³ which will lower the shift by populating phosphorus d orbitals. The strong electronegativity of fluorine and the compactness of its atomic size would make such P-R π bonding less effective in the case of PF_3 .¹⁵⁵ The high shift of PF_3 will then give rise to the deviation in Figure 33.

It has been postulated that the upfield shifts in some metal-phosphite complexes could be interpreted in terms of charge drift from the P substituents.¹³¹ This postulate proved to have serious limitations and inconsistencies when attempts were made to extend it to other, similar complexes.¹³²

Fig. 33. Dependence of coordination shifts on IP's of free ligands.
IP's are taken from Table 58 and coordination shifts from Table 53.

Another interesting feature concerning the coordination shifts in the dirhodium complexes is the linear dependence of $\Delta\delta$ on $\delta(L)$, as shown in Fig. 34. A relation of this type was noticed earlier by Reddy and Schumtzer¹³³ in NiL_4 and $Mo(CO)_3L_3$ (L=trivalent phosphines) where a larger downfield shift was observed for a ligand with a higher shift in its free form. When $L=PCl_3$, the coordination shifts were to upfield in both Ni and Mo complexes, an anomaly attributed to the large changes in hybridization and geometry. A similar correlation was also found by Mann, et. al.¹³⁴ in compounds such as $M(CO)_5L$ (M=Mo, Cr, and W),¹³⁵ mer- $RhCl_3L_3$,¹³⁶ $PdCl_2L_2$,¹³⁷ $PtCl_2L_2$.¹³⁸ Our data presented in Fig. 34 show exactly the reverse trend; the lower the shift of a free ligand, the larger the upfield shift in the complex. No abnormal behavior is seen for PCl_3 or even for sterically bulky PCy_3 , which can be taken as evidence for the absence of geometric adjustment upon coordination to Rh of the latter. Neither the trend in other complexes nor the reverse correlation in the dirhodium compounds is yet explicable at this time.

The $^1J(RhP)$ values in the monoadducts increase systematically from 94.9 to 163.8 Hz as the ligand changes from PCy_3 to PF_3 , in the order of increasing electronegativity of substituent atoms ($C < Cl < O < F$). The two-bond coupling $^2J(RhP)$ is in general proportional to the magnitude of $^1J(RhP)$, with an exception of PCl_3 , for which $^2J(RhP)$ is exceptionally large and comparable with $^1J(RhP)$. The Pople-Santry MO theory shows that the coupling constants between directly bonded atoms arise from the Fermi contact term¹³⁹ and the following approximate expression¹⁰² can be used for the Rh-P coupling

Fig. 34. Dependence of coordination shifts on chemical shifts of free ligands.

$$^1J(\text{RhP}) \propto \gamma_{\text{Rh}} \gamma_{\text{P}} \alpha_{\text{Rh}}^2 \alpha_{\text{P}}^2 |S_{\text{Rh}(5s)}(0)|^2 |S_{\text{P}(3s)}(0)|^2 (\Delta E)^{-1}$$

where γ_{Rh} and γ_{P} are the magnetogyric ratios for the nuclei, α_{A}^2 is A's s character in the bond, $|S(0)|^2$ the s electron density evaluated at the indicated parent nucleus, and ΔE involves the average excitation energy for the singlet-triplet transition of metal. Different views concerning the mechanism by which metal-phosphorus couplings can change have been thoroughly reviewed by Nixon and Pidcock.¹⁰⁶ It is obvious from the above equation that changes in $^1J(\text{RhP})$ with phosphine within the dirhodium series cannot be simply explained by one mechanism or the other because phosphines possess different magnitudes of α_{P}^2 and $|S_{\text{P}}(0)|^2$ and, at the same time, directly modify α_{Rh}^2 and $|S_{\text{Rh}}(0)|^2$, as well as ΔE . If one assumes that the metal dependent variables are relatively constant for all adducts, the increasing trend of $^1J(\text{RhP})$ with increasing electronegativity of substituent groups may be related to the increase in the ligand dependent quantities α_{P}^2 and $|S_{\text{P}}(0)|^2$. It must be mentioned here that there are cases where such correlation breaks down even when metal components appear to be invariant.^{73a} On the other hand, since the existence of Rh-P π bonding cannot be ruled out, as is indicated by the upfield chemical shifts, the loss of metal charge may also increase the contributions of α_{Rh}^2 and $|S_{\text{Rh}}(0)|^2$.

Although the extent to which each of these factors participate in the bond is not certain, the coupling constants do reflect one aspect of the bond--s character--which can be an indirect measure of the bond strength if other contributing factors are held constant. The Rh-P bond distances in the dirhodium complexes decrease in the order $\text{PPh}_3 > \text{P(OMe)}_3 > \text{P(OPh)}_3 > \text{PF}_3$, in fair agreement with the observed Rh-P coupling

constants. A linear correlation between the Rh-P distances and IP's of free ligands was noted in the previous section (Fig. 29), which was ascribed to the gradual shortening of the Rh-P bond as the π acidity of phosphine increases. Thus it is tempting to relate the coupling constants to IP's. It is seen in Fig. 35 that neither $^1J(\text{RhP})$ nor $^2J(\text{RhP})$ correlates well with IP owing to the inexplicable deviation of PCl_3 , but the sum of $^1J(\text{RhP})$ and $^2J(\text{RhP})$ does increase monotonically with increasing IP. Interestingly, despite the same values of $^1J(\text{RhP})$ for $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OPh})_3$, $^2J(\text{RhP})$ for the former is smaller than for the latter. One can deduce from the bond length data for the corresponding bisadducts that the Rh-Rh bond in the 1:1 $\text{P}(\text{OMe})_3$ adduct will be longer than that in the 1:1 $\text{P}(\text{OPh})_3$ adduct. Since the Rh-Rh bond strength is partially mirrored by $^2J(\text{RhP})$, the observed ordering of $^2J(\text{RhP})$, $\text{P}(\text{OMe})_3 < \text{P}(\text{OPh})_3$, is consistent with the bond length order $\text{P}(\text{OMe})_3 > \text{P}(\text{OPh})_3$. Evidently, the drastic reduction of $^2J(\text{RhP})$ in going from monoadducts to mixed ligand or bisadducts, while $^1J(\text{RhP})$ does not change noticeably in comparison, must also be related to further weakening of the Rh-Rh bond as one more axial ligand is attached to the vacant site of the Rh-Rh-P system.

The most interesting aspect of the ^{31}P spectra is the observation of extremely large, long-range couplings between the phosphorus nuclei. Table 54 lists values of $^3J(\text{PP})$ ranging from ~ 300 Hz for trialkylphosphines to ~ 900 Hz for phosphites. These three-bond couplings are almost invariably similar in magnitude to two-bond couplings found in monomers such as $\text{trans-RhX}(\text{CO})(\text{PMe}_2\text{Ph})_2$, 140 $\text{trans-RhCl}_3(\text{CO})(\text{PMe}_2\text{H})$, 141 or even in $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ complexes. 143 It was pointed out that the

Fig. 35. Correlation between the coupling constants and IP's of free ligands. IP's are taken from Table 58.

most significant factor that determines P-P couplings could be the electronegativity of substituent atoms on phosphorus,^{139b} increasing with electronegativity just as with M-P couplings. No such dependence exists here. If there were, the couplings involving PCl_3 would have to be smaller than those involving phosphites (Pauling electronegativity = 3.16 for Cl and 3.44 for O). Instead, the couplings vary linearly with IP's in the series $(\text{MeO})_3\text{P-Rh-Rh-PR}_3$ for $\text{R}=\text{Ph}$, OMe , OPh , and Cl . The overall trend in the series $\text{Ph}_3\text{P-Rh-Rh-PR}_3$ is in keeping with this, with a net difference of approximately 300 Hz between the two series, with the prominent exception of $\text{Ph}_3\text{P-Rh-Rh-PPh}_3$ for which $^3\text{J}(\text{PP})$ is undoubtedly overestimated in the computer analysis (Fig. 35).

When the Fermi contact term is dominant, there is marked dependence on the singlet-triplet excitation energy of the P-P coupling.^{139b,140} In the case of these dirhodium compounds, nothing much can be said about the degree of participation of the energy term, due in part to the lack of information on the signs of P-P couplings. However, the linear dependence of P-P couplings on IP's is a good indication that ΔE is significantly responsible. This is because the energies of unoccupied orbitals, particularly Rh-Rh σ^* , to which the most favorable transition (that will make dominant positive contributions) is likely to occur, are raised in proportion to the phosphorus donor orbital energy (see Fig. 46 for the energy levels). In other words, ΔE will increase with the ligand donor strength, giving rise to a smaller coupling for a stronger σ donor. This is in sharp contrast with $^1\text{J}(\text{RhP})$ which correlates beautifully with electronegativity but not with IP, suggesting that ΔE is less important in the Rh-P coupling.

The Rh-Rh coupling constants determined for bisadducts of P(OMe)_3 and P(OPh)_3 , 7.5 and 6.0 Hz, respectively, are identical within the error limit and comparable with the values of ca. 4 Hz obtained by computer simulation for Rh(I) dimers.^{144a} $^1\text{J(RhRh)}$ in $\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{DPM})(\text{BPh}_4)$ (DPM=bis(diphenylphosphino)methane) has been reported to be 127.8 Hz,^{144b} but the large uncertainty in the reported value, ca. ± 25 Hz,^{144c} precludes comparison with values found in this study.

The trend in ^{13}C chemical shifts of CO adducts is similar in every aspect to that observed for phosphorus ligands. Factors governing the ^{13}C shifts are, by and large, identical to those for ^{31}P shifts. The arguments for the phosphorus ligand adducts should thus as well hold for the CO adducts. It is of particular interest to note that, unlike dirhodium species, virtually all ^{13}C resonances of other metal-carbonyl complexes are to lower field than free CO.^{145,146} Numerous accounts have appeared¹⁴⁷⁻¹⁴⁹ to rationalize the downfield shifts in terms of the paramagnetic term of the screening constant such as the one similar to the equation for the ^{31}P resonance. Considerable pessimism has been expressed concerning limitations on qualitative explanations based on the paramagnetic term alone^{150,151} and the importance of the frequently neglected diamagnetic term has been emphasized.¹⁵¹

$^1\text{J(RhC)}$ for the monoadduct is a little smaller than the expected value of 60-80 Hz for terminal Rh-CO species¹⁴⁶ but comparable with the 40-50 Hz expected for bridging CO groups, such as those, for example, in $\text{Rh}_2(\text{CO})_3(\text{Cp})_2$,¹⁵² $\text{Rh}_2(\text{CPh}_2)_2\text{Cl}_2\text{py}_2(\text{CO})$,¹⁵³ and $\text{Rh}_3(\text{Cp})_3(\text{Ph}_2\text{C}_2)(\text{CO})$.¹⁵⁴ In view of the large three-bond P-P couplings, $^3\text{J(CC)}$ in the bisadduct may not be zero. $^1\text{J(RhC)}$ and $^2\text{J(RhC)}$ in the bisadduct show the expected

decrease from the corresponding values in the monoadduct.

The peaks at 27.6, 41.1, and 199.9 ppm are respectively assigned to methyl, tertiary, and carboxylic carbon of the Me_3CCOO^- bridge (Fig. 26).

C. Discussion of the Role of Bridging Ligands

Although a large number of structural data are available for carboxylate bridged dimers, the effect of tetracarboxylate bridges on the equilibrium metal-metal distances and the role in influencing the metal-metal interactions are not yet clearly understood. As can be seen in Table 57, the tetracarboxylate cage is capable of accommodating a wide range of metal-metal distances (2.1-2.9 Å), indicating that the metal atoms may not be constrained to particular distances imposed by the bridging ligands. The metal-metal distances for a few metals such as Mo(II), Re(III), and W(III) correlate well with those found in dimeric complexes without bridging ligands (see Table 1). For others, encapsulation in the tetracarboxylate framework appears to constrain the metals to a narrow range of distances. For instance, the metal-metal distances in the tetracarboxylate bridged Cr(II) dimers vary from 2.28 Å to 2.54 Å, while in non-bridged dimers the distances are even shorter, ranging from 1.85 Å to 2.21 Å, which suggests that the structural deformation of the carboxylate framework is energetically unfavorable for such short metal-metal distances. In contrast, the metal-metal distances in non-bridged Rh(II) dimers are much longer than those observed for the tetraacetate bridged dimers; 2.79 Å in $\text{Rh}_2(\text{CNC}_6\text{H}_4\text{Me})_8\text{I}_2(\text{PF}_6)_2$ ²⁰ and 2.94 Å in $\text{Rh}_2(\text{DMG})_4(\text{PPh}_3)_2$ ²⁶ vs. 2.39-2.46 Å in tetraacetate dimers. On the other hand, the isoelectronic Co(II) dimer $\text{Co}_2(\text{O}_2\text{CPh})_4(\text{quin})_2$ possesses a comparable metal-metal distance to that found in non-bridged dimers $\text{Co}_2(\text{CNCH}_3)^{+4,22}$ or $\text{Co}_2(\text{CN})_{10}^{-6,23}$. It is also noteworthy that the metal-metal distances in

Table 57. Structural Data for $M_2(O_2CR)_4L_2$

Compound	d(M-M), Å	d(M-L), Å	d(M-O), Å	d(C-O), Å	∠MMO, deg	∠MOC, deg	∠OCO, deg	Ref
$Cu_2(O_2CH)_4(NCS^-)_2$	2.716(2)	2.093(9)	1.983(4)	1.244(8)	83.0(1)	122.7(3)	128.4(5)	172
$Cr_2(O_2CH)_4(py)_2$	2.408(1)	2.308(3)	2.019(3)	1.258(5)	87.6(2)	119.7(4)	125.4(3)	173
$(Cr_2(O_2CH)_4(H_2O)_2)_3 \cdot 10H_2O^e$	2.360(2)	2.210(6)	2.121(5)	1.251(8)	87.9(1)	119.9(4)	124.3(5)	
	2.373(2)	2.268(4)	2.015(4)	1.257(8)	87.9(1)	119.6(4)	124.9(6)	174
$Cr_3(O_2CH)_6(H_2O)_2$	2.451(1)	2.224(2)	2.122(3)	1.257(5)	87.0(2)	120.2(2)	125.6(3)	173
$Mo_2(O_2CH)_4$	2.091(2)	-	2.11(2)	1.29(2)	92.0(4)	117(1)	121(1)	175
$Cu_2(OAc)_4(H_2O)_2$	2.614(2)	2.161(2)	1.969(2)	1.259(2)	84.4(1)	123.0(1)	124.9(1)	176 ^a
$Cu_2(OAc)_4(H_2O)_2$	2.616(1)	2.156(4)	1.969(3)	1.260(6)	84.4(1) ^j	123.1(3)	124.8(4)	177 ^b
$Cu_2(OAc)_4(py)_2^c$	2.645(3)	2.186(8)	1.955(8)	1.24(2)	83.7(4) ⁱ	123.4(9) ⁱ	126(1) ⁱ	66
$Cu_2(OAc)_4(py)_2^d$	2.630(3)	2.13(1)	1.98(1)	1.24(2)	83.6(3) ^j	123.4(7)	125.1(9)	65
$Cu_2(OAc)_4(NCS^-)_2$	2.643(3)	2.08(2)	2.03(1)	1.24(2)	84.0(3)	123(1)	126(1)	172
$Cu_2(OAc)_4(quin)_2$	2.652(2)	2.224(6)	1.977(5)	1.23(1)	83.4(2) ^j	123.6(1)	126(1)	180
$Cu_2(OAc)_4(pyraz)_2$	2.583(1)	2.171(6)	1.964(5)	1.249(7)	84.7(1) ^j	122.7(4)	125.3(6)	181
$Cr_2(OAc)_4(C_5H_{11}N)_2$	2.342(2)	2.338(7)	2.016(3)	1.265(5)	88.4(1)	119.9(3)	123.4(4)	182
$Cr_2(OAc)_4$	2.288(2)	-	2.011(8)	1.261(8)	89.0(5)	119.5(5)	123.1(6)	183
$Cr_2(OAc)_4(HOAc)_2$	2.300(1)	2.306(3)	2.014(3)	1.263(5)	88.9(1)	119.6(3)	123.1(4)	182
$CrMo(OAc)_4$	2.050(1)	-	2.07(1)	1.274(9)	92.3(8)	117.1(4)	121.2(7)	184
$Cr_2(OAc)_4(H_2O)_2$	2.362(1)	2.272(3)	2.018(2)	1.265(4)	88.04(5)	120.4(1)	123.1(2)	50a
$Mo_2(OAc)_4$	2.0934(8)	-	2.119(4)	1.277(8)	91.8(1)	117.5(4)	121.3(6)	185

Table 57. (Continued)

Compound	$\overline{d(M-M)}, \text{\AA}$	$\overline{d(M-L)}, \text{\AA}$	$\overline{d(M-O)}, \text{\AA}$	$\overline{d(C-O)}, \text{\AA}$	$\angle_{MMO}, \text{deg}$	$\angle_{MOC}, \text{deg}$	$\angle_{OCO}, \text{deg}$	Ref
$\text{Cu}_2(\text{O}_2\text{CCF}_3)_4(\text{quin})_2$	2.886(4)	2.109(6)	1.972(6)	1.24(1)	80.6(2)	124.7(6)	129.3(8)	186
$\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{OEt})_2$	2.541(1)	2.244(3)	2.017(2)	1.243(4)	85.6(1)	120.6(2)	127.6(3)	173
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$	2.090(4)	-	2.06(2)	1.26(3)	92.1(4) ^j	115(2)	126.0(2.5)	187
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$	2.129(2)	2.548(8)	2.116(6)	1.26(1)	91.6(2)	115.3(6)	126(1)	63
$\text{Co}_2(\text{O}_2\text{CPh})_4(\text{quin})_2$	2.832(2)	2.102(8)	2.037(7)	1.25(1)	81.6(2) ^j	124.5(1)	126.4(1.0)	189
$\text{Cr}_2(\text{O}_2\text{CPh})_4(\text{PhCO}_2\text{H})_2$	2.352(3)	2.295(7)	2.009(6)	1.27(1)	88.3(2)	120.3(6)	122.8(8)	173
$\text{Re}_2(\text{O}_2\text{CPh})_4\text{Cl}_2$	2.234(2)	2.489(5)	2.02(1)	1.30(2)	90.1(3)	120(1)	121.5(1.5)	189
$\text{Mo}_2(\text{O}_2\text{CPh})_4(\text{digyme})_2$	2.100(1)	2.663(6)	2.107(5)	1.277(8)	91.8(1)	117.3(5)	121.8(7)	190
$\text{Mo}_2(\text{O}_2\text{CPh})_4$	2.096(1)	-	2.107(3)	1.275(5)	91.8(1)	117.4(2)	121.5(4)	191
$\text{Cu}_2(\text{O}_2\text{CCH}_2\text{Cl})_4(2\text{-Mepy})_2$	2.747(3)	2.16(1)	1.975(9)	1.25(2)	82.6(3)	123.6(8)	127.3(1.3)	192
$\text{Cu}_2(\text{O}_2\text{CCH}_2-)_4(\text{H}_2\text{O})_2$	2.610(1)	2.102(7)	1.926(7)	1.256(10)	85.8(1)	124(1)	124.3(9)	193
$\text{Cu}_2(2\text{-BrPhCO}_2)_4(\text{H}_2\text{O})_2$	2.624(7)	2.17(2)	1.99(3)	1.26(3)	84.3(7)	123(2)	124(3)	194
$\text{Cu}_2(\text{C}_9\text{H}_7\text{O}_4)_4$	2.617(3)	2.241(8)	1.962(8)	1.26(1)	84.5(3) ⁱ	122.8(7)	125.5(1.0)	195
$\text{Cu}_2(\text{O}_2\text{CET})_4(\text{py})_2$	2.631(2)	2.15(1)	1.96(1)	1.25(2)	83.9(2) ^j	122.8(8) ^j	127(1)	196
$\text{Cu}_2(\text{O}_2\text{CET})_4(3\text{-Mepy})_2$	2.6312(4)	2.167(2)	1.971(2)	1.25(4)	83.5(1) ^j	123.3(2) ^j	125.4(3)	197
$\text{Cu}_2(\text{O}_2\text{CET})_4(\text{dioxane})_2$	2.5634(4)	2.227(2)	1.953(2)	1.257(4)	85.12(4) ^j	122.3(2) ^j	125.1(3)	178
$\text{Cu}_2(\text{O}_2\text{CCl}_3)_4(2\text{-Clpy})_2$	2.766(3)	2.145(5)	1.957(5)	1.230(7)	81.9(1)	123.8(4)	128.4(6)	179
$\text{Cu}_2(\text{O}_2\text{CCH}_2\text{Cl})_4(\text{quin})_2$	2.724(2)	2.211(7)	1.974(6)	1.24(1)	82.9(2)	123.9(1)	128(1)	180

Table 57. (Continued)

Compound	$d(M-M), \text{\AA}$	$d(M-L), \text{\AA}$	$d(M-O), \text{\AA}$	$d(C-O), \text{\AA}$	$\angle MMO, \text{deg}$	$\angle MOC, \text{deg}$	$\angle OCO, \text{deg}$	Ref
$\text{Cr}_2(\text{O}_2\text{CC}_6\text{H}_9)_4\text{DME}$	2.283(2)	2.283(5)	2.116(4)	1.263(8)	89.2(1)	118.9(4)	123.5(6)	173
$\text{Cr}_2(\text{O}_2\text{CCMe}_3)_4$	2.388(4)	-	2.02(1)	1.26(2)	87.4(4)	120(1)	125(2)	173
$\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_4$	2.115(1)	-	2.125(4)	1.26(1)	91.6(2)	116.4(5)	124.0(3)	188
$\text{Mo}_2(\text{O}_2\text{CCMe}_3)_4$	2.088(1)	-	2.112(6)	1.28(1)	91.9(2)	117.4(3)	121.4(8)	191
$\text{Re}_2(\text{O}_2\text{CC}_3\text{H}_7)_4(\text{ReO}_4)_2$	2.251(2)	2.18(3)	2.02(3)	1.29(6)	89.7(9)	119(3)	123(4)	126
$\text{MoW}(\text{O}_2\text{CCMe}_3)_4\text{I} \cdot \text{CH}_3\text{CN}$	2.194(2)	3.054(2) ^f	2.064(13) ^f	h	90.7(4)	h	h	121
		2.71(2) ^g	2.081(13) ^g					

a. Neutron diffraction method

b. X-ray method

c. Orthorhombic

d. Monoclinic

e. Two independent molecules in one asymmetric unit

f. $M=W$ g. $M=Mo$

h. Unavailable

i. Errors are estimated from σ 's of coordinates

j. Calculated from the coordinates

some dimers such as Mo(II) are independent of the nature of the substituent R, while other dimers such as Cu(II) and Cr(II) show considerable variations.

In the case of Rh(II), two arguments are intuitively evident; 1) if the metal-metal interaction alone determines the metal-metal distance the Rh-Rh bond in the tetraacetate dimer is no doubt extremely strong as compared to that in the nonbridged dimer, or 2) the increase in the Rh-Rh bond distance in going from the bridged to nonbridged dimer is simply due to the release of strong, constraining, "bite" of the acetate framework. The former is Cotton's view that prompted the initial proposal of a triple bond,⁵⁰ whereas the latter view was taken by Norman and Kolari⁵² in support of their argument that the Rh-Rh bond is single.

In the light of this, it is appropriate to examine the role of bridging ligands in determining the metal-metal distances and systematics of changes in the geometry of the acetate framework as the metal-metal distance is varied. Before discussing the trend in the dirhodium complexes, it will be useful to consider which of the geometric measures are the most sensitive functions of the metal-metal distances. It is expected that the internal angles in the carboxylate framework are more sensitive than the bonds because the angular deformation is less demanding than the bond stretching or compression. The M-O and C-O distances are in fact invariant for a given metal atom, but the C-O distance shows a slight negative variation with increasing M-M distance (Fig. 36). The M-M-O angles give an excellent linear correlation with the M-M distances, as shown in Fig. 37. This linear

Fig. 37. Plot of M-M-O angles vs. M-M distances in $M_2(O_2CR)_4L_2$.

correlation requires that the sum of the remaining internal angles must be a linear function of the M-M distance because the $\overline{M-M-O-C-O}$ rings are essentially planar in all complexes. The O-C-O angles are characteristic of the nature of R (Fig. 38). The slopes of the linear plots decrease in the order $H > CH_3 \sim Ph > CF_3$, which is not the order of base strength but roughly the order of the size of the R group. The magnitude of the O-C-O angles parallel the pK_b 's of the carboxylate anions; O-C-O angle and pK_b , respectively; 125.7° and 9.24 for $R=CH_3$,⁹⁹ 125.7° and 10.3 for $R=H$,¹⁰⁰ and 128.3° and 13.8 for $R=CF_3$ ¹⁰¹ (data for $R=Ph$ are not available). It appears that the inductive effect of the R group is the primary factor in determining the size of the O-C-O angle and the flexibility of the O-C-O angle for a given acid is dependent on the size of R. Since for a given M-M distance the M-M-O angle can be assumed to be constant irrespective of the R group, the initial adjustment is made in the O-C-O angle. The remaining ring strain after the M-M-O and O-C-O angles are adjusted would be taken up by the M-O-C angle. In this regard the M-O-C angles are the most flexible or the most easily deformed in response to changes elsewhere in the five-membered ring.

We consider next the dirhodium complexes in relation to other carboxylate bridged dimers. Comparison of the O-C-O angles shows that the geometry of the free anion is closely approximated by the long metal-metal distances of Cu(II) dimers (Fig. 39). Since the M-O-C angle is the most flexible parameter it can be safely assumed that the M-O-C and O-C-O angles in the dicopper systems are the comfortable geometry of the acetate cage that does not require extraordinary strain to

Fig. 38. Plot of O-C-O angles against M-M distances in $M_2(O_2CR)_4L_2$ ($R=CF_3$, CH_3 , H , and Ph), showing the effect of R .

Fig. 39. Plot of O-C-O angles vs. M-M distances in $M_2(OAc)_4L_2$, showing the deviation of dirhodium complexes.

maintain the metal-metal distances of 2.6-2.7 Å. If the Rh-Rh single bond length is assumed to be 2.70 Å, using the normal Rh-O and C-O distances of 2.04 Å and 1.26 Å, one can construct a tetraacetate bridged Rh(II) dimer with the M-O-C and O-C-O angles similar to the values observed in Cu(II) dimers. In other words, if the Rh-Rh single bond is forced into the tetraacetate cage, it would prefer the maximum separation that is allowed within the cage, ca. 2.70 Å, without disturbing the "comfortable" geometry. Thus the fact that the observed Rh-Rh distance is 0.30 Å shorter than this "comfortable" metal-metal distance implies that the Rh-Rh bond is multiple or that the tetraacetate framework fosters additional bonding interactions which yield a much shorter equilibrium Rh-Rh distance.

Of further interest is the effect of different R substituents on the metal-metal distances. The Cu(II)-Cu(II) bond is lengthened by 0.07 Å in going from $\text{Cu}_2(\text{OAc})_4(\text{NCS}^-)_2$ to $\text{Cu}_2(\text{O}_2\text{CH})_4(\text{NCS}^-)_2$ and by 0.24 Å in going from $\text{Cu}_2(\text{OAc})_4(\text{quin})_2$ to $\text{Cu}_2(\text{O}_2\text{CCF}_3)_4(\text{quin})_2$, in marked contrast with the Mo(II)-Mo(II) bond which remains unaltered as R is changed from CH_3 to CF_3 . The inevitable expansion of the O-C-O angle in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ is properly balanced by the decrease in the M-O-C angle. A drastic increase in the M-M distance is also seen in the dichromium systems when $\text{R}=\text{CH}_3$ is replaced with CF_3 ; 2.36 Å in $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ and 2.54 Å in $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{OEt}_2)_2$ (the effect of different axial ligands is uncertain but it is not the major contributor to the lengthening). These examples show that the degree that varying carboxylates modify the metal-metal distance is largely dependent on the relative metal-metal bond strength. If the metal-metal bond is strong, then the

tetracarboxylate framework will undergo an angular adjustment, with the metal-metal bond distance remaining unaltered. On the other hand, if the metal-metal bond is weak as in Cu(II) dimers, then it is likely that the metal-metal bond will be expanded or compressed as required to approximate the "comfortable" geometry of the tetracarboxylate framework. It will be of future interest to see if the replacement of the acetate with the trifluoroacetates in the dirhodium system gives significant changes in the Rh-Rh bond distance and to assess thereby the relative bond strength.

D. Trans Influence and Rh-Rh Bond

1) Trans Influence

The trans influence deals with the structural effect of a ligand on the metal-ligand bond trans to it in the ground state of a complex, in particular, the degree of weakening or strengthening of the trans bond. In its simplest case, it is believed to arise from the rehybridization of metal σ -orbitals in response to changes in orbitals on the ligand used in σ -bonding.¹⁰² Venanzi and Syrkin¹⁰³ proposed hypothetical sd hybrids for the metal complexes. If a ligand forms a strong covalent bond with the metal, the orbital used by the metal will have a high s -character because the order of stability of the metal orbital is $(n-1)d > ns > np$ (n =principal quantum number). The migration of electron density to the ligand from the metal reduces the charge for the formation of a covalent bond with the trans ligand, causing the trans bond to be weakened. In addition to the σ -bonding, the π -interaction between the metal and the ligand is known to play an important role in the trans influence. For example, phosphorus ligands have vacant d_π orbitals that can share the metal d_π electrons. The drift of the Md_π electrons into the Pd_π orbitals can, through the synergic effect,¹⁰⁴ increase the donor capacity which in turn enhances the inductive contribution to the trans influence.^{105,107,138}

The trans influence of various ligands has been studied by means of infrared, nmr, and x-ray diffraction methods. Of these, the measurement of nmr coupling constants has been the most widely used method.^{102,108} Since the couplings are largely dependent on changes in s -character in the bond, a covalent bond richer in s -character would

be expected to have a larger coupling constant.¹⁰⁹ Thus the observation of variation of coupling constants with different trans ligands would yield an insight into the trans influence in terms of the strengths of s-characters, which would of course not account for the overall bond strengths. Infrared and x-ray methods should supply more reliable results than the nmr method because the stretching frequencies and bond lengths are assumed to be more directly related to the bond strengths, irrespective of the formal bonding scheme. The force constants for most complexes that have been examined by vibrational spectroscopy are not available. The mass effects of ligands and the possible vibrational couplings set limits to the use of stretching frequencies as measures of bond strengths. In the following discussion of the dependence of trans influence on the nature of the bond in the trans relationship, we will follow the commonly made assumption that these effects are not significant and that a lower frequency corresponds to a weaker bond.

Church and Mays^{108d} have shown that in trans-PtCl(PEt₃)₂L⁺ the ir stretching frequency of the Pt-Cl bond is 30 cm⁻¹ greater when L=P(OPh)₃ than when L=PEt₃. In cis-PtCl₂LL' (L, L'=PBu₃ and PPh₃, or PPh₃ and P(OPh)₃),^{108b} $\nu(\text{Pt-Cl})$ decreases in the order P(OPh)₃ > PPh₃ > PBu₃ in the trans position. Consistent with this, the crystal structures of cis-PtCl₂(PBu₃)(P(OPh)₃)¹¹⁰ and cis-PtCl₂(CO)(PPh₃)¹¹¹ show that the Pt-Cl bond distances are considerably longer for PBu₃ trans and PPh₃ trans in respective cases. The trans influence order inferred from these results is then

A similar trans influence ordering was also obtained in the diffraction studies of a series of $\text{cis-PtCl}_2\text{PEt}_3\text{L}$, where $\text{L}=\text{PEt}_3$, CO , P(OPh)_3 , and PF_3 .¹¹²

On the other hand, examination of the CO stretching frequencies in metal carbonyl complexes indicates that the above order can be reversed for strongly π -interacting trans ligands. With a stronger π -acceptor in the trans position, the CO frequency is always larger. A good example of this is $\text{cis-MoL}_3(\text{CO})_3$ where $\nu(\text{CO})$ decreases with PF_3 , PCl_3 , P(OPh)_3 , and PPh_3 , in the order given.¹¹³ The correlation between the stretching frequencies and the metal-CO bond strengths can be envisaged as follows: The phosphorus ligands compete with CO for the metal d_{π} electrons. As the π -acidity of the phosphorus ligand increases, the back donation from the metal to the empty antibonding π^* orbital of CO will decrease, resulting in a longer M-CO bond. With fewer electrons in the $\pi^*(\text{CO})$ orbital, the C-O bond becomes stronger and hence a higher $\nu(\text{CO})$ is expected. A clearer picture of the trans influence ranking of this sort can be obtained by comparing the structures of $\text{Cr(CO)}_5\text{L}$ where $\text{L}=\text{CO}$,¹¹⁴ P(OPh)_3 , and PPh_3 ¹¹⁵; the Cr-CO distance trans to L decreases in the order $\text{CO} > \text{P(OPh)}_3 > \text{PPh}_3$ (1.909, 1.861, and 1.844 Å, respectively). Therefore, the trans influence in the metal-carbonyl complexes is in a reversed order from that for the Pt-Cl complexes;

We have taken a few examples to demonstrate the dependence of the trans influence on the nature of the trans bond. The order is such that the trans influence diminishes with increasing π -acidity

for the Pt-Cl bond and increases with increasing π -acidity for the M-CO bond. In addition, the order $\text{PR}_3 > \text{P(OR)}_3 > \text{CO}$ is generally observed, with very few exceptions, for trans bonds that do not involve π interactions, such as M-Cl, M-C(alkyl), M-N, and M-H in square planar or octahedral environments.¹¹⁶

The observed trans influence data can be rationalized by use of simple qualitative orbital pictures for a linear triatomic system X-M-L, as depicted in Fig. 40. If the trans ligand X is a strong σ -bonder with no π -accepting ability, then the M-X bond strength is mainly dependent on the σ -donor strength of L and the M-L π interaction will exert no appreciable influence on the M-X bond. Consequently, the M-X bond becomes stronger as L is replaced with a weaker σ -donor (Fig. 40a) and the trans influence parallels the basicity order of L. If, on the other hand, X is a strong π -acceptor ligand, then it will compete with L for the $\text{Md}\pi$ orbital density and hence the M-X bond will be weakened as the π -acidity of L increases (Fig. 40b). However, complications arise from the simultaneous contributions to the effect; the M-X bond can be either stronger or weaker depending on whether the σ effect outweighs the π effect or vice versa. The trans influence will follow the π acidity order only when the strengthening through σ interaction is overshadowed by the weakening through π interaction.

This sort of interpretation of the bonding interaction is of course a highly idealized one, with other energetics involved, such as orbital contraction and expansion caused by the flow of charge, the synergic contribution, steric effects, and the effect of cis

Fig. 40. Qualitative interaction diagram of trans influence
 a) for X with no π acceptor ability
 b) for X forming a strong π bond with M.

ligands, being ignored. Nevertheless, the extrapolation of the linear triatomic fragment, by substituting X with M, to the binuclear metal-metal bonded system would be very informative in elucidating the bonding implications between the metal centers.

2) Rh-Rh Bond

The Rh-Rh bond distances are summarized in Table 55, along with the bond parameters for the water^{50a} and triphenylphosphine⁷⁵ adducts. It is seen that the Rh-Rh bond is weakened with increasing basicity of the σ donor ligands, H₂O, pyridine, and NHEt₂. A similar trend is observed for the π acceptor ligands, CO and phosphorus ligands (Fig. 41). The most remarkable feature is the fact that all of the ligands with no π acceptor character exert a weaker trans influence than the π acceptors, particularly CO and PF₃, which are the weakest σ donors in the series.

A simple qualitative picture of trans influence similar to the one discussed in the previous section suggests that the net lengthening of the Rh-Rh bond for the π acceptor ligands is due to the M π -L π interactions, which would require a filled M-M π as the donor orbital. If the Rh-Rh bond is single, then the M-M π^* orbital is filled and the acceptor ligands will interact with it in preference to the low-lying π bonding orbital. It is in general true that the M-L π back-bonding occurs to a greater extent with a M-M π^* than with a M-M π because the antibonding orbital lies at a higher energy level than the bonding orbital and the π^* electron density is steered more into the M-L region, while the π electrons are concentrated more in the M-M region. Thus, for a given π acid, there is a better energy match and a more effective

Fig. 41. Correlation between Rh-Rh distances and base strengths of ligands as measured by ionization potentials. IP's are taken from Table 58.

Fig. 42. Orbital diagram for the interaction of L a) with a M-M π orbital, b) with a M-M π^* orbital.

overlap for the $M-M \pi^* \rightarrow L_\pi$ type interaction. This is more clearly illustrated in Figure 42, along with simple orbital interaction diagrams to demonstrate the greater stabilization of the antibonding π orbital. The $M-M \pi^* \rightarrow L_\pi$ interaction would be expected to strengthen the M-M bond and, hence, the M-M bond would be shorter for the π acids, contrary to the experimental data. Therefore, the net separation of approximately $0.04 \text{ \AA}$ between the donor and acceptor ligands in Figure 41 must be ascribed to the additional weakening caused by $Rh-Rh \pi \rightarrow L_\pi$ interactions.

It was noted earlier that in mononuclear complexes the trans influence order is $CO > PF_3 > P(OR) > PR_3$ when the trans ligands maintain strong π bonding with the metal and the order is reversed when such interactions are of little importance. In view of the similarity of the M-M-L system to the X-M-L fragment, the observed trans influence ordering for the π acids would seem inconsistent with the π bonding model. It is known that the degree of π interaction is a sensitive function of the internuclear distance, declining much more rapidly with increasing metal-ligand distance than the σ interaction, which remains relatively constant over a wide range of metal-ligand distances.⁸⁸ The Rh-L distances in the dirhodium complexes are $0.1-0.2 \text{ \AA}$ longer than normal M-L distances found in Rh(I) or Rh(III) compounds (Table 55), owing to the strong trans influence of the Rh-Rh bond on the Rh-L bond. At these long distances, the Rh-L π overlap is less effective than it is when the metal-ligand distances are normal and the Rh-L bond strength is determined mainly by the $M \leftarrow L \sigma$ bond, with small contributions from the π component. The striking evidence for this is the relative

stabilities of the adducts. The PF_3 adduct is most labile, despite the shortest Rh-P distance, while the PPh_3 adduct is quite stable. The P(OPh)_3 and P(OMe)_3 adducts are intermediate. The point is that the bond strength follows the basicity order of the π acceptor ligands, leading to the trans influence ordering $\text{PPh}_3 > \text{P(OMe)}_3 > \text{P(OPh)}_3 > \text{PF}_3 > \text{CO}$ (the position of PPh_3 is uncertain due to a steric modification of the Rh-Rh bond length; see the Description of Structures).

McWeeny, et. al.¹⁰⁵ have proposed that the M-L bond strength may be related to $S^2/\Delta E$ where S is the overlap integral and ΔE the energy gap between the donor and acceptor orbitals and the trans influence varies in proportion with this quantity. Calculations for various metals show that the metal($p\sigma$)-ligand hybrid(σ) overlap integrals remain relatively constant for a given ligand donor atom in going from d^6 to d^8 metals. Thus it is not unreasonable to approximate S for $\text{Rh(II)}(d^7)$ with that for $\text{Rh(III)}(d^6)$. Taking the ligand lone pair ionization potentials and the theoretical value of -4.78 eV ⁵² as the donor levels of ligands and the metal σ^* acceptor level, respectively, we can calculate $S^2/\Delta E$ as given in Table 58. Once again, a plot of $S^2/\Delta E$ against the Rh-Rh distance yields two distinct lines for the two ligand groups (Fig. 43). The deviation of the point for PPh_3 may be attributed to the reduced trans influence due to the steric elongation of the Rh- PPh_3 bond as was mentioned in the description of structures of phosphorus ligand adducts. In the absence of the enhanced trans influence by the involvement of the π components, the points for the π acids would fall on the line representing the σ donors because it is the Rh-Rh σ bond that is mainly affected by the changes

Table 58. Estimates of $S^2/\Delta E$ for Rh-L Bonds in $\text{Rh}_2(\text{OAc})_4\text{L}_2$

<u>L</u>	<u>VIP^a</u> eV	<u>S^{2b}</u>	<u>ΔE^c</u> eV	<u>$S^2/\Delta E$</u> eV ⁻¹	<u>$\bar{d}(\text{Rh-Rh})$</u> Å
H ₂ O	-14.0 ^f	0.1600	9.22	0.0174	2.386
py	-9.88	0.2209	5.10	0.0410	2.396
NHET ₂	-8.63	0.2025	3.85	0.0526	2.402
CO	-13.79	0.3025	9.01	0.0336	2.419
PF ₃	-12.27	0.2500	7.49	0.0334	2.422
P(OPh) ₃	-9.7 ^d	0.2500	4.9	0.051	2.443
PPh ₃	-7.88	0.2500	3.10	0.0806	2.449
P(OMe) ₃	-9.25	0.2500	4.47	0.0559	2.456

a. Vertical ionization potential;ref 122.

b. Overlap integrals are taken from ref 105.

c. Energy gap between the Rh-Rh σ^* ($=-4.78$ eV;ref 52) and the ligand VIP.

d. Estimated from a linear plot of VIP's vs. $\nu(\text{CO})$ in $\text{Ni}(\text{CO})_3\text{L}$ where L is PPh_3 (2068.9 cm^{-1}), $\text{P}(\text{OMe})_3$ (2079.5 cm^{-1}), $\text{P}(\text{OPh})_3$ (2085.3 cm^{-1}), and PF_3 (2110.8 cm^{-1}), after C. A. Tolman, J. Am. Chem. Soc., 92, 2953-2956(1970).

f. A weighted mean of the a_1 (-14.7 eV) and b_2 (-12.6 eV) lone pairs of H₂O, assuming that the oxygen atom utilizes 70 % a_1 and 30 % b_2 upon coordination to the metal.

Fig. 43. Plot of Rh-Rh distances vs. $S^2/\Delta E$.
The deviation of the point for PPh₃ originates from steric interaction.

in the $Mp\sigma-L\sigma$ interactions. In this respect, the plot seems to indicate that $S^2/\Delta E$ is underestimated for the π acids. In addition, the expected trans influence order based on the magnitudes of $S^2/\Delta E$ is $PPh_3 > P(OMe)_3 > NHEt_2 > P(OPh)_3 > py > CO > PF_3 > H_2O$, in contradiction to the observed order $PPh_3 > P(OMe)_3 > P(OPh)_3 > PF_3 > CO > NHEt_2 > py > H_2O$ (the observed Rh-Rh distance for the PPh_3 adduct may be shorter by 0.01-0.02 Å because of the steric elongation of the Rh- PPh_3 bond).

Inclusion of a quantity which will account for the π component, such as $S^2/\Delta E_{\pi}$, would cause the π acceptors to fall on the line extended from the σ donors (dotted line in Fig. 43), making the magnitude of trans influence a smooth, continuous linear function of overall $S^2/\Delta E$.

Certainly, the foregoing argument is a very naive and oversimplified interpretation of orbital energetics. The uncertainty in the ligand acceptor levels, the degree of involvement of metal 5s and $4d_{z^2}$ orbitals in the metal-metal and metal-ligand bonding interactions, and the nature of hybridization of phosphorus ligands defies quantitative analysis of the observed trans influence ordering. However, the strikingly different behavior apparent in Figures 41 and 43 clearly shows that there is a significant back-donation to the axial ligands from a filled metal-metal bonding π level, which in turn will destabilize the metal-metal bond, causing a lowering of the metal-metal level. This would augment $S^2/\Delta E$ for the σ part of the Rh-L bond and thereby complement the weakening of the Rh-Rh bond.

We now consider the MO schemes proposed by Cotton,²⁸ Dubicki and Martin,⁵¹ and Norman and Kolari,⁵² in connection with the observed trans influence data. As was alluded in the introduction, the shortcoming of

Fig. 44. Proposed MO diagrams for $Rh_2(O_2CR)_4$.

a. Cotton's; ref 28.

b. Norman and Kolar's; ref 52.

c. Dubicki and Martin's; ref 51.

the MO picture in Fig. 44a is the fact that the energy level ordering is not peculiar to the dirhodium system but was derived for an M_2X_8 species of D_{4h} symmetry, in which fourteen electrons from the d^7 - d^7 metals were successively placed to fill up to the δ^* orbital, yielding a net bond order of three. The σ_n and σ'_n nonbonding orbitals in this diagram are primarily of $4d_{z^2}2s5p$ hybrid character directed outward along the metal-metal axis. In the MO scheme derived from extended Hückel calculations, these non-bonding orbitals are much higher in energy and empty ($7a_{1g}$ and $5a_{2u}$ in Fig. 44c). The two pairs of electrons which were in Cotton's σ_n and σ'_n orbitals now occupy the π^* orbital, giving rise to a bond order of one. The $X\alpha$ -SW levels (Fig. 44b) are much the same as those from the extended Hückel method, except that the level ordering is slightly different and the nonbonding orbitals arising from the mix-in of Rh $5s5p$ orbitals are not at all present. The fundamental difference between these MO schemes is that, apart from the disagreement in the resultant bond order, the highest filled orbital with a proper symmetry to form a back-bonding with a π acceptor is π in Cotton's scheme and π^* in the others. Evidently, the experimental data cannot be explained by the $X\alpha$ -SW MO picture nor by the extended Hückel configuration.

Despite the inconsistency with the structural data, the MO levels derived from the $X\alpha$ -SW and extended Hückel methods predict the proper sensitivity of the spectral bands to the nature of the axial ligands.^{51,52} In particular, the transition $^1A_{1g} \rightarrow ^1E_u(\pi^* \rightarrow \sigma^*)$ is most sensitive to the donor strengths, shifting to a higher energy when the ligand strength increases, as would be expected from the destabilization of the σ^*

level. Expectations are then that a lowering of the π^* level would have the same effect on this transition. This is indeed what is observed for the adducts of π acceptors where the metal-metal donor level is stabilized through the backbonding. A good example is the CO adduct for which the absorption maximum appears at 490 nm, much higher in energy than those of purely σ donors such as NHEt_2 ($\lambda_{\text{max}} = 542 \text{ nm}$). The absorption maxima of the 1:1 adducts always occur, without exceptions, at a lower energy region than those of the 1:2 adducts,¹²³ in accordance with the metal-metal acceptor(donor) orbital being destabilized(stabilized) to a lesser degree by a single ligand than by two identical ligands. If one views that axial ligands as single atom donors or acceptors such that the approximate symmetries for the 1:1 and 1:2 adducts are C_{4v} and D_{4h} , as in the case of linear axial ligands(e.g., CO), the spectral shifts can be qualitatively rationalized in terms of energy levels involved. The a_{2u} and e_g levels under the D_{4h} symmetry transform into a_1 and e levels under the C_{4v} structure. The interaction of a single ligand would lower the a_1 level, while it raises the e level(Fig. 45). The transition energy for $e \rightarrow a_1$ in the 1:1 adduct will then be smaller than that for $e_g \rightarrow a_{2u}$ in the 1:2 adduct. Furthermore, a recent study of single-crystal polarized absorption spectra for the water adduct¹²⁴ has shown that the bands in the visible region generally possess the polarizations predicted by the $X\alpha$ -SW calculations; the Rh-Rh $\pi^* \rightarrow \sigma^*$ transition is x,y-polarized and the Rh-Rh $\pi^* \rightarrow \text{Rh-O } \sigma^*$ transition z-polarized.

Fig. 45. The visible spectra of the CO adducts.
 1; an equilibrium mixture of 1:1 and 1:2 adducts in CH_2Cl_2 .
 2; solution 1 was purged with N_2 gas for 10 min.

All that is required to explain the trans influence data is that the highest filled level of π symmetry must be π -bonding rather than π -antibonding in nature. Neither the triple bond formulation nor the single bond scheme is strongly favored, although the extraordinary shortness and low sensitivity of the Rh-Rh bond to the axial ligands reflect the unusual strength which appears to argue for a multiple bond. In view of the ramification of the experimental results and conflicting MO schemes, it seems quite necessary to propose a new MO scheme which will be consistent with structural data as well as the spectral behavior.

Assuming that MO's for the dimer are formed by the interaction of ligand MO's with MO's for the pure metal-metal bond such as those for d^3-d^3 or d^4-d^4 systems, MO levels of different orderings can be constructed, depending upon the relative position of the ligand and metal-metal only MO's. The highest occupied MO's for RCO_2^- (C_{2v} symmetry) are $(1b_1)^2(4b_2)^2(6a_1)^2(1a_2)^2$. Of these, b_1 and a_2 orbitals are π in

character delocalized over O-C-O linkage. b_2 and a_1 orbitals are mainly of oxygen p_π orbitals which will interact most strongly with M-M π^* and π levels. A set of four degenerate orbitals are obtained for the D_{4h} symmetry by a linear combination of each of the C_{2v} symmetry orbitals; b_1 transforms into $(a_{2g})(b_{2g})(e_u)$, b_2 into $(a_{2u})(b_{2u})(e_g)$, a_1 into $(a_{1g})(b_{1g})(e_u)$, and a_2 into $(a_{1u})(b_{1u})(e_g)$.

The interaction diagram of these symmetry orbitals with the d-derived metal-metal MO's is depicted in Figure 46. The level ordering on the right hand side of the metal-metal MO's is similar to that determined by X α -SW calculations, with the HOMO being e_g which has a large amount of Rh-Rh π^* . The levels on the left side are generated by arbitrarily lowering the ligand levels so that the energy match between Rh-Rh $\pi(e_u)$ and the ligand e_u orbitals is the greatest. The HOMO π^* in Fig. 46b has now fallen below the π level in Fig. 46a, as the ligand levels are moved downward.

We conclude that the level ordering is very much dependent on the relative positions of interacting orbitals. The observed trans influence data require that the highest occupied π MO be bonding. Thus the MO diagram in Figure 46a appears to be a better description of the electronic structure of the dirhodium species. Since the transitions $A_{1g} \rightarrow B_{2g}(b_{1u} \rightarrow a_{2u})$ and $A_{1g} \rightarrow E_g(e_u \rightarrow a_{2u})$ are not dipole allowed, the placement of $b_{1u}(\delta^*)$ or $e_u(\pi)$ orbitals above e_g would not create additional bands in the visible region. However, the sensitivity of the $A_{1g} \rightarrow E_u(e_g \rightarrow a_{2u})$ transition to the π acceptor ligands will be diminished because it is the e_u orbital that will most strongly interact with the axial ligand π orbitals and the spectral shift is indirect and secondary in contrast with the MO scheme in Figure 46b where the e_g level is directly stabilized. In other words, the stabilization of the e_g level is induced by the weakening of the Rh-Rh bond through Rh-Rh $\pi(e_u)$ -L π interaction. This will also lead to the expected blue shift.

Fig. 46. Qualitative MO diagram for $\text{Rh}_2(\text{OAc})_4$. Levels that are mainly of ligand characters are omitted for clarity.

The problem with this MO picture is that it still does not explain the unusual shortness of the Rh-Rh bond. Since the MO's contain different amounts of metal and ligand characters, the Rh-Rh bond order can be taken as the algebraic sum of the metal contributions. In this case, the Rh-Rh bond is no more than single(σ only), just as in the d-derived MO's for Rh_2^{+4} , unless some of the M-M electrons are lost through extensive delocalization over the bridging ligands. Without the heavy delocalization and extensive mixing of the M-M orbitals with the ligand electrons, the resultant bond order will be exactly the same as whatever one chooses for the "metal-metal only" configuration. For instance, if a particular orbital such as e_g just below e_u in Figure 46a comprises, e.g., 90 % of the M-M π^* , then the remaining 10 % must be found in the counterpart e_g just below b_{1u} . The only way to achieve a bond order higher than single, which will account for the strong Rh-Rh bond, is the inexact cancellation of the metal components in the filled bonding and antibonding orbitals of π or σ symmetry⁴⁰ so that the metal contributions to the bonding orbitals are in excess.

Alternatively, the extra strength of the Rh-Rh bond may be explained by introducing the concept of configuration interaction of the kind proposed by Rundle¹²⁷ in order to rationalize the dimerization of the d^8 square planar complexes such as Ni(II), Pd(II), Pt(II), and Au(III). The bond order of these d^8 - d^8 dimers is formally zero based on the d-derived configuration. The existence of non-bridged dimers as well as bridged analogues led to the conclusion that the metal-metal bonding arose from a partial promotion of inner d electrons to

the vacant s and p orbitals, allowing a small contribution of d^2sp^3 type hybridization to the ground state. This idea is of course somewhat analogous to Cotton's MO scheme in which the 5s and 5p orbitals are imbedded in the 4d orbitals, forming non-bonding levels σ_n and σ_n^* , insofar as the vacant s and p orbitals drop into proper energy range to strengthen the metal-metal bonding interaction. A recent study on $\text{Cu(I)}-\text{Cu(I)}(d^{10}-d^{10})$ systems by Mehrota and Hoffmann¹²⁸ shows that the mixing of metal s and p orbitals with d orbitals converts the closed-shell repulsion between the d^{10} centers into a slight attraction by making the metal-metal σ orbital more bonding and the σ^* less antibonding.

The degree of stabilization of the metal-metal bond afforded by this mechanism depends entirely upon the energy separation between the vacant virtual orbitals and filled orbitals. The close proximity of the virtual orbitals will facilitate the mixing and dissipation of the higher-lying d orbital electrons. The possibility of the ligands providing a means of channelling some of the metal electrons into their own low-lying virtual orbitals cannot be completely ruled out. A simpler way of looking at this is that such mixing ultimately provides electron deficient d manifolds of the metal atoms. Thus formally d^n-d^n complexes become $d^{n'}-d^{n'}$ dimers where $n' < n$, leading to enhanced bonding interactions for the seemingly non-interacting or weakly interacting metal-metal bonds. This appears to be in particular true for some of the d^7-d^7 , d^8-d^8 , and d^9-d^9 complexes, bridged or non-bridged. For example, one should examine the results of the structures for the dirhodium compounds in this study, $\text{Co}_2(\text{O}_2\text{CR})_4\text{L}_2(d(\text{Co}-\text{Co})=2.83 \text{ \AA})$,²⁴

$\text{Rh}_2(\text{OSCR})_4\text{L}_2$ ($d(\text{Rh-Rh})=2.55 \text{ \AA}$)²⁷, $\text{Ni}_2(\text{OSCR})_4\text{L}_2$ (d^8-d^8 , $d(\text{Ni-Ni})=2.49 \text{ \AA}$)¹⁹, and other d^8-d^8 dimers of the form $\text{M}_2(\text{S}_2\text{CR})_4$ with $\text{M}=\text{Ni}$ and Pd where the M-M distances are $2.56 \text{ \AA}$ ²¹ and $2.72 \text{ \AA}$ ³³ respectively. No one can dispute that the Co-Co bond is weak, perhaps no more than single, as in non-bridged Co(II) dimers, $\text{Co}_2(\text{CNMe})_{10}^{+4}$ and $\text{Co}_2(\text{CN})_{10}^{-6}$ ($d(\text{Co-Co})=2.74 \text{ \AA}$ ²² and $2.79 \text{ \AA}$ ²³), wherein the Co-Co bond is not constrained by the bridging ligands. The replacement of one oxygen atom with one sulfur atom increases the M-M distance by approximately $0.1 \text{ \AA}$ due to the bulkiness of the sulfur atom. From this, we can deduce the hypothetical M-M distances in the non-existent $\text{Ni}_2(\text{O}_2\text{CR})_4$ and $\text{Pd}_2(\text{O}_2\text{CR})_4$ to be ca. $2.4 \text{ \AA}$ and $2.5 \text{ \AA}$, which are much shorter than the values expected for single bonds ($2.49 \text{ \AA}$ in metallic Ni and $2.75 \text{ \AA}$ in metallic Pd), but the latter more so. Thus the existence of the metal-metal bonding interactions in these formally non-bonding d^8-d^8 dimers cannot be denied. An interesting aspect is that in going from the first to second row transition metals within a triad the M-M interaction becomes stronger as evidenced by the decrease in the M-M distances relative to covalent radii. This can be readily rationalized by the diffuseness of the second row transition metal d orbitals which can interact more effectively with the virtual orbitals. Theoretical studies^{1,129} of a number of dimers have also shown that the availability of virtual orbitals for the first transition series is small compared to the second- and third-row metals. Moreover, non-bridged d^9-d^9 dimers of, e.g., Ni(I) ³², Pd(I) ⁴⁸ and Pt(I) ⁴⁹ which have even shorter M-M distances than those in the above mentioned, bridged Ni(II), Pd(II), and Pt(II) dimers cannot be explained without such heavy mixing of virtual and

filled orbitals of metals and ligands involved.

3) Summary

The trans influence order of the axial ligands, as determined by the lengthening of the Rh-Rh bond, is

The most important result is that all π acceptor ligands (CO and phosphorus ligands) exert significantly larger trans influence than σ donors with no or weak π accepting power (H_2O , py, and NHEt_2). Within each ligand group, the trans influence increases linearly with increasing basicity of ligands (the shorter Rh-Rh bond for PPh_3 than for P(OMe)_3 , despite the stronger basicity of PPh_3 , is ascribed to the steric enlongation of the Rh- PPh_3 bond). The observed ordering is rationalized on the basis of qualitative trans influence theory and the larger trans influence for the π acids is viewed as arising from the interaction of a filled Rh-Rh π orbital with ligand acceptor orbitals. This requires that the Rh-Rh bond be multiple, rather than single, with substantial π character, although theoretical⁵² and spectroscopic^{51,53,124} studies suggest a single bond formulation. The extreme shortness and high strength of the Rh-Rh bond is attributed in part to such multiple bonding between the metal centers. The heavy mixing of ligand and metal orbitals and configuration interaction between ligand and metal orbitals or within the metal centers are believed to provide a means of enhancing the bonding interaction between the metal atoms.

APPENDIX

A. Computer Programs

I. Syntex Programs(Syntex P1 diffractometer softwares)

1. Reflection Centering
2. Autoindexing
3. Unit Cell Least Squares
4. Autocollection

II. CRYM Programs: "Crystallographic Computing System", Department of Chemistry, California Institute of Technology, Pasadena, California 91109.

This program has been partially modified by Dr. G. G. Christoph, Mr. M. A. Beno, and Mr. T. Brown, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

1. Initial Data Processing
2. Wilson Statistics
3. Absorption Correction(for the pyridine adduct only)
4. Structure Factor and Least squares
5. Patterson, Fourier, and Difference Fourier
6. Hydrogen Positions
7. Distances, Angles, and Plane Calculations

III. RAGGLS: "Rigid and Generalized Group Least Squares", written by Dr. G. G. Christoph, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

1. Refinement of the Structure of the PF_3 Adduct

IV. EMPPSI: A program that utilizes ψ scan data to correct for the absorption effect, written by Mr. M. A. Beno and Dr. G. G. Christoph, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

1. Absorption Corrections for NHEt_2 , CO, and PF_3 Adducts

V. ORTEP: "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Oak Ridge National Laboratory Publication No. ORNL-3794, Rev., 1965

1. Drawings of Perspective Views and Packing Diagrams

B. Nmr Transition Frequencies*

1:1 Adducts

<u>Ligand</u>	<u>Observed Frequencies</u>		<u>Ligand</u>	<u>Observed Frequencies</u>	
	Hz	ppm		Hz	ppm
PCy ₃	-1183.2	-32.48	PF ₃	2350.6	64.52(1)
	-1217.0	-33.41		2273.2	62.39(1)
	-1278.8	-35.10		2186.9	60.02(1)
	-1311.2	-35.99		2109.5	57.90(1)
PPh ₃	-1305.4	-35.83		787.5	21.61(3)
	-1337.2	-36.70		710.1	19.49(3)
	-1401.9	-38.48		623.8	17.12(3)
	-1434.8	-39.38		546.4	15.00(3)
P(OMe) ₃	1584.0	43.47		-778.5	-21.37(3)
	1538.7	42.23		-855.9	-23.49(3)
	1436.3	39.42		-942.3	-25.86(3)
	1391.0	38.18		-1019.7	-27.99(3)
P(OPh) ₃	766.9	21.05		-2341.6	-64.27(1)
	707.8	19.43		-2419.0	-66.39(1)
	619.2	17.00		-2505.4	-68.76(1)
	560.2	15.37		-2582.8	-70.89(1)
PCl ₃	2442.8	67.04	CO	3466.5	153.22
	2337.9	64.17		3456.2	152.76
	2317.2	63.61		3425.3	151.39
	2212.4	60.72		3415.0	150.94

* ³¹P nmr transition frequencies are relative to 85 % H₃PO₄.

¹³C nmr transition frequencies are relative to TMS.

Relative intensities of the transitions are identical, unless otherwise specified in the parentheses.

1:2 Adducts1) $\text{Cy}_3\text{P-Rh-Rh-PCy}_3$

1 2 3 4

Chemical Shifts(Hz)	$\begin{smallmatrix} >T \\ T \end{smallmatrix}$	Cal. Freq.	Relative Intensity	Exp. Freq.
$V(1) = -516.800$	10 14	- 327.332	0.034	Unobserved
$V(2) = 50000$	7 13	- 817.560	0.036	
$V(3) = 50000$	15 16	- 560.337	1.996	-560.1
$V(4) = -516.800$	9 15	- 560.334	1.996	
	3 6	- 522.561	1.962	-522.7
	4 11	- 522.333	1.964	
Coupling Constants(Hz)	11 14	- 511.291	1.965	-510.9
$J(1,2) = 85.00$	6 13	- 511.107	1.963	
$J(1,3) = 2.00$	1 5	- 473.337	2.003	-473.5
$J(1,4) = 300.00$	5 8	- 473.333	2.003	
$J(2,3) = 5.00$				
$J(2,4) = 2.00$				
$J(3,4) = 85.00$				

2) $\text{Ph}_3\text{P-Rh-Rh-PPh}_3$

1 2 3 4

Chemical Shifts(Hz)	$\begin{smallmatrix} >T \\ T \end{smallmatrix}$	Cal. Freq.	Relative Intensity	Exp. Freq.
$V(1) = -691.300$	7 14	-1071.206	0.024	Unobserved
$V(2) = 50000$	10 13	-1061.333	0.026	
$V(3) = 50000$	15 16	- 736.339	1.996	-736.1
$V(4) = -691.300$	9 15	- 736.336	1.996	
	3 11	- 696.333	1.972	-696.4
Coupling Constants(Hz)	4 6	- 696.207	1.974	
$J(1,2) = 88.00$	6 14	- 686.472	1.975	-686.1
$J(1,3) = 2.00$	11 13	- 686.338	1.973	
$J(1,4) = 370.00$	1 5	- 646.339	2.003	-646.9
$J(2,3) = 5.00$	5 8	- 646.336	2.003	
$J(2,4) = 2.00$	3 10	- 321.339	0.027	Unobserved
$J(3,4) = 88.00$	4 7	- 311.473	0.025	

3) (MeO)₃P-Rh-Rh-P(OMe)₃

1 2 3 4

Chemical Shifts(Hz)	ν	τ	Cal. Freq.	Relative Intensity	Exp. Freq.
V(1)=3643.4	10	14	2793.171	0.012	2798.7
V(2)=50000	7	13	2813.056	0.013	2812.5
V(3)=50000	9	12	3578.345	1.994	3576.5
V(4)=3643.4	12	16	3578.353	1.994	3576.5
	3	11	3637.552	1.935	3637.5
	4	6	3637.667	1.936	
Coupling Constants(Hz)	6	14	3643.950	1.937	3649.3
J(1,2)= 134.0	11	13	3649.041	1.936	
J(1,3)= -4.1	2	8	3708.243	2.005	3708.4
J(1,4)= 832.0	1	2	3703.253	2.005	
J(2,3)= 7.5	3	7	4473.538	0.014	4474.3
J(2,4)= -4.1	4	10	4433.446	0.013	4488.6
J(3,4)= 134.0					

4) (PhO)₃P-Rh-Rh-P(OPh)₃

1 2 3 4

Chemical Shifts(Hz)	ν	τ	Cal. Freq.	Relative Intensity	Exp. Freq.
V(1)= 2873.6	7	13	1973.100	0.009	1971.8
V(2)=50000	10	14	1935.050	0.009	1983.6
V(3)=50000	15	16	2306.504	1.994	2804.7
V(4)=2873.6	9	15	2306.514	1.994	
	3	11	2369.047	1.939	2869.6
	4	6	2369.096	1.939	
Coupling Constants(Hz)	6	13	2377.912	1.990	2877.5
J(1,2)= 130.0	11	14	2377.934	1.990	
J(1,3)= 4.0	1	5	2940.504	2.005	2940.5
J(1,4)= 890.0	5	8	2940.517	2.005	
J(2,3)= 6.0	3	10	3761.931	0.010	3763.5
J(2,4)= 4.0	4	7	3773.309	0.010	3775.3
J(3,4)= 130.0					

5) $\text{Cl}_3\text{P-Rh-Rh-PCl}_3$

<u>Observed Frequencies(Hz)</u>	<u>Relative Intensity</u>
5464.9	1
5390.5	2
5316.0	1

6) OC-Rh-Rh-CO

1 2 3 4

<u>Chemical Shifts(Hz)</u>		<u>Cal. Freq.</u>	<u>Relative Intensity</u>	<u>Exp. Freq.</u>
V(1)= 3833.45	7 13	13.515	0.237	13.590
V(2)=50000	10 13	13.515	0.237	13.590
V(3)=50000	12 16	13.539	0.992	13.590
V(4)= 3833.45	15 16	13.539	0.992	13.590
	9 15	13.540	0.992	13.590
<u>Coupling Constants(Hz)</u>	9 12	13.540	0.992	13.590
J(1,2)= 32.528	3 11	13.562	0.237	13.590
J(1,3)= 7.181	3 6	13.562	0.237	13.590
J(1,4)= 0.0	4 11	25.230	0.703	25.360
J(2,3)= 11.765	4 6	25.230	0.703	25.360
J(2,4)= 7.181	7 14	25.327	0.703	25.360
J(3,4)= 32.528	10 14	25.327	0.703	25.360
	6 13	41.460	0.712	41.540
	11 13	41.460	0.712	41.540
	3 10	41.507	0.712	41.540
	3 7	41.507	0.712	41.540
	4 10	53.225	0.291	53.300
	4 7	53.225	0.291	53.300
	2 8	53.243	1.003	53.300
	5 8	53.243	1.003	53.300
	1 5	53.243	1.007	53.300
	1 2	53.243	1.007	53.300
	6 14	53.272	0.291	53.300
	11 14	53.272	0.291	53.300

Add 3800 Hz to the frequencies listed above.

Mixed Ligand Adducts1) $\text{Ph}_3\text{P-Rh-Rh-P(OMe)}_3$

	1	2	3	4	>T			Relative	
Chemical Shifts(Hz)	T				T		Cal. Freq.	Intensity	Exp. Freq.
V(1)= -582.87					15	16	- 905.174	0.363	- 904.690
V(2)= 50000					10	13	- 904.600	0.372	- 904.690
V(3)= 49000					11	14	- 821.435	0.363	- 821.993
V(4)= 3448.36					5	8	- 320.839	0.372	- 321.993
					9	12	- 379.099	1.123	- 379.001
					3	6	- 378.525	1.124	- 379.001
Coupling Constants(Hz)					4	7	- 295.411	1.134	- 294.339
J(1,2)= 84.04					1	2	- 294.814	1.130	- 294.339
J(1,3)= 0.0					12	16	3131.153	1.126	3131.504
J(1,4)= 526.08					7	14	3135.369	1.129	3135.440
J(2,3)= 5.0					6	13	3269.267	1.129	3269.325
J(2,4)= 3.86					2	8	3273.455	1.131	3273.260
J(3,4)= 138.68					9	15	3657.233	0.866	3657.190
					4	11	3661.444	0.864	3661.130
					3	10	3795.341	0.876	3795.015
					1	5	3799.530	0.374	3793.953

2) $\text{Ph}_3\text{P-Rh-Rh-P(OPh)}_3$

	1	2	3	4	>T			Relative	
Chemical Shifts(Hz)	T				T		Cal. Freq.	Intensity	Exp. Freq.
V(1)= -578.23					15	16	- 914.437	0.343	- 914.060
V(2)= 50000					10	13	- 913.681	0.343	- 914.060
V(3)= 49000					11	14	- 827.632	0.343	- 827.290
V(4)= 2899.16					5	8	- 826.894	0.343	- 827.290
					9	12	- 371.739	1.153	- 371.360
					3	6	- 370.932	1.143	- 371.360
Coupling Constants(Hz)					4	7	- 234.984	1.160	- 234.590
J(1,2)= 87.21					1	2	- 234.197	1.155	- 234.590
J(1,3)= 0.0					12	16	2577.436	1.151	2577.440
J(1,4)= 542.70					7	14	2592.160	1.156	2592.150
J(2,3)= 5.0					6	13	2705.402	1.152	2705.400
J(2,4)= 14.27					2	8	2720.094	1.156	2720.104
J(3,4)= 128.72					9	15	3120.134	0.841	3120.140
					4	11	3134.853	0.838	3134.850
					3	10	3248.101	0.852	3248.095
					1	5	3262.792	0.849	3262.802

3) $\text{Ph}_3\text{P-Rh-Rh-PCl}_3$

	1	2	3	4	T		Cal. Freq.	Relative Intensity	Exp. Freq.
Chemical Shifts(Hz)					15	16	842.795	0.362	842.800
V(1)= -364.24					10	13	842.312	0.364	842.800
V(2)= 50000					11	14	748.704	0.364	747.600
V(3)= 49000					5	8	748.212	0.366	747.600
V(4)= 5545.26					9	12	35.233	1.133	34.700
					3	6	34.622	1.123	34.700
Coupling Constants(Hz)					4	7	53.630	1.130	53.100
					1	2	59.299	1.137	53.100
J(1,2)= 94.41					12	16	5103.055	1.132	5104.500
J(1,3)= 0.0					7	14	5133.465	1.128	5133.700
J(1,4)= 807.51					6	13	5199.351	1.127	5197.300
J(2,3)= 5.0					2	8	5234.752	1.133	5233.900
J(2,4)= 34.93					9	15	5910.567	0.861	5910.400
J(3,4)= 96.93					4	11	5945.300	0.861	5944.300
					3	10	6007.041	0.867	6007.800
					1	5	6042.264	0.867	6044.400

4) $\text{Cy}_3\text{P-Rh-Rh-P(OMe)}_3$

	1	2	3	4	T		Cal. Freq.	Relative Intensity	Exp. Freq.
Chemical Shifts(Hz)					15	16	690.041	0.855	683.740
V(1)= -356.19					10	13	639.358	0.859	633.740
V(2)= 50000					11	14	603.964	0.854	603.180
V(3)= 49000					5	8	603.249	0.859	603.180
V(4)= 3408.50					9	12	148.019	1.141	148.640
					3	6	147.336	1.136	148.640
Coupling Constants(Hz)					4	7	61.942	1.148	62.010
					1	2	61.228	1.143	62.010
J(1,2)= 86.54					12	16	3038.656	1.140	3038.190
J(1,3)= 0.0					7	14	3089.115	1.143	3038.190
J(1,4)= 542.02					6	13	3224.518	1.141	3224.040
J(2,3)= 5.0					2	8	3224.946	1.144	3224.040
J(2,4)= 0.0					9	15	3630.678	0.853	3631.600
J(3,4)= 136.54					4	11	3631.137	0.850	3631.600
					3	10	3766.540	0.864	3767.450
					1	5	3766.967	0.861	3767.450

5) (PhO)₃P-Rh-Rh-P(OMe)₃

	1	2	3	4	>T T	Cal. Freq.	Relative Intensity	Exp. Freq.
Chemical Shifts(Hz)								
V(1)= 3031.83					15 16	2222.116	0.049	2221.930
V(2)= 50000					10 13	2269.145	0.098	2271.105
V(3)= 49000					11 14	2300.696	0.014	
V(4)= 3312.35					5 8	2356.987	0.049	2355.767
					9 12	3082.266	1.945	3082.230
					12 16	3126.851	1.945	3127.570
Coupling Constants(Hz)					3 6	3129.296	1.399	3127.570
J(1,2)= 130.47					4 7	3160.344	1.936	3161.040
J(1,3)= 4.40					7 14	3172.822	1.935	3172.860
J(1,4)= 860.15					1 2	3217.136	1.956	3213.134
J(2,3)= 5.0					6 13	3225.010	1.901	3224.040
J(2,4)= -5.92					2 8	3261.719	1.956	3261.450
J(3,4)= 140.79					9 15	3987.001	0.049	3935.996
					4 11	4032.971	0.013	4033.250
					3 10	4085.161	0.101	4036.410
					1 5	4121.868	0.049	4121.350

6) (MeO)₃P-Rh-Rh-PCl₃

	1	2	3	4	>T T	Cal. Freq.	Relative Intensity	Exp. Freq.
Chemical Shifts(Hz)								
V(1)= 2865					15 16	2121.669	0.532	2116
V(2)= 50000					10 13	2129.590	0.591	
V(3)= 49000					11 14	2240.002	0.569	2241
V(4)= 5280					5 8	2243.178	0.578	
					3 7	3227.576	0.022	
					9 12	3236.667	1.411	3251
Coupling Constants(Hz)					3 6	3244.858	1.331	
J(1,2)= 124					4 7	3354.729	1.411	3373
J(1,3)= 5.0					1 2	3363.176	1.426	
J(1,4)= 1100					4 6	3372.011	0.023	
J(2,3)= 5.0					6 14	4799.943	0.013	
J(3,4)= 70					12 16	4806.222	1.412	4823
J(2,4)= 30					7 14	4817.125	1.413	
					6 13	4873.069	1.339	4893
					2 8	4883.715	1.425	
					7 13	4390.350	0.017	
					9 15	5921.219	0.583	
					4 11	5931.851	0.565	5953
					3 10	5938.337	0.595	
					1 5	5998.712	0.577	

Experimental frequencies are estimated
by the centers of the broad peaks in Fig.25.

C. Calculated and Observed Structure Factors

Data for centric space groups(py, NHET_2 , CO, P(OMe)_3 , and P(OPh)_3 adducts) contain F_{obs} 's, F_{cal} 's(with signs), and standard deviations of F_{obs} 's, in the order given. Data for acentric space groups(PF_3 and $(\text{NO})(\text{NO}_2)$ adducts) contain F_{obs} 's, F_{cal} 's, and phase angles, in the order given. The printing scale is 10 for all data.

	<u>From(page)</u>	<u>To(page)</u>
$\text{Rh}_2(\text{OAc})_4(\text{py})_2$:	225	229
$\text{Rh}_2(\text{OAc})_4(\text{NHET}_2)_2$:	230	235
$\text{Rh}_2(\text{OAc})_4(\text{CO})_2$:	236	240
$\text{Rh}_2(\text{OAc})_4(\text{PF}_3)_2$:	241	242
$\text{Rh}_2(\text{OAc})_4(\text{P(OPh)}_3)_2$:	243	253
$\text{Rh}_2(\text{OAc})_4(\text{P(OMe)}_3)_2$:	254	260
$\text{Rh}_2(\text{OAc})_4(\text{NO})(\text{NO}_2)$:	261	265

[illegible]

10	166	-183	14	4	192	223	12	6	80	-7	27	13	743	-733	10	-1	682	694	8	-12	438	-449	9		
11	120	-189	19	5	1638	1639	19	7	88	-173	14	14	619	-622	9	0	237	235	6	-11	560	508	9		
12	195	-197	14	6	143	-164	16	8	24	76	-47	30	15	634	-654	10	1	872	-874	7	-10	346	328	9	
13	212	-118	14	7	1684	-1896	19	9	198	224	-77	14	16	479	-494	10	2	627	-634	7	-9	159	-132	14	
14	65	-126	37	8	146	94	16	10	-32	-42	53	17	450	-456	10	3	811	811	7	-8	236	-268	11		
15	70	-86	37	9	1212	1210	14	11	95	-98	30					4	590	686	7	-6	663	-663	9		
16	85	30	33	10	69	-61	32									5	695	-701	8	-6	1069	1063	13		
				11	1113	-1126	13		2	20	L					6	854	-860	10	-5	1167	-1169	14		
				12	105	56	20										7	838	841	7	-4	1026	-1033	12	
				13	777	784	19										8	446	464	10	-3	1167	1166	13	
				14	31	-68	56		-9	83	79	34	-16	62	-167	42	9	446	464	10	-3	811	831	10	
-14	388	374	11					-8	627	623	10	-16	82	-119	27	10	10	446	464	10	-3	1167	1166	13	
-13	-90	-45	30					-7	189	-148	10	-13	235	-274	12	11	138	-131	17	-2	811	831	10		
-12	827	-538	9		2	16	L	-6	734	-148	10	-12	302	-504	16	11	414	403	8	0	261	-273	8		
-11	68	49	32					-5	182	-174	17	-11	213	-215	12	12	419	425	9	1	613	642	8		
-10	745	753	9	-12		683	686	10	-4	756	766	10	-10	225	210	11	3	557	-548	9	2	870	902	10	
-9	28	53	49	-11		113	-91	21	-2	56	-136	16	-9	318	326	9	14	477	-484	9	3	1250	-1280	14	
-8	524	-515	8	-10		162	-75	10	-2	10	694	-710	14	114	-125	17	15	543	386	11	4	1102	-1175	13	
-7	138	-124	16	-9		139	119	19	-1	-18	112	60	-7	18	-14	9	16	233	233	14	5	1125	135	13	
-6	617	623	8	-8		563	565	9	0	921	935	11	-6	238	-219	8	17	218	-212	17	6	7	1062	-1061	12
-5	106	112	19	-7		77	-88	29	1	75	-119	31	-5	712	678	8									
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-2	116	1157	14	-4		1095	1157	14	4	725	747	15	-2	591	-591	7	-13	850	856	11	12	-27	9		
-1																									

6	166	-164 15		4	20	L	-12	183	-197 16	13	453	-459 9	5	1164	1149 14	2	808	-797 10	
7	1281	-1190 14					-11	89	-75 26	14	376	-377 10	6	719	712 9	3	738	-761 9	
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9	923	923 11	-6	595	-589 10		-9	104	81 21	16	266	276 15	8	343	-343 9	5	728	726 9	
10	42	-61 45	-5	179	114 17		-8	83	-87 26				9	553	560 8	6	699	608 9	
11	896	-846 11	-4	779	778 10		-7	296	-304 9		5	7	10	404	401 9	7	863	-833 11	
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13	1005	992 12	-2	636	-622 10		-5	140	143 7		-14	439	448 11	12	443	-527 9	9	508	508 9
			-1	-31	44 52	-4	80	1	21	-13	470	475 10	13	499	496 10	10	513	508 9	
4	16	L	0	578	600 9	-3	277	248 8	-12	643	-647 10	14	428	418 10	11	564	-570 9		
			1	89	-52 28	-2	654	641 8	-11	731	-739 10	15	340	-338 12	12	513	-517 10		
-11	99	-91 30	2	787	-708 10	-1	188	188 9	-10	980	972 12				13	640	616 10		
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-4	1013	1017 12				6	355	360 7	-3	1552	-1537 18	-9	20	44 55	-9	478	-483 10		
-3	163	-121 14		5	1	L	7	435	433 7	-2	1511	1511 18	-8	204	-194 13	-8	703	710 10	
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4	1113	1126 13	-10	769	-791 10	14	43	137 48	5	1600	-1585 19	-1	162	157 14	-1	634	-641 9		
5	95	-108 24	-9	768	771 10	15	194	293 17	6</										

8	130	108 22	0	76	-116 22	-8	33	-32 46	-13	91	-13 82		1	72	62 32		
9	123	-106 13	1	1785	-1746 19	-7	1189	-1286 14	-12	64	91 49	-11	658	653 10	2	-96	-16 23
10	77	-34 33	2	81	-41 29	-6	38	-10 41	-11	161	176 19	-10	1123	-136 47	3	220	-235 33
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									13	207	205 16						
									14	78	86 86						
6 0 L			-9	1	74 25												
			-8	285	290 10												
			-7	-477	0 26												
			-6	-465													

-5	121	-83	20	-1	140	-86	17	-4	-89	36	81	8	220	-226	12	7	795	797	10	9	13	L		
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13	23	-32	58	17	998	-991	12	-14	787	-787	10	0	475	477	8	0	388	-384	9	9	497	-501	11	
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-9	97	37	27	21	891	891	11	-18	897	-887	11	4	436	443	8	-5	454	-437	9	-5	634	-624	10	
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-7	-71	-18	32	23	1076	-1081	13	-20	897	-887	11	6	473	-484	9	-3	531	312	11	-3	494	511	10	
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-5	187	27	21	25	811	813	10	-22	897	-887	11	8	418	425	9	-1	532	-219	15	-1	591	-568	9	
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-2	-43	-23	9	28	77	92	34	-25	897	-887	11	11	191	206	16	2	532	383	11	2	591	571	10	
-1	312	-319	9	29	935	923	12	-26	897	-887	11	12	201	195	16	3	532	383	11	3	611	-615	10	
0	83	8	25	30	60	-84	44	-27	897	-887	11	13	296	-291	13	4	532	383	11	4	536	-492	10	
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3	83	-96	25	33	503	-516	10	-30	897	-887	11	16	140	95	20	7	532	383	11	7	220	-228	16	
4	127	-183	12	34	-16	53	67	-31	897	-887	11	17	-72	-61	33	8	532	383	11	8	134	-127	23	
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Rh₂(OAc)₄(PF₃)₂

241

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								18	263	256	-176					19							
								19	310	314	-85												
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6	199	202	-178
8	11	L	
0	-67	46	5
1	356	845	-96
2	469	456	-71
9	8	L	
1	181	161	92
2	373	337	-177
3	165	142	-86
4	181	180	-176
5	897	891	-87
6	70	44	180
7	283	281	-87
8	-89	58	-178
9	511	518	93
10	39	63	2

	9	1	L
0	543	829	-88
1	189	93	48
2	271	265	-132
3	447	437	11
4	246	233	137
5	159	128	99
6	146	146	167
7	782	776	177
8	59	72	125
9	318	321	-150
10	135	163	65

	9	2	L
0	475	436	-86
1	247	232	138
2	250	246	-124

3	188	172	126
4	177	162	118
5	815	803	-79
6	284	255	59
7	310	311	-28
8	203	202	100
9	401	389	61

	S	L	
0	119	66	-87
1	333	329	177
2	544	529	176
3	192	197	35
4	329	313	160
5	328	320	47
6	112	84	-111
7	210	191	174
8	205	208	-107
9	222	226	-71

	9	4	L
0	549	547	-87
1	373	362	101
2	108	94	-39
3	605	590	109
4	491	480	61
5	78	70	77
6	247	250	23
7	192	203	1
8	73	34	-131

	9	5	L
0	139	114	93
1	536	533	-171
2	410	405	164
3	171	163	-69
4	144	129	34

5	321	299	25
6	369	366	-36
7	143	159	2
8	366	346	-115
9 6 L			
0	199	193	-57
1	308	297	51
2	195	197	73
3	413	411	193
4	371	377	62
5	194	184	126
6	375	365	-54
9 7 L			
0	-47	26	92
1	159	158	-117
2	195	91	178

3	293	286	-90
4	482	473	11
5	60	43	-111
9 8 L			
0	72	36	-86
1	235	233	-18
2	243	244	107
10 0 L			
0	154	152	-176
1	524	494	-86
2	93	91	4
10 1 L			
0	204	191	-177
1	317	299	-155

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