N-HETEROCYCLIC CARBENES: FROM HETEROCYCLYNES TO POTENTIAL RADIOPHARMACEUTICALS

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N-HETEROCYCLIC CARBENES: FROM HETEROCYCLYNES TO POTENTIAL RADIOPHARMACEUTICALS

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Dissertation

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ABSTRACT

This dissertation discusses the synthesis of different N-heterocyclic carbene precursors, the synthesis of an N-heterocyclic carbene from the precursor, the synthesis of N-heterocyclic carbene complexes of platinum and rhodium, as well as the transfer of N-heterocyclic carbenes from silver to rhodium, and to a smaller extent about the synthesis of previous heterocyclynes. In Chapter 1, the properties and preparation of N-heterocyclic carbenes and carbene salts are discussed. The bonding of N-heterocyclic carbenes as opposed to the bonding of Fischer and Schrock carbenes to metal centers is reviewed. The synthesis of platinum complexes of N-heterocyclic carbenes is illustrated. The synthesis of some of the many heterocyclynes with platinum at the corners is also discussed. The synthesis of the first silver N-heterocyclic carbene complex to use silver(I) oxide is discussed as well as the transfer of the carbene from silver to other metals with an emphasis on the transfer to rhodium. The synthesis of the various rhodium complexes of N-heterocyclic carbenes is also discussed. In Chapter 2 the synthesis of the first bis(N-heterocyclic carbene) complex of platinum is discussed as well as the synthesis of the building blocks to form the heterocyclyne. The high yield synthesis of the heterocyclyne composed of N-heterocyclic carbene platinum complexes at the corners and butadiyde fragments on the periphery is illustrated. In Chapter 3 the syntheses of the N-heterocyclic carbene complexes of silver are reported as well as the first transfer of a carbene from silver to rhodium trichloride hydrate, a necessary step in the direction of using N-heterocyclic carbene complexes of rhodium as radiopharmceuticals. An alternate approach to the synthesis of a rhodium N-heterocyclic carbene complex is also discussed.

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DEDICATION

To My Parents Geza G. Berczy and Catherine S. Berczy

Who

Gave me love and encouragement throughout my college career.

To my beloved husband Claro G. Quezada who gave me love, encouragement, understanding, and support. To my precious children Cristian A. Quezada and Nicolas J. Quezada who are my pride and joy in my life.

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ABBREVIATIONS AND ACCRONYMS

Å	Angstrom
Anal.	analysis
α	crystallographic unit-cell angle between axes b and c
β	crystallographic unit-cell angle between axes a and c
γ	crystallographic unit-cell angle between axes a and b
δ	scale (NMR) ppm
χ	angle (diffractometry)
ω	angle (diffractometry)
Φ	angle (diffractometry)
Ψ	angle (diffractometry)
σ	bond referring to bonding between sigma orbitals
π	bond referring to bonding between pi orbitals
a	crystallographic unit cell axis a
anal.	Analysis
b	crystallographic unit cell axis b
n-Bu	*n*-Butyl
C	celcius
c	crystallographic unit cell axis c
calcd.	Calculated
COD	cyclo-1,5-octadiene
d	doublet (NMR spectra) lattice spacing (crystallographic)
DFT	density functional theory
dcpe	1,2-bis(dicyclohexylphosphino) ethane
depe	1,2-bis(diethylphosphino)ethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dppbz	1,2-bis(diphenylphosphino) benzene

dppe	1,2-bis(diphenylphosphino) ethane
dppf	1,2-bis(diphenylphosphino) ferrocene
dppp	1,3-bis(diphenylphosphino) propane
ed	edition
Ed.	editor
EMIM	1-ethyl-3-methylimidazolium
ESI	electro spray ionization
et. al.	and others
F(000)	scaling coefficient for structure factors
F_c	calculated structure factor
F_o	observed structure factor
h	crystallographic index
h	hour
Hz	hertz
I	integrated intensity
IMes	1,3-bis(mesityl)imidazole
i-Pr	isopropyl
L	general ligand
^{n}J	nuclear spin-spin coupling constant through bonds
K	crystallographic index
l	crystallographic index
MeCN	acetonitrile
MeOH	methanol
min	minutes
mL	milliliter
MLCT	metal-to-ligand charge transfer
mmol	millimole
m/z	mass-to-charge ratio
n-Bu	*n*-butyl
NHC	N-heterocyclic carbene
nm	nanometer
NMR	nuclear magnetic resonance
OTf	trifluoromethanesulfonate
p	page
Ph	phenyl
pp	pages
ppm	parts per million
q	quartet (spectral)
R	organic group
R, R	residual based on F_o

RT	room temperature
s	singlet (spectrum)
S	goodness of fit
sat.	saturated
t	tertiary triplet (spectrum)
$t_{1/2}$	half-life
THF	tetrahydrofuran
TMEDA	tetramethylethylene diamine
TMSB	trimethylsilyl butadiyde
U	temperature factor
unsat.	unsaturated
wR2	weighted residual based on I

CHAPTER I

THE SYNTHESIS OF VARIOUS N-HETEROCYCLIC CARBENE PLATINUM, SILVER, AND RHODIUM COMPLEXES

Introduction

Although the synthesis of N-heterocyclic carbene metal complexes was first accomplished by Öfele[1] and Wanzlick[2] in 1968, it was not until the discovery of a stable, isolable free carbene by Arduengo[3] in 1991 that they became important in mainstream organometallic chemistry. Today, it is much easier to use the air and water stable precursors to carbenes, the carbene or imidazolium salts.

The Properties and Uses of N-heterocyclic Carbenes

N-heterocyclic carbenes (Figure 1-1) (furthermore referred to NHC or NHCs) are interesting ligands to organometallic chemists because of their unique properties. They bind to metals in a variety of oxidation states, to both hard and soft metals, and they bind with a strong σ donation and little or no π back bonding. These properties make NHC metal complexes much different than the electrophilic Fischer carbene[4] (Figure 1-2) or the nucleophilic Schrock carbene[5] (Figure 1-3) metal complexes. They have been compared to phosphines in their binding nature.[6]

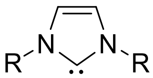


Figure 1-1 An example of an N-heterocyclic Carbene

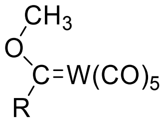


Figure1- 2 An example of a Fischer carbene

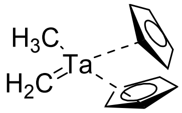


Figure 1-3 An example of a Schrock carbene

The stability of NHCs is due in large part to the nature of the substituents directly attached to the carbene center. Figure 1-4 illustrates the fact that σ acceptors and π donors directly attached to the carbene greatly increase the stability.[7] The original isolated NHC employed steric bulk at the N atoms to prevent dimerization,[8] and aromaticity in the ring contributed to the stability.[9] Figure 1-5 demonstrates the stability gained as the conjugation to the carbene increases.[10]

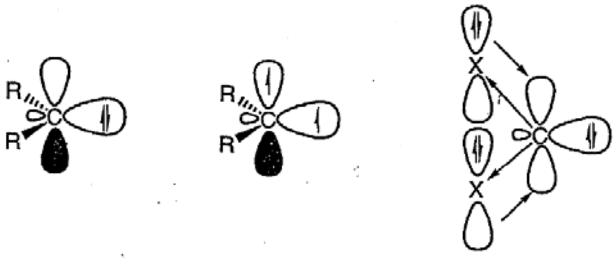


Figure 1-4 Stabilization of the carbene by σ acceptors and π donors (taken from reference 7)

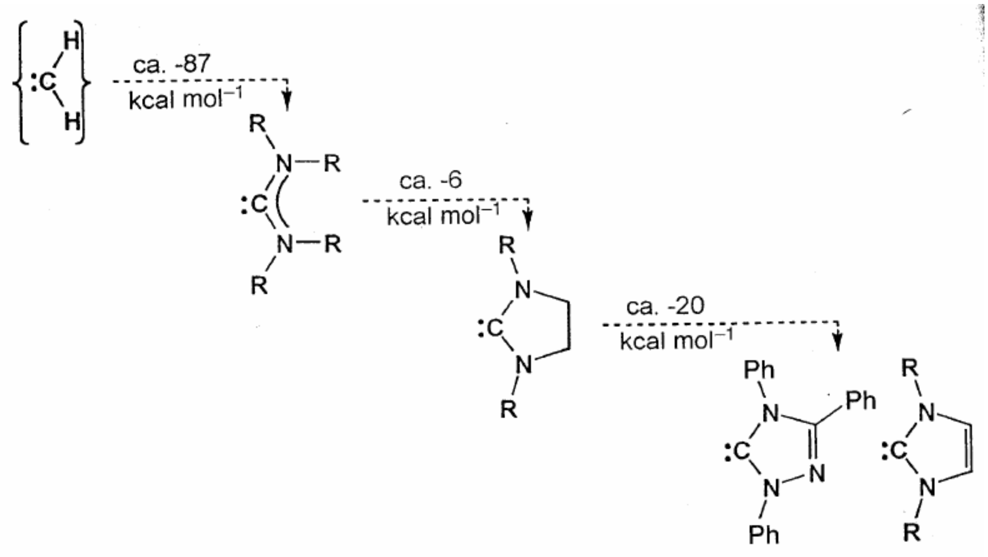
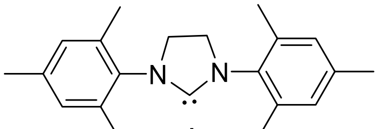


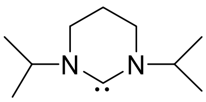
Figure 1-5 Stabilization of the carbene by nitrogen atoms and aromaticity (taken from reference 10)

Later the first saturated types of NHCs, **1**, (Figure 1-6) were introduced,[11,12] followed by the 6-membered type,[13,14] **2**, (Figure 1-7) and acyclic NHCs,[15,16] **3**, (Figure 1-8). These types of NHCs are more electron rich, but also lack the aromatic character.



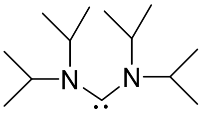
1

Figure 1-6 Saturated NHC



2

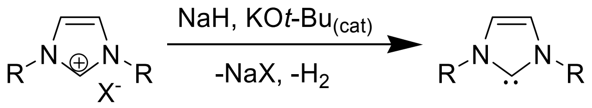
Figure 1-7 6-membered NHC



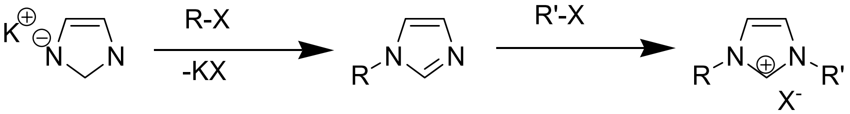
3

Figure 1-8 Acyclic NHC

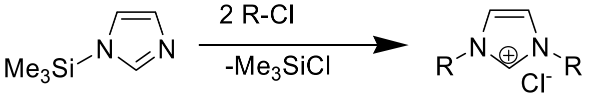
NHCs are most easily handled as their air-stable counterparts, imidazolium salts. Equation 1-1 demonstrates the formation of a carbene from the corresponding imidazolium salt. Deprotonation of the imidazolium salt by a strong base, NaH, and a catalytic amount of potassium *tert*-butoxide affords the carbene. Equations 1-2 and 1-3 express two different ways to synthesize unsaturated imidazolium salts. The first method (Equation 1-2) involves a reaction between potassium imidazole and a primary halide to give the substituted imidazole, followed by a second addition of a primary halide to yield the final imidazolium salt.[17,18,19] The second route (Equation 1-3) involves a reaction between a trimethylsilyl-substituted imidazole and two equivalents of a primary alkyl chloride. The trimethylsilyl group is displaced, forming the volatile trimethylsilyl chloride and the alkyl substituted imidazolium salt.[20] One limitation imposed by the previously mentioned syntheses is that it is necessary to only use primary alkyl halides, as the use of secondary and tertiary alkyl halides results in excessive amounts of elimination by-products.



Equation 1-1

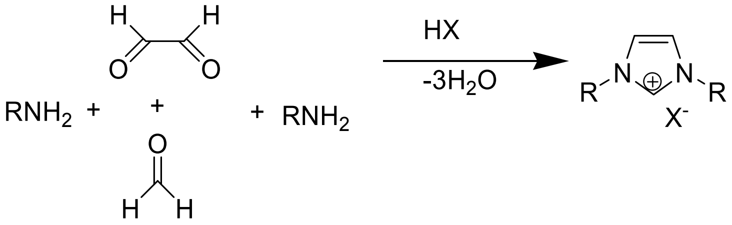


Equation 1-2



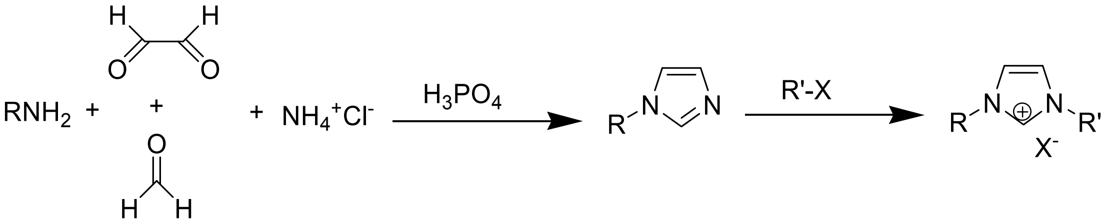
Equation 1-3

In order to introduce bulkier substituents onto the nitrogen atoms in the ring, a reaction between glyoxal, formaldehyde, and two primary amines in the presence of acid can be utilized[21,22,23] (Equation 1-4).



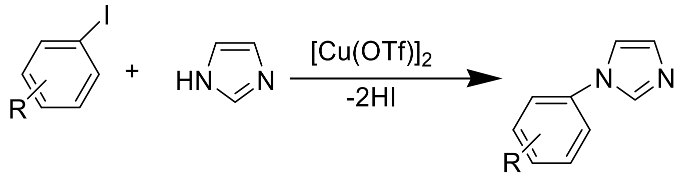
Equation 1-4

A combination of the previous two methods allows for the synthesis of a bulkier imidazolium salt by first preparing a substituted imidazole through the formaldehyde/glyoxal route and a subsequent alkylation using a primary alkyl halide (Equation 1-5).[24]



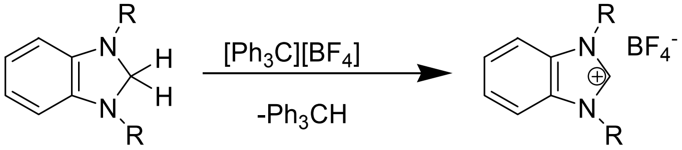
Equation 1-5

A variation of this method[25] involves a reaction between an aryl halide and imizadole in the presence of copper(I) triflate to yield an aryl substituted imidazole, followed by alkylation (Equation 1-6).



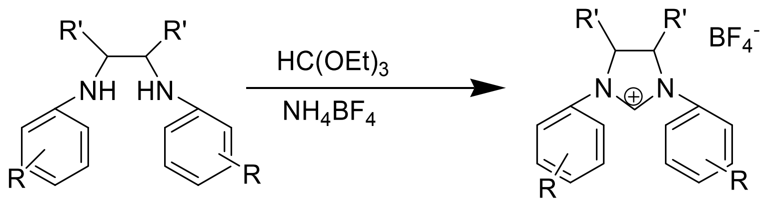
Equation 1-6

In the case of benzimidazolium salts, the simple route involves hydrogen abstraction by treatment with tritylium tetrafluoroborate (Equation 1-7).[26]



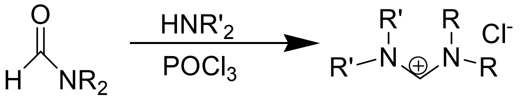
Equation 1-7

NHCs with saturated backbones, imidazolidinium salts, are readily accessible via a reaction between a secondary diamine and $HC(OEt)_3$ in the presence of an ammonium salt (Equation 1-8).[27,28]



Equation 1-8

Acyclic NHCs are easily synthesized via a condensation reaction between a formamide and an amine (Equation 1-9).[29]

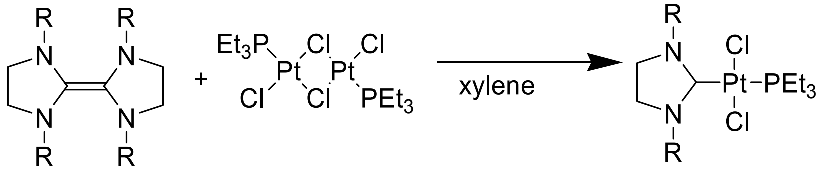


Equation 1-9

Metal complexes of NHCs are now known for most metals.[10,30,31] We will restrict our discussion to NHC metal complexes involving Pt and Rh, and a short discussion on the vast array of Ag carbenes.

Platinum Complexes of N-heterocyclic Carbenes

Much of the early work involving NHC Pt complexes was done by Lappert and his coworkers in the early to mid 1970s. The first example of a transition metal NHC is illustrated in Equation 1-10. Treatment of the NHC dimer **4a** or **4b** with *trans*-$[Et_3P]_2Pt_2Cl_4$ in refluxing xylene afforded the *trans* NHC Pt complexes **5a** and **5b**.[32,33,34,35]



4a: R = Me
4b: R = Ph

5a: R = Me
5b: R = Ph

Equation 1-10

A subsequent publication discussed the *cis/trans* isomerization of **5b** (Figure 1-9).[36] Lappert *et al* determined that the *trans* complex could be converted to the *cis* conformation, **6**, thermally. Furthermore, the two conformations possessed different properties. The *cis* form was white, whereas the *trans* form was yellow. The solubility of the *trans* form was greater than that of the *cis* form in non-polar solvents. The melting point for the *cis* configuration was greater than that for the *trans* form. The *J* coupling between the ^{31}P and the ^{195}Pt was greater for the *cis* than for the *trans* form. The bond length of the Pt-Cl bond was greater for the *cis* form, while the bond length of the Pt-P bond was greater for the *trans* form. This suggested that the *trans* influence of the phosphorus is about the same as for the carbene and greater than that for the chloride.

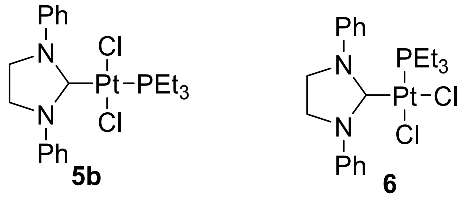
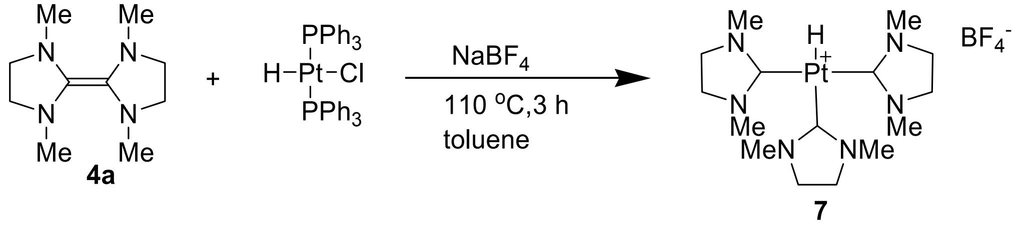


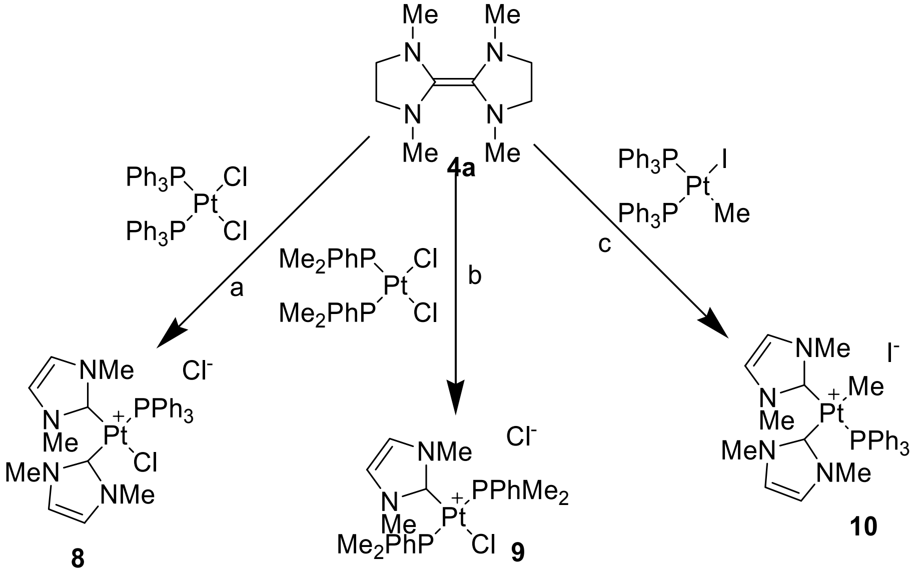
Figure 1-9 A view of the cis and trans isomers of **4b**

Lappert *et al*, also reported the synthesis of **7**[37] (Equation 1-11). Combination of the NHC dimer **4a** with *trans*($(PPh_3)_2PtHCl$) in the presence of $NaBF_4$ in toluene at 110 °C for 3 h afforded **7** in 80% yield as a white powder with a melting point of 183-185 °C. This reaction demonstrated that an NHC could displace a neutral ligand such as a phosphine.



Equation 1 -11

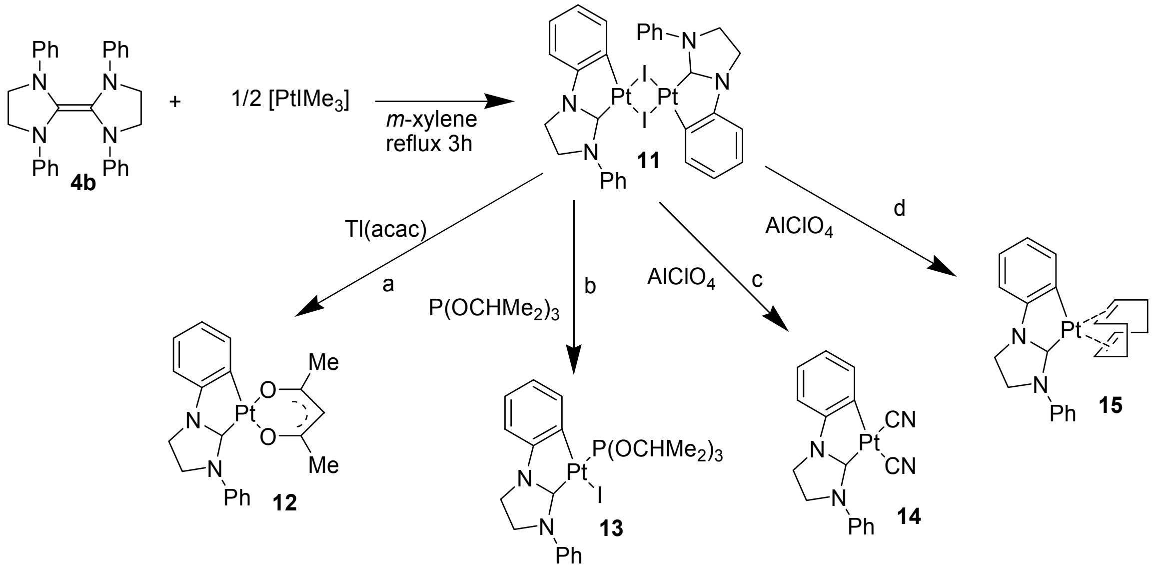
In a subsequent publication, Lappert *et al* further demonstrated the ability of an NHC to displace a neutral ligand[38] (Scheme 1-1).



a = toluene, reflux 3 h
b = toluene, reflux 1 h
c = toluene, reflux 2 h

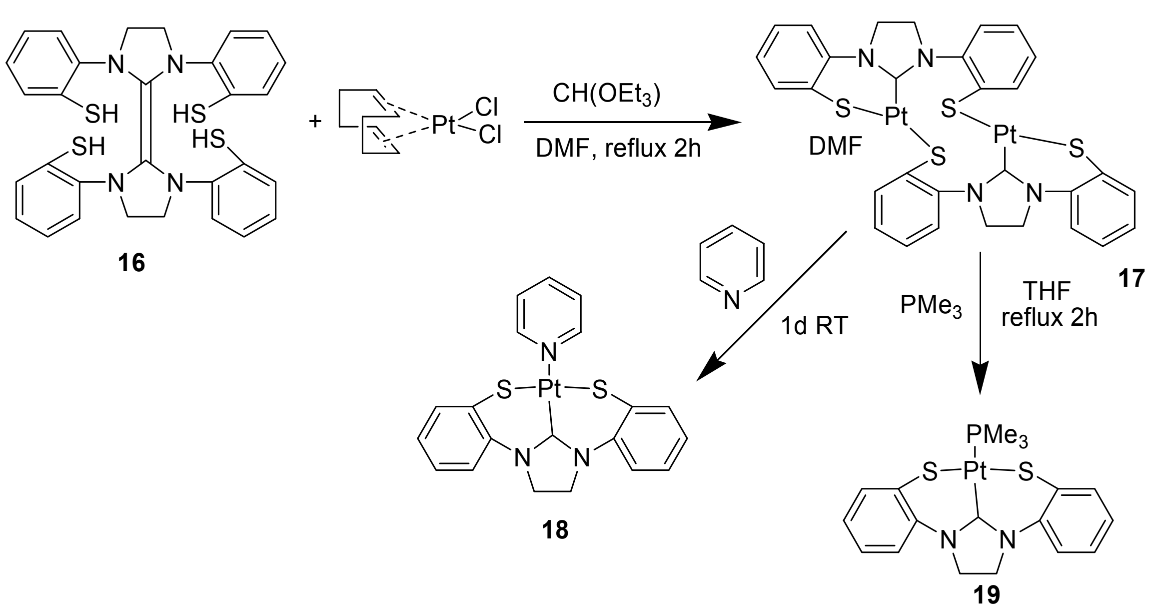
Scheme 1-1 The demonstration that NHCs displace neutral ligands

Sugino *et al* contributed to the synthesis of Pt NHC complexes with their work in 1981 (Scheme 1-2).[39] They demonstrated the formation of fine green crystals of the Pt NHC dimer complex **11** after refluxing **4b** and half of an equivalent of $PtIMe_3$ in xylene for 3 h. Subsequent reactions proved that **11** could react a) in refluxing CH_2Cl_2 with Tl(acac) to form fine yellow needles of **12**, b) with triisopropyl phosphite in THF at RT to form **13** as yellow microcrystals after 24 h, c) with a solution of silver perchlorate in a 50:50 benzene/acetonitrile mix at RT to form yellow crystals of **14** after 24 h, or d) with silver perchlorate and cyclo-1,5-octadiene (COD) in a 50:50 benzene/CH_2Cl_2 mix at RT to form orange microcrystals of **15** after 2 h.



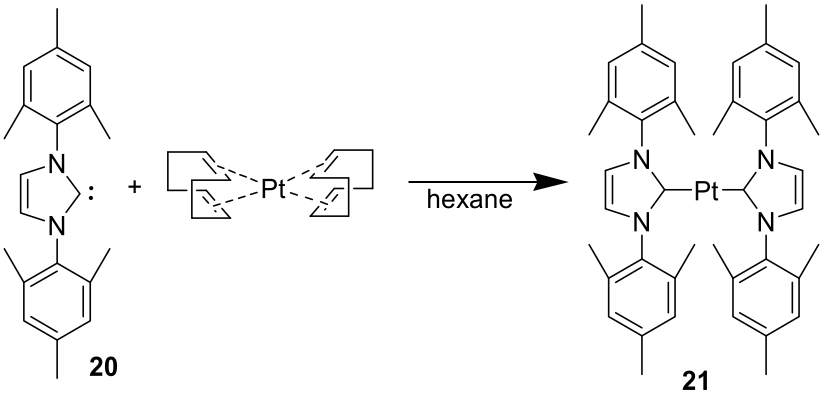
Scheme 1-2 The synthesis of various Pt NHC complexes by Sugino *et al* in 1981

Moll *et al* followed a similar pattern which involved the reaction of the NHC dimer containing pendant thiol groups, **16**, with (COD)PtCl$_2$ in DMF in the presence of CH(OEt)$_3$ (Scheme 1-3).[40, 41] In this reaction, a boiling solution of **16** and CH(OEt)$_3$ in DMF was added dropwise to a solution of (COD)PtCl$_2$ in DMF. After boiling the solution for a further 2 h and a subsequent organic workup, **17** was obtained as a fine green powder in 70% yield. Further reaction of **17** with pyridine gave **18** as a green powder in 62% yield, and reaction of **17** with trimethylphosphine gave **19** as a yellow powder in 67% yield.



Scheme 1-3 The reaction of a bis(NHC) with pendant thiol groups with (COD)$PtCl_2$

It was not until Arduengo *et al* introduced the first isolable crystalline carbene in 1991[3] that renewed interest in Pt NHC commenced. Arduengo *et al* published the first successful synthesis of a Pt NHC complex using a free carbene[42] (Equation 1-12). To a partially dissolved solution of Pt(0)$(COD)_2$ in hexane was added dropwise a solution of the free carbene, **20**, in hexane. Following stirring at RT for 30 minutes and a subsequent organic workup, **21** was obtained as a yellow powder in 70% yield with a melting point of 247 ^{0}C.



20

21

Equation 1-12

Cloke *et al* was interested in the remarkable two coordinate metal-NHC complexes such as **21**.[43] He investigated the bonding using photoelectron spectroscopy and density functional theory (DFT) calculations. He concluded that the NHC provided a predominately strong σ donation to the metal and little or no π back bonding by the metal, which was indicated by the fact that the π orbital are essentially unperturbed upon complexation (Figure 1-10).

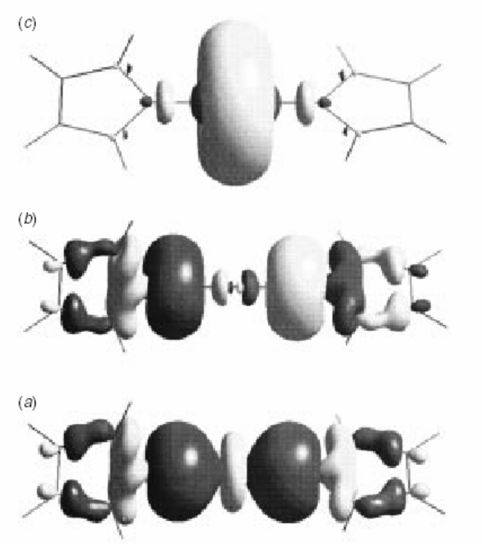
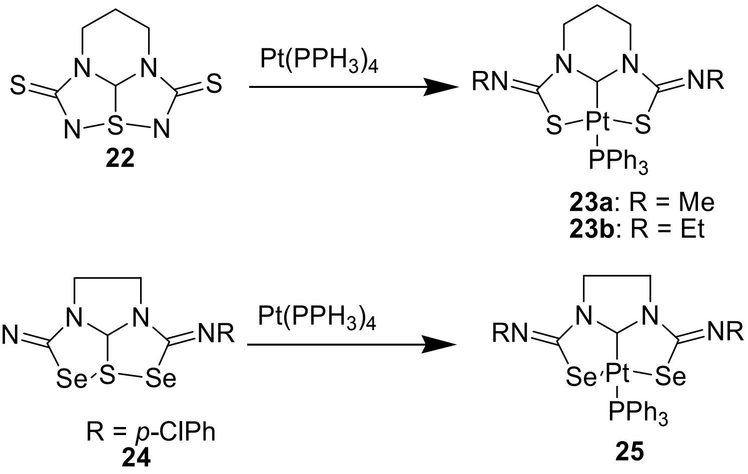


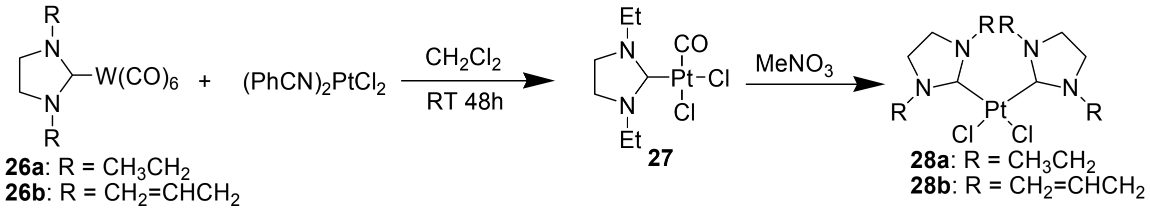
Figure 1-10 DFT calculations showing the bonding between a metal and an NHC (taken from reference 42)

Iwasaki *et al* reported the synthesis of the NHC Pt complexes **23a**, **23b**, and **25** using a unique type of carbene precursor, **22** (Scheme 1-4).[44, 45] They reported that the S-N bond is moderately weak and is easily broken by the electrophilic Pt metal as it attacks the carbene center.



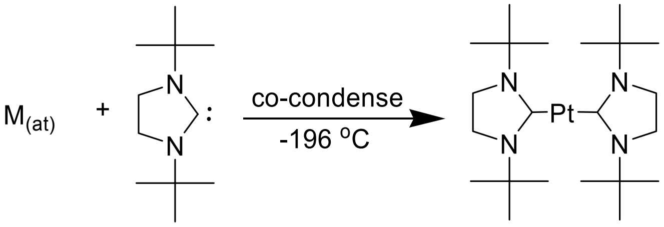
Scheme 1-4 The synthesis of the Pt NHC complexes **23a,b** and **25**.

In 1998, Peng *et al* reported the first example of a carbene transfer from W to Pt (Equation 1-13).[46,47] Reaction of **26a** with $(PhCN)_2PtCl_2$ in CH_2Cl_2 at RT for 48 h afforded the Pt NHC complex, **27**, in 93% yield. This showed that both the NHC and the carbonyl were transferred. Treatment of **27** with $MeNO_3$ resulted in a disproportionation reaction to form **28a**. Alternatively, **28b** can be synthesized directly from **26b** without the formation of the carbonyl intermediate.



Equation 1-13

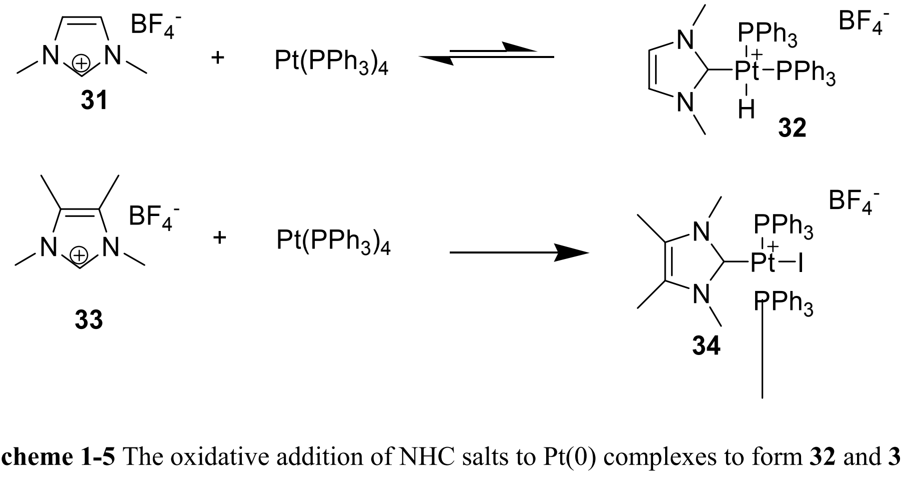
Cloke *et al* reported the synthesis of the Pt NHC, **30**, via a co-condensation of Pt metal and an excess of the free carbene, **29** (Equation 1-14).[48] Pt complex **30** was obtained as a yellow crystalline powder in 25% yield. It decomposed after a few minutes of exposure to moisture.



29 **30**

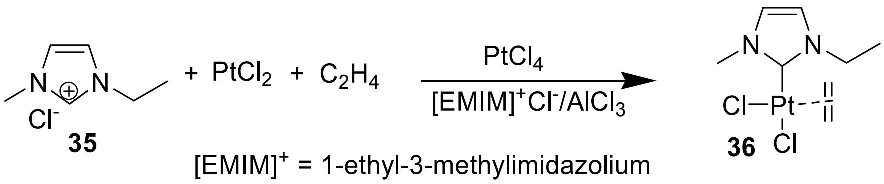
Equation 1-14

Cavell *et al* studied the oxidative addition of an NHC salt to Pt(0) to form Pt(II) (Scheme 1-5).[49,50] They determined that such reaction would be an exothermic process based on DFT calculations. They confirmed their results experimentally, showing that a reaction between **31** and Pt(PPh)$_4$ forms the NHC Pt(II) complex **32**, and similarly, a reaction between **33** and Pt(PPh)$_4$ forms NHC Pt(II) complex **34**.



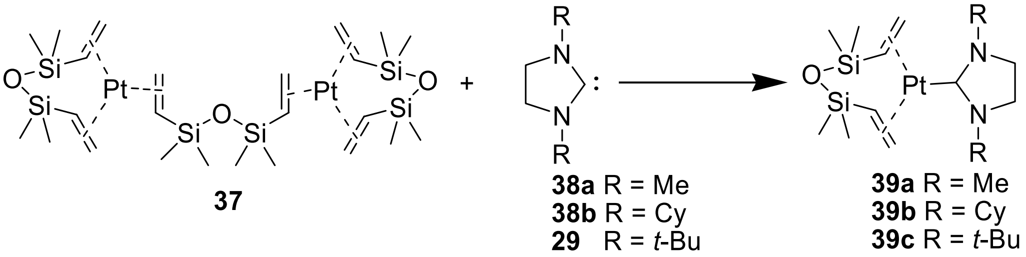
Scheme 1-5 The oxidative addition of NHC salts to Pt(0) complexes to form **32** and **34**.

Winterton and coworker studied the effects of Pt(II) and Pt(IV) salts on the effects of ionic liquids (Equation 1-15).[51] They determined that the presence of the salts had no effect on the thermal behavior of the ionic liquid up to 200 °C. However, they also serendipitously discovered the synthesis of **36**. During their investigation, they heated $PtCl_2$, a catalytic amount of $PtCl_4$, and ethylene in the basic ionic liquid $[EMIM]^+Cl^-/AlCl_3$ to 200°C at a pressure of 50 atm and produced the Pt NHC complex **36** as brown crystals in 26% yield with a melting point of 193 °C. They speculated that the $PtCl_4$ most likely assisted in the formation of bis(1-ethyl-3-methylimidazolium)tetrachloroplatinate(II), which is likely to be an intermediate in the overall reaction. They stated that it was necessary to use a basic ionic liquid to facilitate the abstraction of the carbonium proton. The reaction did not proceed in either acidic or neutral ionic liquids. The presence of ethylene at a pressure above 30 atm was also necessary for the formation of **36**. This indicated that the Pt-C bond was stabilized by the alkene.



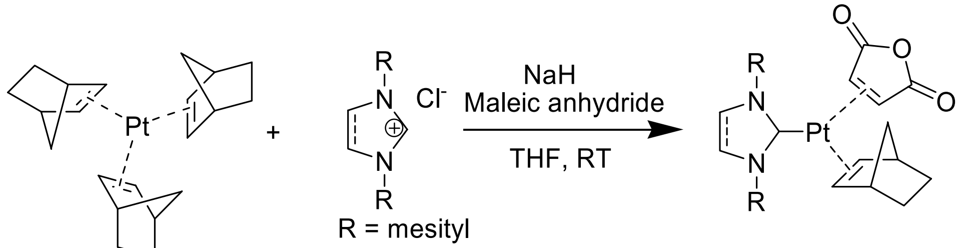
Equation 1-15

Since the synthesis of the first Pt NHC, there have been many patents on the uses of these complexes for catalysis.[52, 53, 54, 55, 56, 57] One such complex was published by Declercq *et al* for use as a hydrosilylation catalyst (Equation 1-16).[58] Karstedt's catalyst, **37**, classically has been used for hydrosilylation reactions. However, it has some problems including the formation of isomers, dehydrocondensation adducts, the reduction of alkenes, and the formation of colloidal platinum that causes undesired side reactions and discolorations in the final product. In order to circumvent these problems, Declercq *et al* decided to synthesize the NHC platinum complexes, **39a-c**, and test their effectiveness. The platinum NHC complexes, **39a-c**, were synthesized by adding the free carbene, **38a,b** or **29**, to a solution of **37**. After workup, platinum complexes **39a-c** were obtained in 54%, 60%, and 90% yields respectively. They also found that the platinum NHC catalysts outperformed the original Karstedt's catalyst. Although the platinum NHC complexes were slightly less reactive, they produced a greatly reduced amount of the undesired byproducts previously mentioned, and they did not produce any colloidal platinum.



Equation 1-16

Elsevier and coworkers were also studying platinum NHC complexes as potential catalysts for hydrosilylation (Equation 1-17).[59, 60] The Pt(0) complex, **40**, was added to a suspension of **41a** or **41b** and NaH in THF, and the solution was stirred for 18 h. After filtering the solution, maleic anhydride was added to the filtrate, and it was stirred for ten minutes. The solvent was removed *in vacuo* yielding **42** as a light yellow powder in 74% yield. They initially applied two NHCs onto the platinum, but later determined that this complex was too stable to act as a catalyst. They found that **42** had a very high activity, and that it produced virtually no dehydrogenative silation.



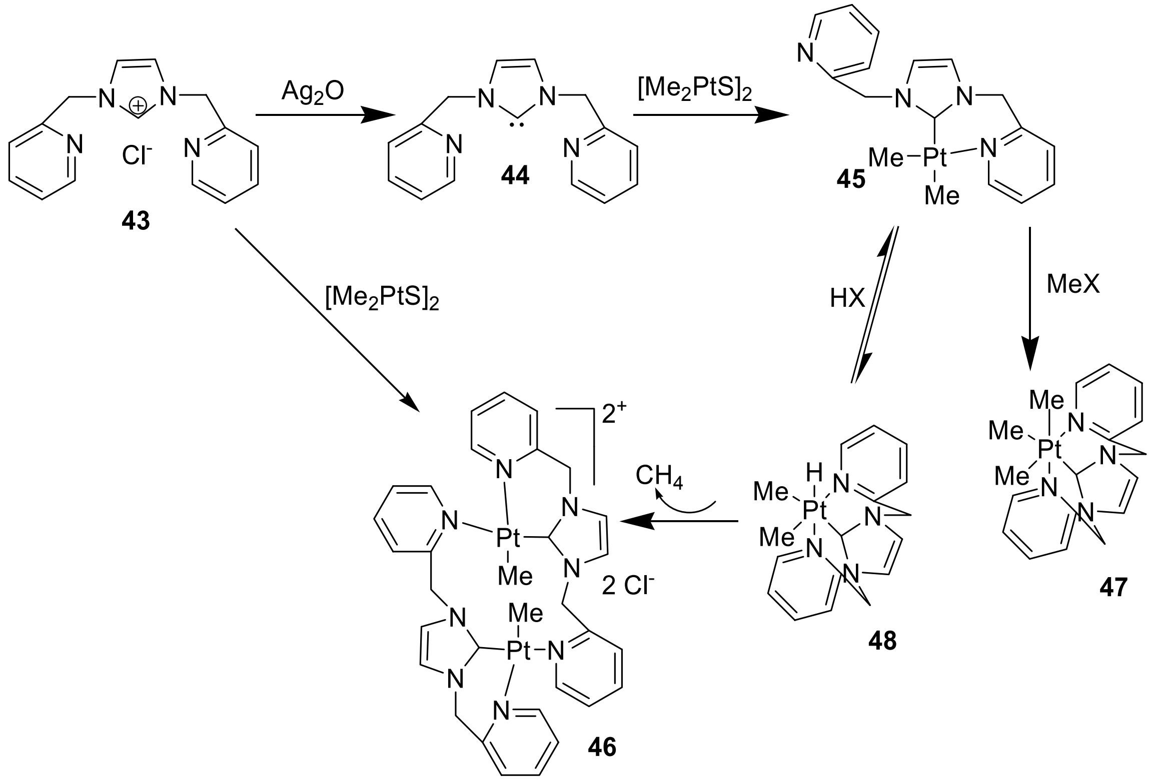
40

R = mesityl
41a unsat. carbene
41b sat. carbene

R = mesityl
42a unsat. carbene
42b sat. carbene

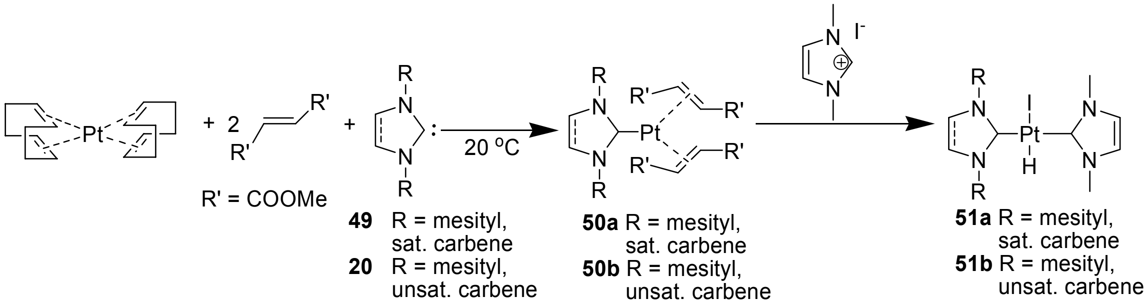
Equation 1-17

Puddephatt *et al* utilized transfer of a carbene from Ag to Pt to synthesize **45** (Scheme 1-6).[61] The carbene salt, **43**, was treated with Ag_2O to yield the Ag carbene complex, **44**, which the authors depicted as the free carbene since the exact structure was not known. The carbene was transferred from Ag to Pt using the dimethyl Pt complex $[Me_2PtS]_2$ by displacing the more labile sulfide ligands. Complex **45** was obtained as a red-orange powder in 57% yield. The authors describe **45** as being slightly air-sensitive and reactive towards oxidative addition. Complex **46** was synthesized by simply mixing **43** and $[Me_2PtS]_2$ in THF at rt for four days. Excess diethylether was added to precipitate **46** as a pale tan powder in 59% yield. The oxidative addition of MeI to **45** gave **47**, which is stable at rt in solution for at least one month. Alternatively, the oxidative addition of the protic acid HCl in acetone at -78 ^{o}C gave the hydrido(dimethyl)Pt complex **45**, which is stable for one week at -78 ^{o}C, for greater than seven hours at -60 ^{o}C, and for greater than one hour at -40 ^{o}C. The reductive elimination of methane occurs to give an alternative route to **46**.



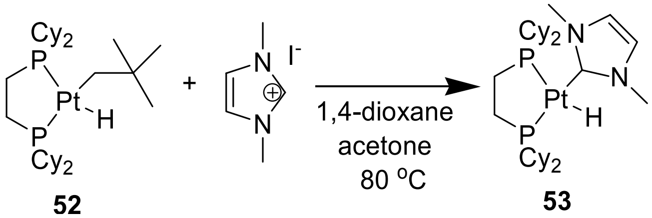
Scheme 1-6 The transfer of an NHC from Ag to Pt to form **45**, and subsequent reactions to form **46**, **47**, and **48**.

Elsevier and his coworkers were studying the C-H activation of imidazolium salts by Pt[62] (Equation 1-18). They synthesized **50a,b** via the addition of the appropriate free carbene, **49,** or **20**, to a solution containing Pt $(COD)_2$ and two equivalents of the alkene in THF at rt. The Pt complexes **50a** and **50b** were obtained as white solids in 55% and 73% yields respectively. They showed that **50a** and **50b** were reactive towards C-H insertion. This was demonstrated by the addition of 1,1'-dimethylimidazol-2-ylidene iodide to a solution of **50a** or **50b** in a solution of THF. The C-H bond of the carbonium carbon was activated, forming the first examples of the thermally stable bis(NHC)Pt hydrido complexes, **51a** and **51b**. In the same publication, Elsevier and coworkers compared the ability of their NHC Pt complexes to activate C-H bonds with the ability of the Whitesides complex, **52**, which is well known for its ability to activate C-H bonds.[63,64] The Whitesides method is shown in Equation 1-19. The combination of 1,1'-dimethylimidazol-2-ylidene iodide with **52** in a solution of 1,4-dioxane/acetone at 80 °C overnight produced **53** as a very reactive Pt(0) intermediate in a 90% yield.



49 R = mesityl, sat. carbene
20 R = mesityl, unsat. carbene
50a R = mesityl, sat. carbene
50b R = mesityl, unsat. carbene
51a R = mesityl, sat. carbene
51b R = mesityl, unsat. carbene

Equation 1-18

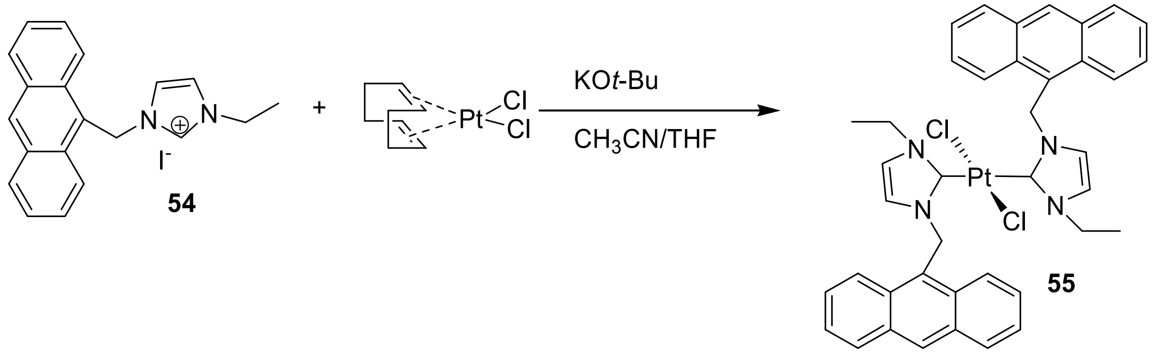


52 **53**

Equation 1-19

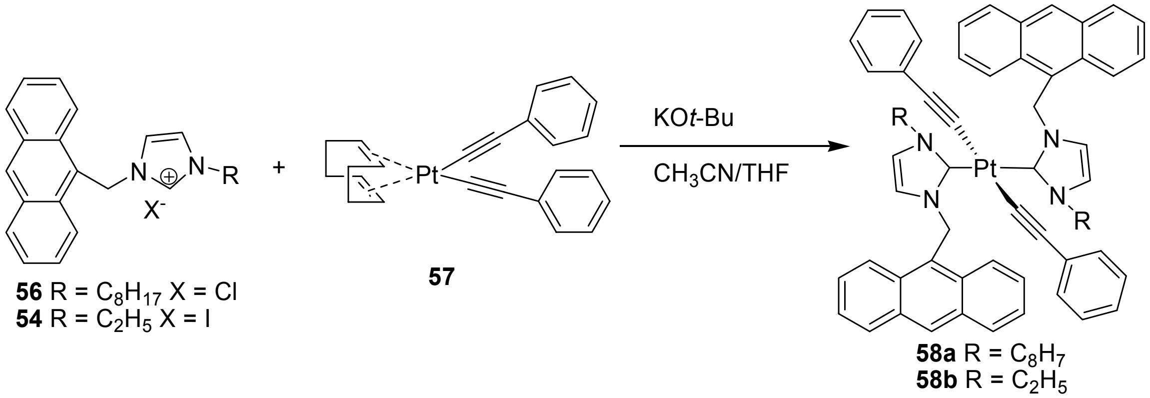
Zhang and coworkers were interested in the photophysical properties of Pt NHC complexes. They synthesized a variety of optically active Pt NHC complexes by using an anthracene substituent on the NHC salt. The synthesis of the first complex, **55**, is outlined in Equation 1-20.[65] The combination of **54** and (COD)PtCl$_2$ in CH$_3$CN/THF in the presence of potassium *t*-butoxide afforded **55** as a fine yellow powder in 55% yield.

They concluded that the luminescence of the platinum complex, **55**, was stronger than that of **54** due to the electron withdrawing effect of platinum.



Equation 1-20

In a subsequent publication Zhang *et al* reported the synthesis and the luminescent properties of **58a** and **58b** (Equation 1-21).[66] This synthesis is similar to the previous one. The combination of **56** or **54** with **57** in a solution of CH$_3$CN/THF in the presence of potassium *t*-butoxide afforded **58a** and **58b** as pale yellow powders in 91% and 52% yields respectively. The electron absorption spectra of the two platinum complexes were measured. Complex **58a** exhibited two bands, at approximately 315 nm, for anthracene, and at 340-400 nm for the metal to ligand charge transfer (MLCT) transition. Complex **58b** exhibited an anthracene-type band at 350-500 nm that was similar to but weaker than that of **58a**. This was attributed to the transfer of electrons through the Pt atom from phenyl acetylene to the imidazolium ring.



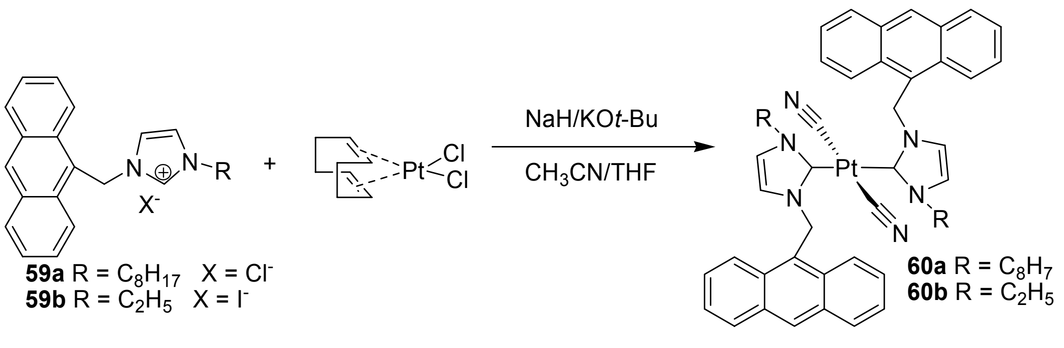
56 R = C_8H_{17} X = Cl
54 R = C_2H_5 X = I

57

58a R = C_8H_7
58b R = C_2H_5

Equation 1-21

Zhang *et al* also reported the synthesis of **60a** and **60b** (Equation 1-22).[67] After refluxing **59a** or **59b**, (COD)$PtCl_2$ NaH and *t*-BuOK in CH_3CN/THF for 8 h, a brown solution formed. After organic workup, **60a** or **60b** was obtained as a pale yellow powder in 43% and 49% yields respectively. This synthesis demonstrated that the H^- derived from NaH could cleave the C-C bond in CH_3CN under the catalysis of Pt(II), and the CN^- could be captured by the Pt(II).

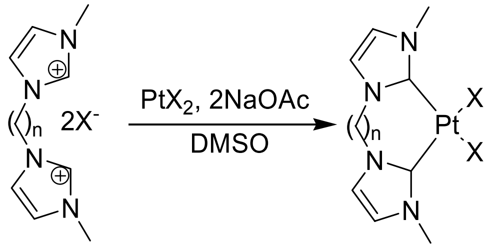


59a R = C_8H_{17} X = Cl^-
59b R = C_2H_5 X = I^-

60a R = C_8H_7
60b R = C_2H_5

Equation 1-22

Herrmann *et al* published the synthesis of the chelating NHC platinum complexes **62a-c** (Equation 1-23)[68] after we had submitted our paper[69] with the exact same synthesis of the platinum complex. After heating **61a-c** with PtX_2 and sodium acetate in DMSO at 75 ^{o}C for 1 h a yellow solution was obtained. After organic workup, **62a-c** were obtained as slightly yellow powders in 70%, 64% and 72% yields respectively. This route was new and improved on the previous syntheses of NHC complexes that had to be handled in an inert atmosphere and prepared via the free carbene or in an ionic liquid. This synthesis took place in one pot in air and using simple reagents, a great improvement over the previous syntheses.



61a n = 1, X = I
61b n = 1, X = Br
61c n = 2, X = I

62a n = 1, X = I
62b n = 1, X = Br
62c n = 2, X = I

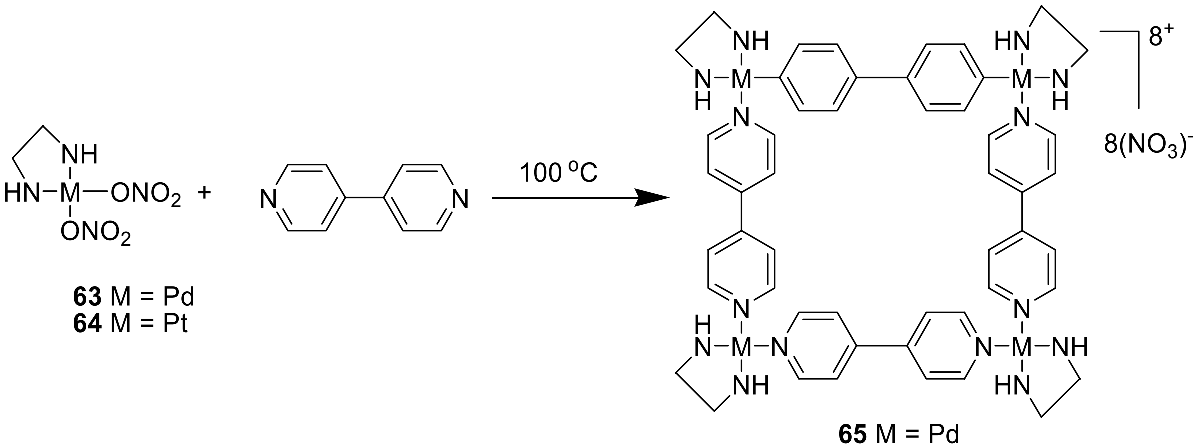
Equation 1-23

Macrocyclic Rings

A cyclyne is defined as a cyclic system that contains one or more alkyne units.[70,71,72] Inclusion of one or more heteroatoms (any element other than carbon) into the ring will result in a heterocyclyne.[73] Our focus will be on heterocyclynes that incorporate Pt.

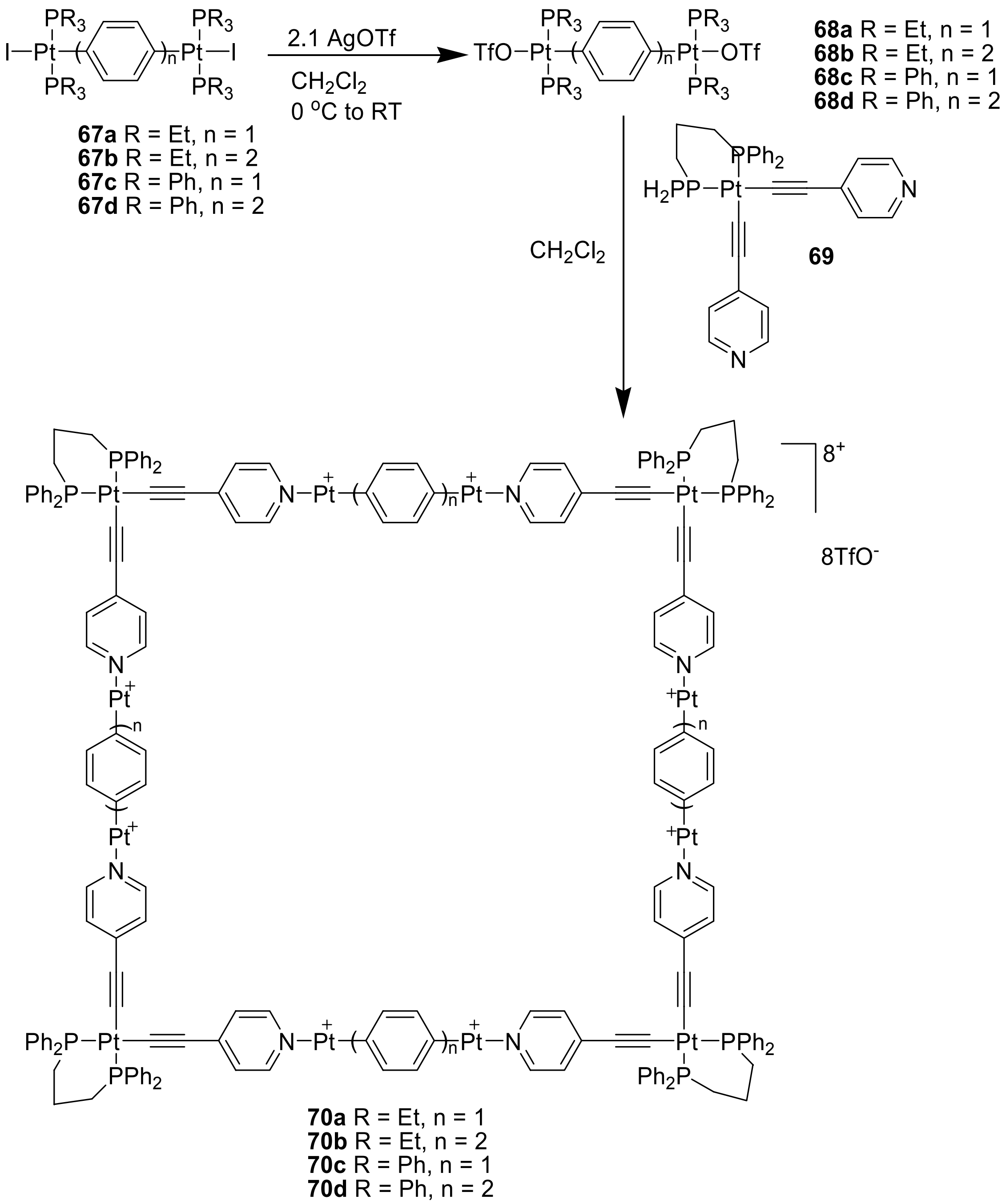
The convergent synthesis of heterocyclynes using a self-assembly approach was developed separately by Fujita[74] and Stang.[75] The self assembly approach required the use of rigid rod-like structures to form the sides of the square and square planar complexes (in this case Pt(II) complexes) to form the corners. With these building blocks, the reaction was thermodynamically driven to form the squares, often in high yields. Others have also reviewed this chemistry.[76,77]

Fujita *et al* were inspired to construct molecular squares for the application of recognizing specific organic moieties in solution and binding to them in a similar manner to crown ethers.[78] The rigid framework could be tailored to recognize specific molecules. The synthesis of Fujita's squares begins with the square planar Pd or Pt complexes **63** or **64**. Combination of **63** or **64** with 3,3'-bipyridine in a mixture of methanol, ethanol, and water at 100 °C afforded charged squares **65**[78] and **66**[79,80] (Equation 1-24). Interestingly, if the reaction was run at rt, only oligomers were observed. By raising the temperature, the thermodynamically favored squares formed, and were isolable after a few weeks.



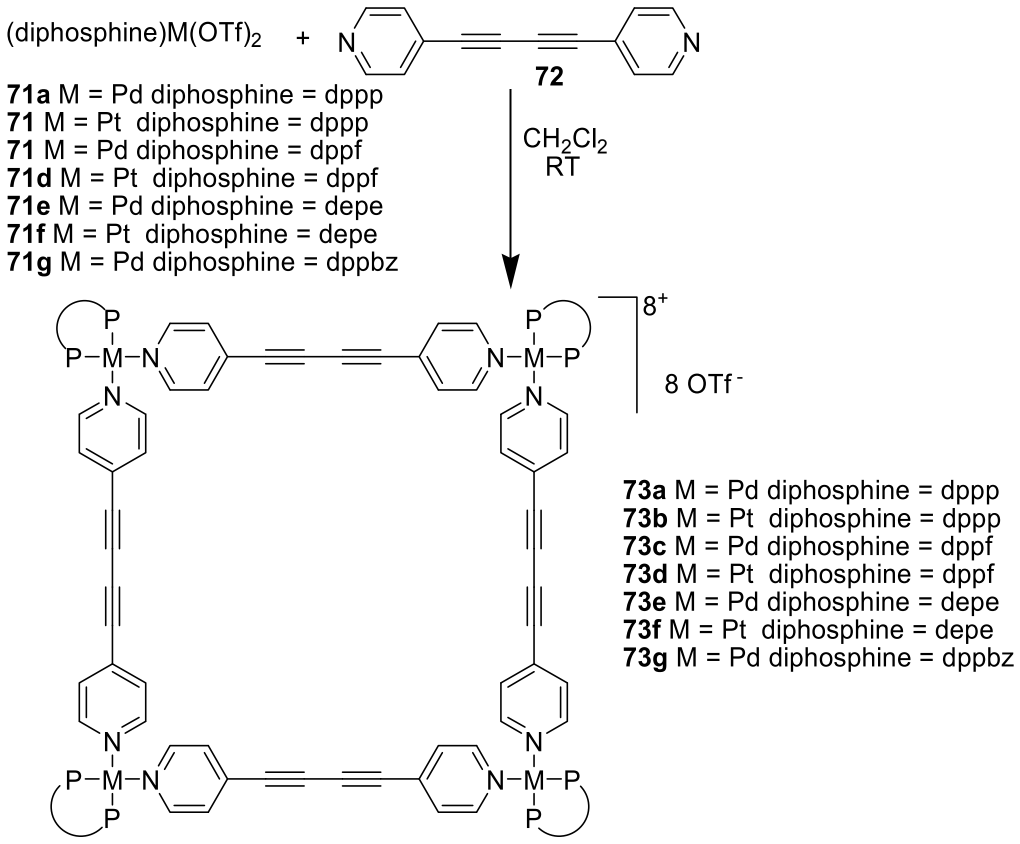
Equation 1-24

Stang *et al* were also interested in the potential applications of molecular squares. They designed the convergent self assembly of the squares shown in Scheme 1-7. [75,81,82,83] The iodide ligands in **67a-d** were converted to the triflate ligands in **68a-d**. The combination of **68a-d** with **69** in CH_2Cl_2 afforded the squares **70a-d** in 94%, 97%, 58% and 86% yields respectively.



Scheme 1-7 The synthesis of the heterocyclic macrocycles **70a-d**.

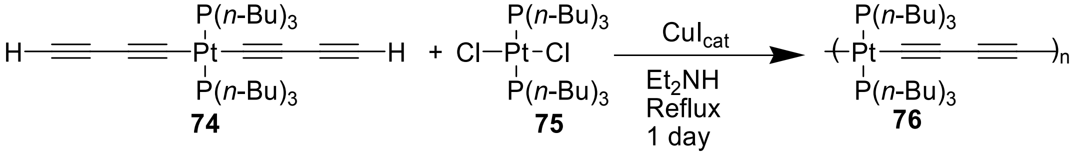
Rossell and coworkers followed a similar approach to Stang's work in the construction of their squares (Equation 1-25). [84] The combination of the (diphosphino)metal(bistriflate) **71a-g**, with **72** in methylene chloride at rt afforded the charged square complexes **73a-g**.



Equation 1-25

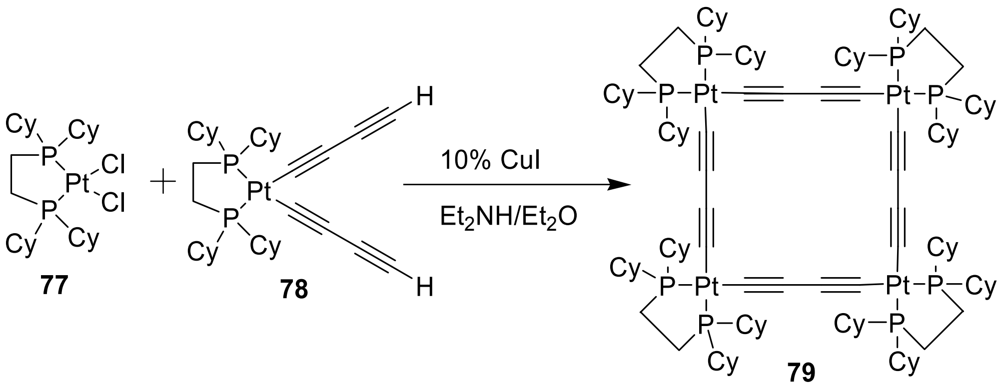
Because the molecular squares made by Fujita and Stang were charged, the presence of the counter anions blocked access to the square, and all attempts to reduce the charge to the neutral species resulted in decomposition of the square.[85] It was highly desirable to produce neutral molecular squares, and work on Pt acetylene polymers by

Hagihara, Takahashi, and Sonogashira paved the way. The synthesis of their polymers is shown in Equation 1-26.[86,87,88,89,90,91,92] The combination of **74** with **75** in diethyl amine under the catalysis of Cu(I) afforded the polymer **76** as a pale yellow polymer in 95% yield. In this experiment the amine not only acts as the solvent, but it also acts as a base to capture the acidic HI/HCl side products.

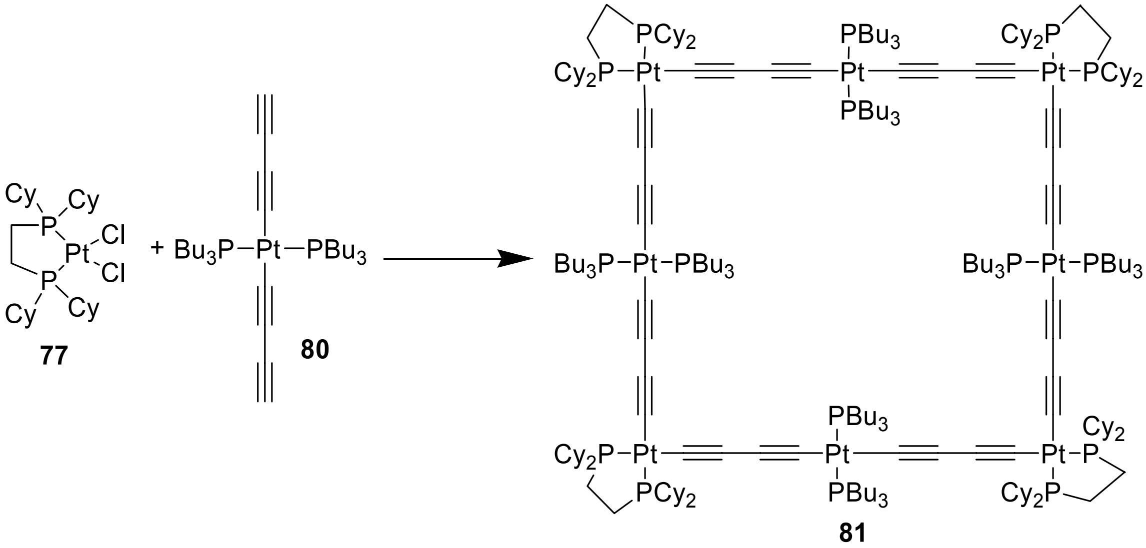


Equation 1-26

The first squares composed of Pt at the corners and butadiyne sections on the periphery were reported by Youngs *et al* (Equation 1-27).[93] Chelating phosphines on **77** and **78** were used in order to enforce the required cis geometry for the formation of the square. The condensation of **77** with **78** in Et_2NH/Et_2O in the presence of a catalytic amount of CuI at RT for five days afforded the square **79** in 98% yield as a yellow powder. In the same publication, the synthesis of the larger square **81** was reported (Equation 1-28). Cis and trans geometries at the Pt were required for the synthesis of **81**. Combination of **77** with **80** in Et_2NH in the presence of a catalytic amount of CuI at rt for 36 h afforded **81** as a yellow powder in 80% yield.

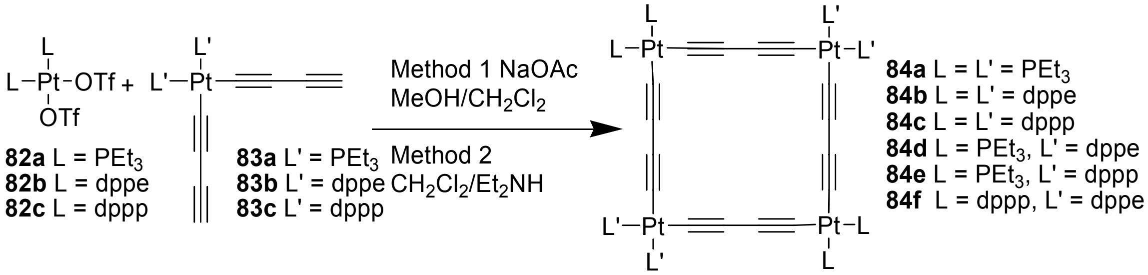


Equation 1-27



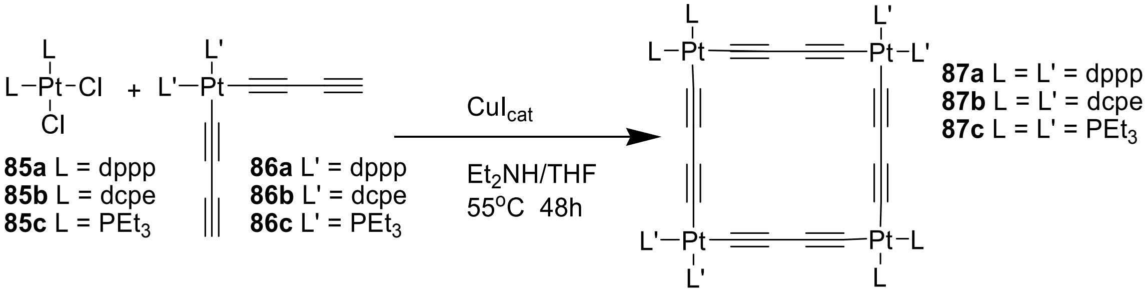
Equation 1-28

Bruce *et al* also published the synthesis of similar squares but via a different route (Equation 1-29).[94] They found that using the Cu(I) catalyzed route resulted in the formation of polymers rather than squares, while the combination of $L_2Pt(OTf)_2$ and the bis(butadiyde)platinum complexes resulted in rapid decomposition presumably due to the formation of triflic acid. Instead, they used the latter route but diluted the reactions and used weak bases such as NaOAc or Et_2NH. The different squares were synthesized via two different methods. Method one involved dissolving **82a-c** in CH_2Cl_2 followed by the addition of NaOAc in MeOH. To this was added **83a-c** in CH_2Cl_2 via syringe pump over 2 h. After workup, the squares **84a-c** were obtained as cream powders in 70%, 72%, and 73% yields respectively. Method two involved the addition of **83a-c** in CH_2Cl_2 via syringe pump over 2 h to a solution containing **82a-c** in CH_2Cl_2/Et_2NH. However, using this method always resulted in the ammonium salt Et_2NH_2OTf being associated with the squares. The salt could be removed by washing with a NaOAc solution. After workup, squares **84a-f** $\cdot$ **[Et$_2$NH$_2$][OTf]** were obtained as cream powders in 63%, 58%, 68%, 56%, 57%, and 60% yields respectively.



Equation 1-29

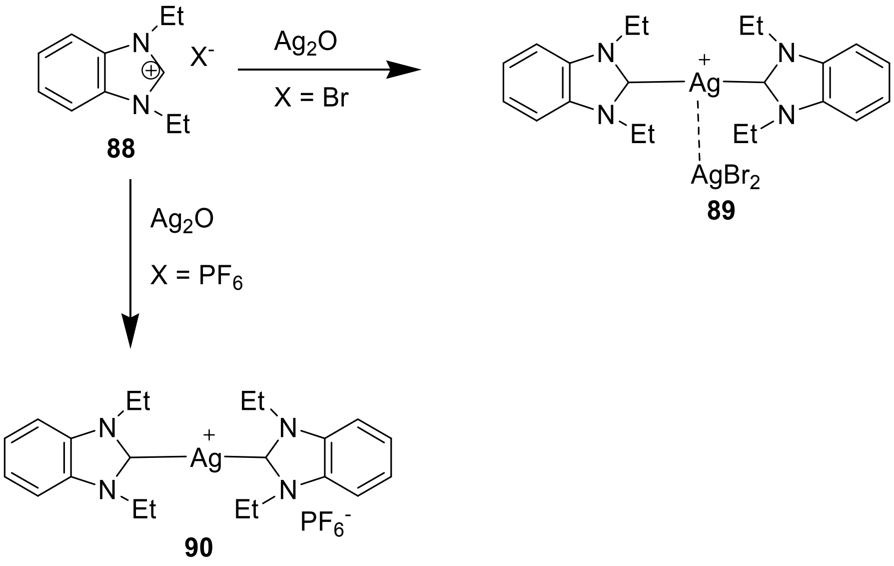
More recently, Anderson and co-workers published the synthesis of the squares **87a-c**[95] (Equation 1-30). Their squares were prepared in a manner similar to that of Youngs *et al.*[93] The combination of **85a-c** with **86a-c** in Et_2NH/THF in the presence of a catalytic amount of CuI at 55 °C for 48h afforded the squares **87a-c** in 78%, 86%, and 77% yields respectively. Unlike the squares made by Bruce *et al*[94] where the Pt atoms deviate from the mean plane by only 0.08Å, square **87a**, the only one that was successfully crystallized and characterized by x-ray diffraction, puckers into a wide V formation when looked at from a side-on view.



Equation 1-30

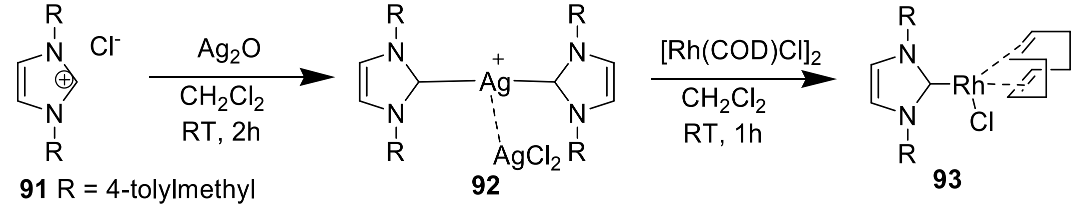
The Transfer of Carbenes From Ag to Rh.

The first example of a silver NHC complex made from Ag_2O was synthesized by Lin and co-workers (Equation 1-31).[96] In the first reaction, **88** was added to a stirring suspension of Ag_2O in CH_2Cl_2. After 2 h, the black precipitate gradually faded to give **89** as a white solid in 89% yield after workup. In the second reaction, Ag_2O and aqueous NaOH were added to a solution of **88** in CH_2Cl_2 with $[Bu_4N]PF_6$ present as a phase transfer catalyst. After stirring for four h, the solution became clear with a black precipitate. After filtering off the precipitate and workup, **90** was obtained as a white powder in 89% yield. This synthesis marked the beginning of the easy, air-stable synthesis of silver carbenes.



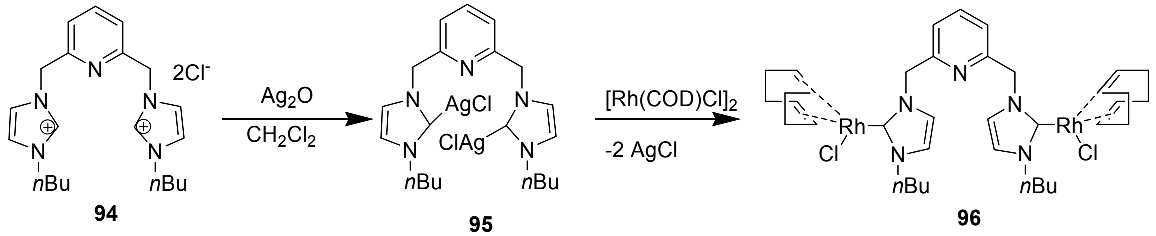
Equation 1-31

The first examples of carbene transfer from silver to rhodium were accomplished by both Crabtree and Youngs simultaneously. Crabtree *et al* utilized the following method to synthesis their NHC rhodium complex, **93** (Equation 1-32).[97] The imidazolium salt, **91**, and Ag_2O were stirred in CH_2Cl_2 for 2 h. After workup, **92** was obtained as colorless crystals in 95% yield. The combination of **92** and $[Rh(COD)Cl]_2$ in CH_2Cl_2 at rt for 1 h afforded **93** after workup as a yellow powder in 95% yield.



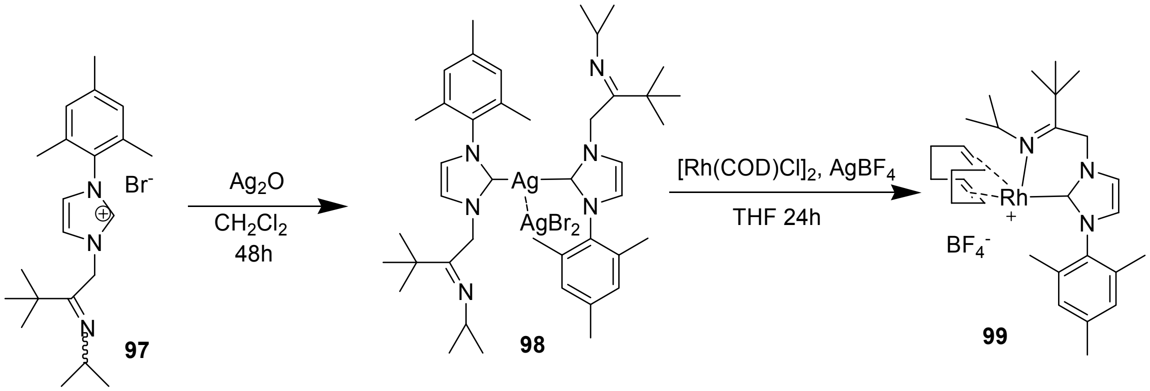
Equation 1-32

Youngs and co-workers used a different ligand, but virtually the same route (Equation 1-33).[98] A suspension of **94** and Ag_2O in CH_2Cl_2 was stirred at rt for 2 h. After workup, the silver complex **95** was isolated. It was reported to be stable in light and air up to its melting point. It was also pointed out that there was a lack of ^{107}Ag-carbene and ^{109}Ag-carbene coupling, which indicated that there was dynamic behavior in solution, therefore the silver complex should be useful as a carbene transfer agent. The theory was tested on rhodium. The carbene was transferred from **95** to rhodium under an atmosphere of nitrogen. The silver complex **95** and $[Rh(COD)Cl]_2$ were combined in a solution of MeCN. After stirring as rt for 1 h, and following organic workup, the rhodium complex, **96**, was obtained as a light yellow solid in 65% yield.



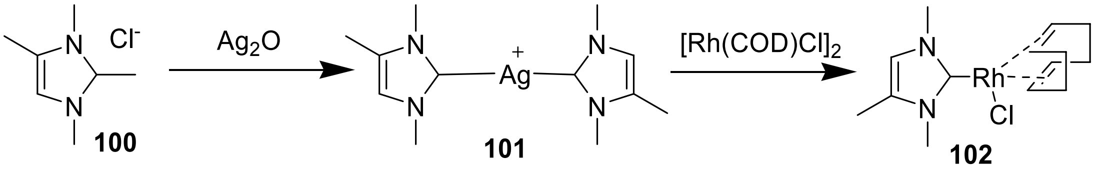
Equation 1-33

Coleman *et al* also demonstrated the transfer of a carbene from silver to rhodium (Equation 1-34).[99] After stirring **97** and Ag_2O in CH_2Cl_2 for 48 h, **98** was obtained as a pale brown solid in 77% yield. The combination of **98** with $[Rh(COD)Cl]_2$ and $AgBF_4$ in THF for 24 h afforded **99** as an orange solid in 45% yield.



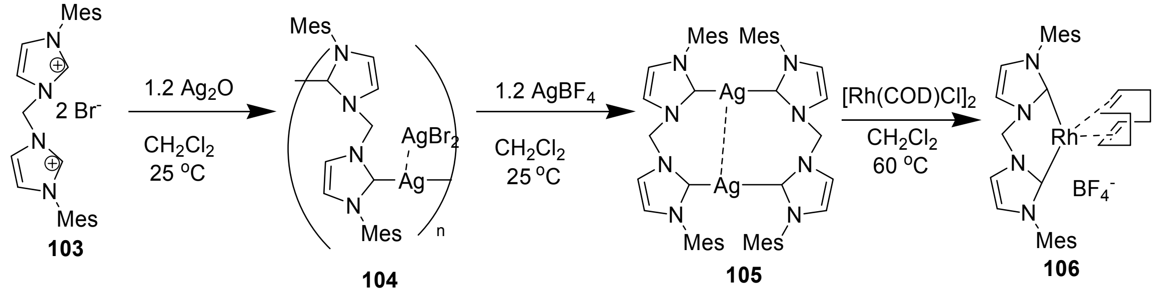
Equation 1-34

Crabtree and co-workers were studying the abnormal binding behavior of NHCs through the backbone at either C4 or C5 (Equation 1-35).[100] They wanted to make a rhodium NHC complex bound at C4(5) via transmetallation, so they decided to block the normal binding site, C2, with a methyl group to avoid competition reactions. However, they did not observe the expected product, but rather ended up with **102** in 25% yield, in which the carbene was bound at the normal C2 position.



Equation 1-35

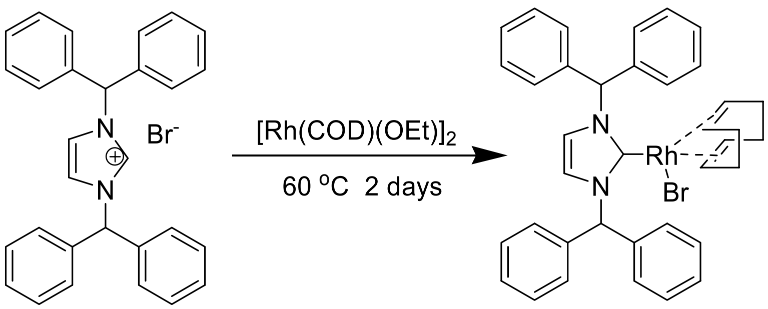
Wanniarachchi and co-workers performed a similar transmetallation reaction, but instead used a chelating NHC[101] (Equation 1-36). The combination of 1.2 equivalents of Ag_2O with **103** in CH_2Cl_2 at 25 °C resulted in the formation of an uncharacterizable brown amorphous solid, **104**, which turned out to be a mixture of oligomers. The addition of 1.2 equivalents of $AgBF_4$ in CH_2Cl_2 at 25 °C remedied the situation and produced **105** as colorless crystals. The transfer of the NHC from silver to rhodium took place in CH_2Cl_2 at 60 °C between **105** and $[Rh(COD)Cl]_2$ to yield **106** as orange crystals.



Equation 1-36

The Synthesis of N-heterocyclic Carbene Complexes of Rhodium

The synthesis of rhodium compounds not via transmetallation occurs almost exclusively with the use of $[Rh(COD)Cl]_2$. Herrmann and co-workers demonstrated the first synthesis of a rhodium NHC directly from $[Rh(COD)Cl]_2$ (Equation 1-37). [102] The $[Rh(COD)Cl]_2$ was suspended in ethanol while four equivalents of sodium acetate were added to form $[Rh(COD)(OEt)]_2$, which is thought to be only an intermediate and is observed by a color change from orange to bright yellow in five minutes. Next, four equivalents of **107** were added to the solution, and it was stirred at 60 °C for two days. After workup, **108** was isolated in 94% yield.

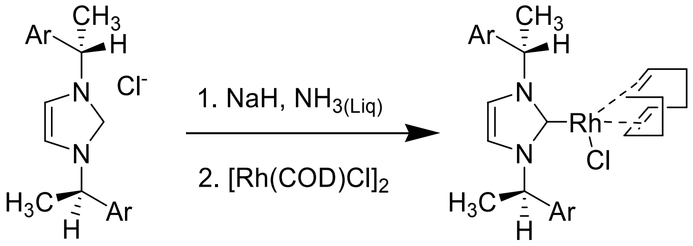


107

108

Equation 1-37

In another paper, Herrmann and co-workers were interested in using a chiral rhodium NHC complex for asymmetric catalysis (Equation 1-38).[103] The deprotonation of **109a** or **109b** took place in a mixture of THF and liquid ammonia with NaH. After stirring for 1 h, a slightly yellow solution was obtained. After removing the NH_3, the volume of the THF was increased to 40 ml and decanted from a precipitate. The free carbene was not isolated, but used without further purification. This solution was added to a solution of $[Rh(COD)Cl]_2$ in THF and stirred at rt for 35 minutes. After workup, **110a** and **110b** were obtained as yellow crystals. They found that **110a** and **110b** were active as catalysts for hydrosilylation reactions without an induction period and even at low temperature. They also concluded that the Rh-carbene bond is strong as no dissociation was observed even after two weeks of reaction time.[104]

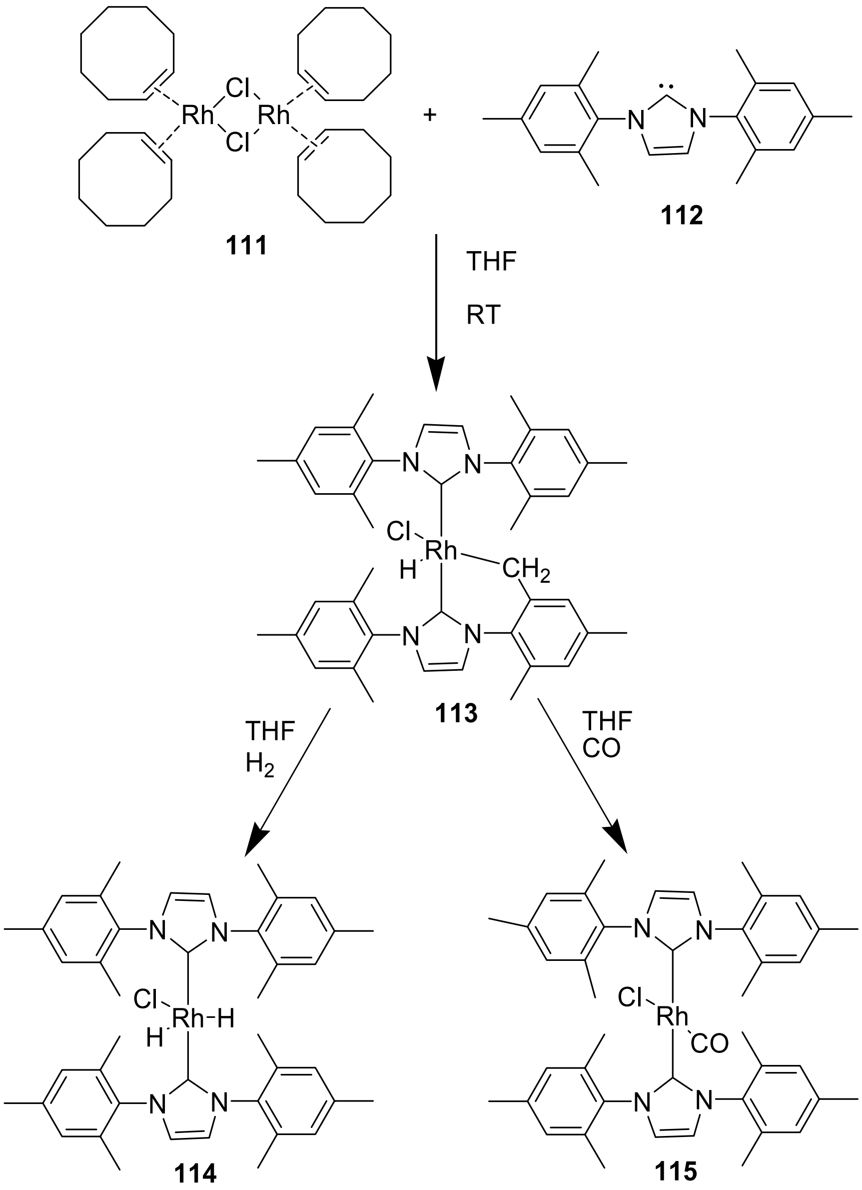


109a R = Ph
109b R = naphthyl

110a R = Ph
110b R = naphthyl

Equation 1-37

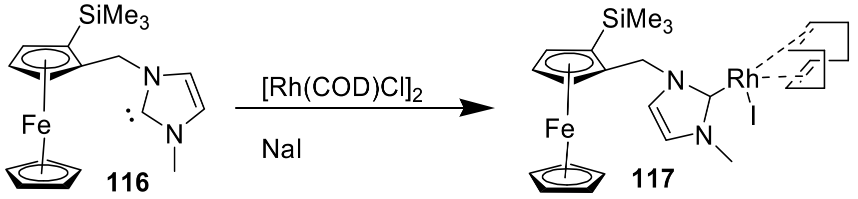
Nolan *et al* synthesized the rhodium complex **113** directly from the free carbene **112** (Scheme 1-8).[105] The combination of **111** with IMes, **112**, in THF at rt for 60 minutes afforded **113** after workup as a yellow powder in 82% yield. Treatment of a solution of **113** in THF with H_2 for 60 minutes afforded **114** as a light yellow powder in 93% yield. Alternatively, treatment of a solution of **113** in THF with CO for 60 minutes afforded **115** as a white powder in 86% yield.



Scheme 1-8 The synthesis of **113**, **114**, and **115**.

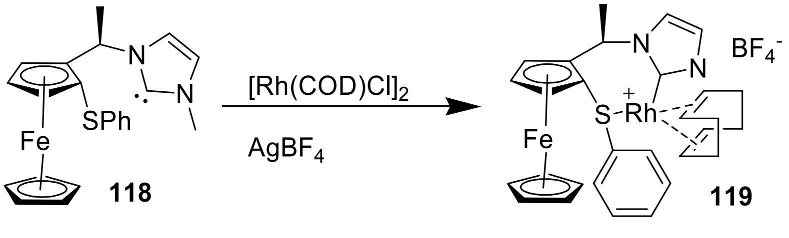
Bohm *et al* were also interested in asymmetric catalysis. They synthesized the first planar planar chiral Rh NHC, **117**, complex for this purpose (Equation 1-38).[106] To a solution of the free carbene **116** in THF was added a solution of [Rh(COD)Cl]$_2$ and NaI in THF. After stirring at RT for 24 h and workup, diastereomers of **117** were obtained.

The major diastereomer was extracted and crystallized with hexane/methyl-*t*-butylether to yield **117** as yellow crystals in 62% yield. Preliminary studies indicated that **117** was a good candidate for use as a hydrosilylation catalyst.



Equation 1-38

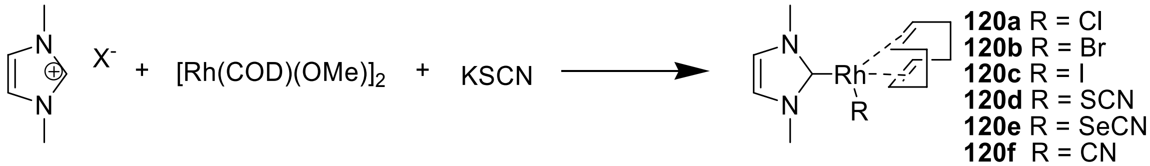
Chung and co-workers synthesized a Rh NHC complex containing ferrocene as well and tested it for its catalytic activity (Equation 1-39) [107]. The combination of **118**, $AgBF_4$, and $[Rh(COD)Cl]_2$ in CH_2Cl_2 afforded **119** in 34% yield after workup. The catalytic activity of **119** was tested in the hydrogenation of dimethyl itaconate at 50 °C under 10 atm of H_2. Disappointingly, **119** gave only a 44% yield with 18% ee after 12 h.



Equation 1-39

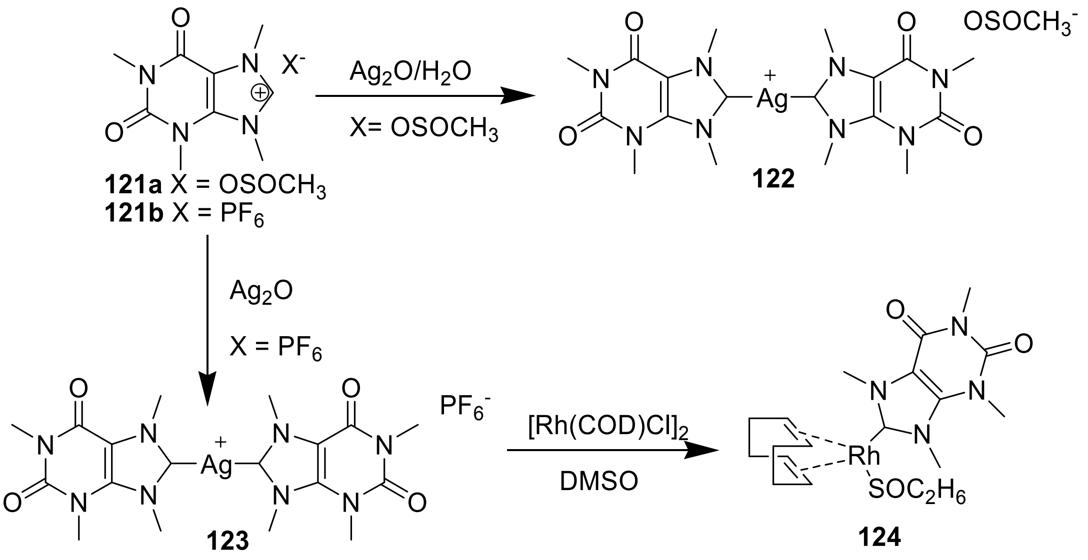
Baker and co-workers were interested in synthesizing pseudo-halo Rh NHC complexes.[108] A sample reaction is shown in Equation 1-40. The condensation of 1,3-dimethyl-2-ylidene *p*-toluene sulfonate with $[Rh(COD)(OMe)]_2$ and LiCl in CH_2Cl_2 and

MeCN afforded **120a** as a yellow solid in 63% yield after stirring for 12 h at RT. The combination of 1,3-dimethyl-2-ylidene bromide with [Rh(COD)(OMe)]$_2$ in CH_2Cl_2 at RT for 2 h afforded **120b** as a yellow solid in 95% yield. The synthesis of **120c** was analogous to that of **120b**, except 1,3-dimethyl-2-ylidene iodide was used instead. Complex **120c** was obtained as a yellow powder in 95% yield. The combination of 1,3-dimethyl-2-ylidene hexafluorophosphate with [Rh(COD)(OMe)]$_2$ and KCSN in CH_2Cl_2/MeCN after stirring for 18 h afforded **120d** as a yellow solid in 89% yield. The synthesis of **120e** was analogous to that of **120d**, except that KSeCN was used. **120e** was obtained as an orange solid in 60% yield. The combination of 1,3-dimethyl-2-ylidene hexafluorophosphate with [Rh(COD)(OMe)]$_2$ and KCN in MeCN for 14 h afforded **120f** as a yellow solid in 73% yield.



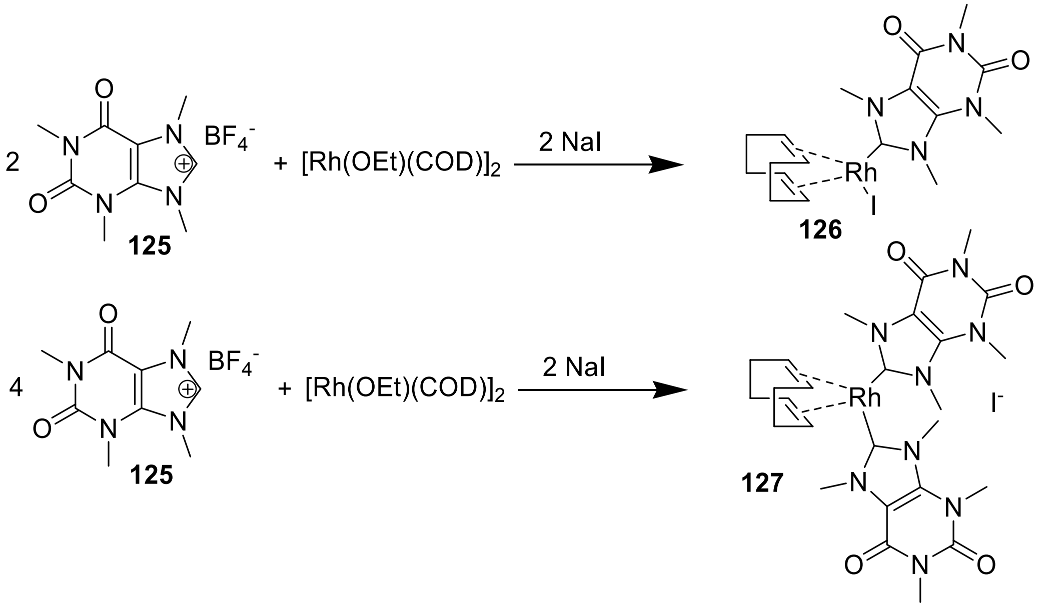
Equation 1-40

The first example of the transfer of methylated caffeine from Ag to Rh was reported by Youngs and co-workers (Scheme 1-9).[109] The combination of methylated caffeine methyl sulfate with Ag_2O in H_2O afforded the Ag NHC complex **122**. Complex **122** was reported to be stable in light and water for 5 days. Alternatively, the combination of methylated caffeine hexafluorophosphate with Ag_2O in DMSO yielded **123**, which is stable in DMSO and light for months. The addition of $[Rh(COD)Cl]_2$ to a solution of **123** in DMSO afforded the Rh complex **124**, which is stable in air up to its melting point.



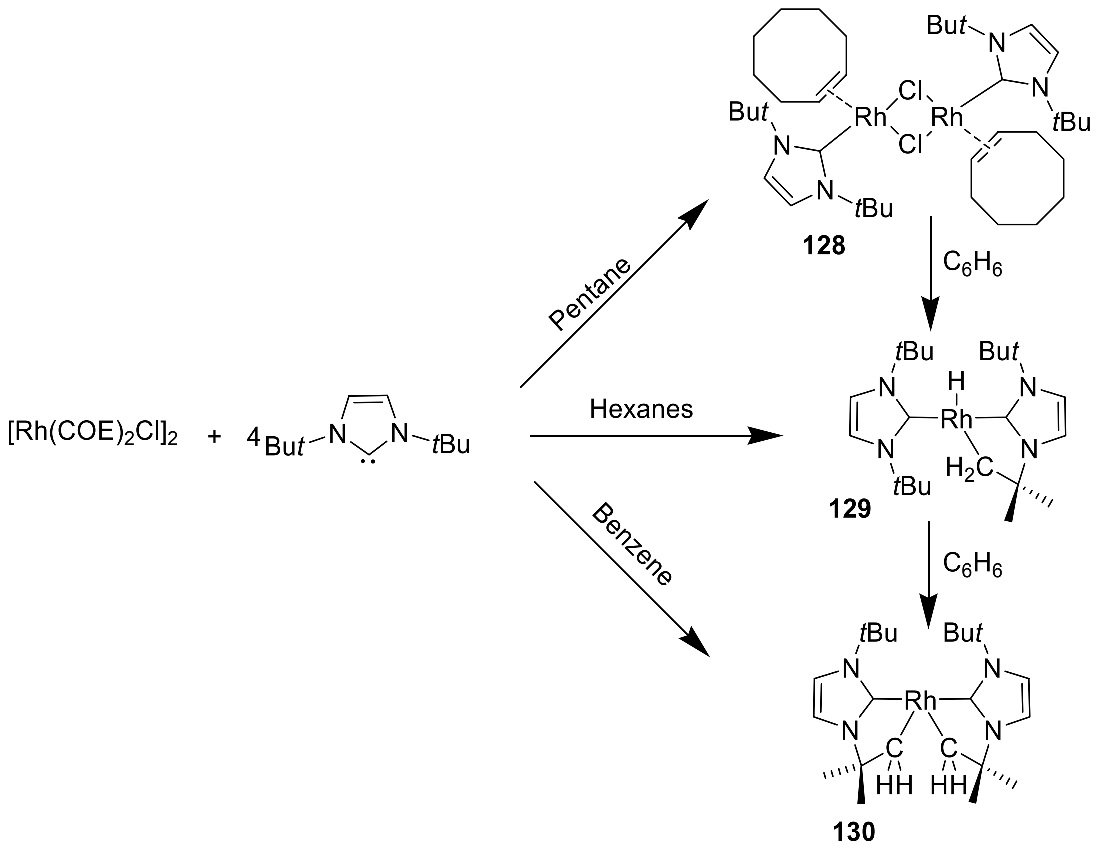
Scheme 1-9 The first synthesis of Ag and Rh complexes of methylated caffeine.

Shortly after the publication on methylated caffeine complexes of Ag and Rh[109] was released, Herrmann *et al* also published their work with methylated caffeine (Equation 1-41).[110] NaH in EtOH was added to a suspension of $[Rh(COD)Cl]_2$. After 30 minutes, methylated caffeine and NaI were added and the solution was stirred for 24 h for the formation of **126** in 88% yield and for 48 h for the formation of **127** in 93% yield.



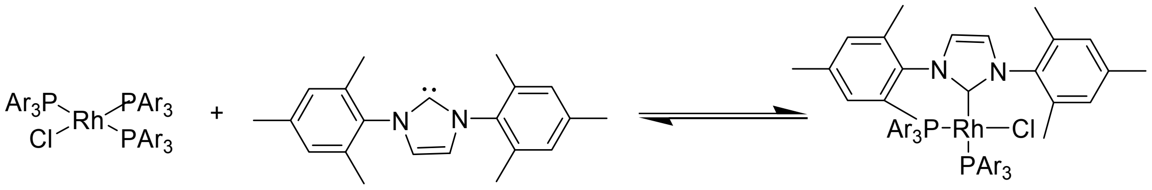
Equation 1-41

Nolan *et al* demonstrated that the synthesis of their rhodium NHC was solvent dependent (Scheme 1-10).[111] If the reaction was conducted in pentane, after 30 minutes of stirring, a yellow precipitate was observed. After workup, it was characterized as **128**. If the reaction was conducted in hexanes however, **129** was formed. Complex **129** contains an agostic hydride, and is the immediate precursor to **130**. Alternatively, running the reaction in benzene yielded the final product, **130**. Complex **130** was the result of C-H bond activation by Rh(III), which is uncommon. This publication marks the first time that two immediate precursors to a C-H activated product have all been characterized by x-ray crystallography.



Scheme 1-10 The synthesis of **128**, **129**, and **130**.

Crudden *et al* demonstrated the irreversible Rh-carbene bond cleavage, proving that the Rh-carbene bond is not inert to further reaction (Equation 1-42). [112] In a typical experiment, **131a** or **131b** and **112** were dissolved in deoxygenated toluene. The solution was stirred for 16 h, and, following workup, **132a** or **132b** was obtained in 87% and 78% yield respectively. Though the Rh-carbene bond is thought to be strong, heating **132a** or **132b** in halogenated solvents to 60 ^{0}C in the presence of excess phosphine caused the carbene to be displaced by phosphine, reversing the reaction. The displacement also takes place in aromatic solvents at 80 °C , though at a much slower rate with a $t_{1/2}$ of three weeks.



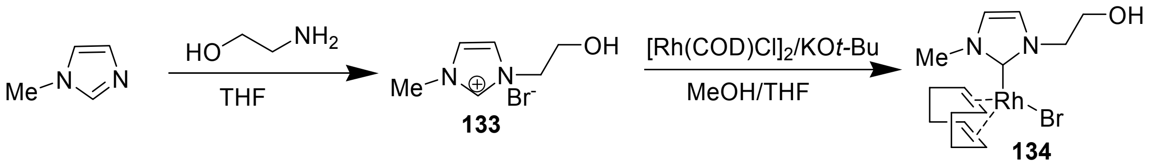
131a Ar = Ph
131b Ar = *p*-tolyl

112

132a Ar = Ph
132b Ar = *p*-tolyl

Equation 1-42

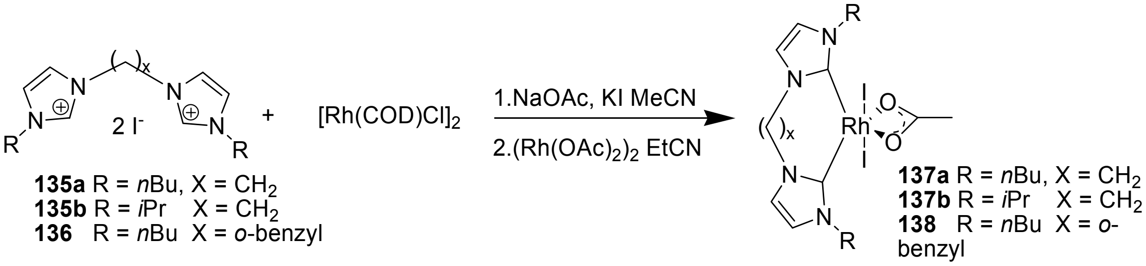
Weberskirch and co-workers were interested in immobilizing a Rh NHC catalyst on a polymer surface.[113] For this, they needed an NHC with a pendant hydroxyl group. The synthesis of **134** is illustrated in Equation 1-43. The synthesis of the asymmetric imidazolium salt **133** took place in THF at reflux overnight. Subsequent workup afforded **133** in 74% yield. The Rh complex **134** was then made by combining **133** with $[Rh(COD)Cl]_2$ in MeOH/THF in the presence of potassium *tert*-butoxide as previously described.[23]



Equation 1-43

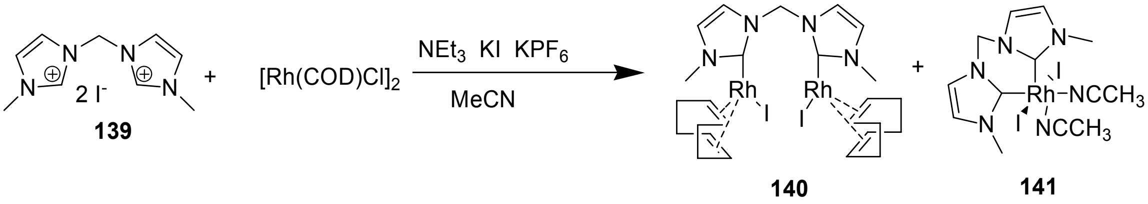
Crabtree *et al* are the major contributors in the synthesis of bis(imidazolium), bis NHC, rhodium complexes. They first published the synthesis of **137a,b** and **138** in 2002

(Equation 1-44).[114] The syntheses were accomplished in two ways. The first method involved refluxing **135a,b** or **136** and $[Rh(COD)Cl]_2$ in acetonitrile in the presence of sodium acetate and potassium iodide for 16 h to yield **137a,b** or **138** in 46-78% yield. The second method utilized $(Rh(OAc)_2)_2$ with **136a,b** or **137** in refluxing propionitrile for 10 h to give **137a,b** or **138** in approximately 50% yield. In all cases, the bis NHC Rh complexes had to be purified by column chromatography.



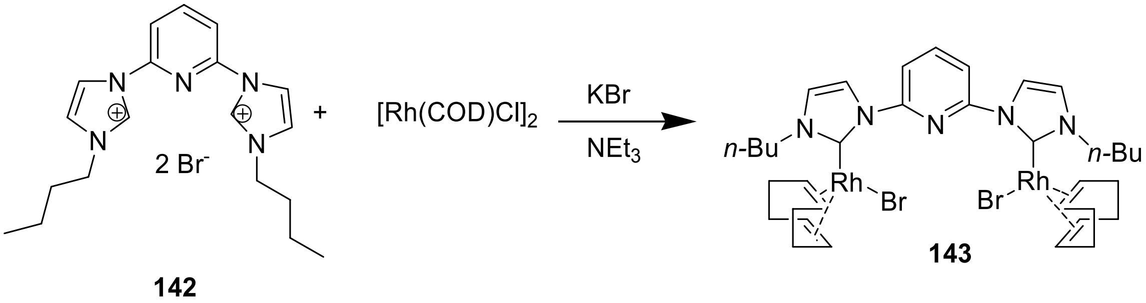
Equation 1-44

Peris *et al* slightly changed the reaction conditions to include triethylamine in place of sodium acetate to give the dirhodium complex **140** and the bis NHC Rh complex **141**.[115] The ratio of **140** to **141** depends on the exact reaction conditions used. Running the reaction in air without degassing the acetonitrile at 40 ^{o}C for 1 h afforded **140** in greater than 80% yield. If the same reaction was run at RT for 1 h, both **140** (30%) and **141** (61%) were formed. If the reaction was performed anaerobically, only **140** was obtained, proving that oxygen was required for the oxidation of Rh(I) to Rh(III).



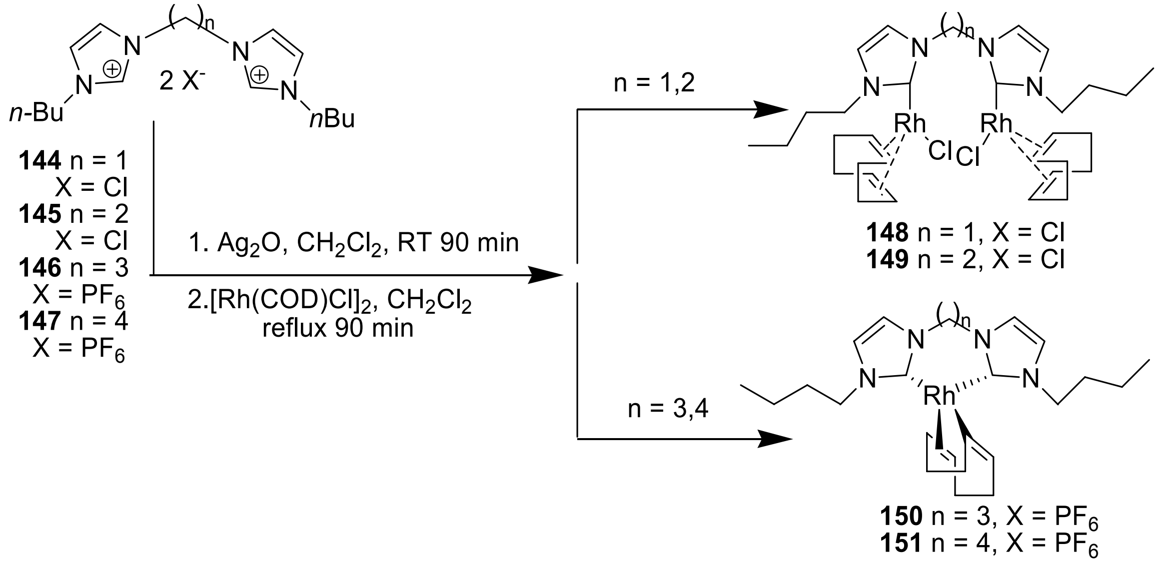
Equation 1-45

Peris *et al* were interested in using the bis NHC Rh complexes for catalysis.[116,117] The synthesis of **143** is outlined in Equation 1-46. The condensation of **142** with $[Rh(COD)Cl]_2$ and KBr in triethylamine afforded the dirhodium NHC complex **143** in 72% yield after workup. Indeed **143** proved to be a good catalyst for the hydroformylation of styrene in particular. Quantitative yields were observed for low catalyst loading at 80 °C and 80 bar. Increased amounts of catalyst were needed to achieve quantitative conversion at 40 °C.



Equation 1-46

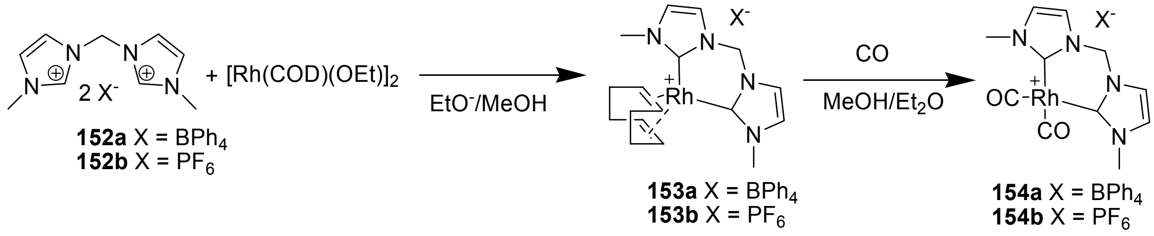
Crabtree and co-workers discovered that the length of the linker between the two NHC units played a big difference in the reaction chemistry. Complexes **148-150** were synthesized in a 2-step reaction via transmetallation (Scheme 1-11).[118] The first step involved the synthesis of the NHC silver complexes by stirring **144-147** with Ag_2O in CH_2Cl_2 at rt for 90 minutes. After filtering off any unreacted Ag_2O and other solids, the filtrate containing the Ag complexes was used for the next step without further purification. $[Rh(COD)Cl]_2$ was added to the filtrate containing the Ag complexes, and the solution was stirred at reflux for 90 minutes. After workup, **148-151** were obtained in 5%, 66%, 70%, and 30% yields, respectively.



Scheme 1-11 The synthesis of **148-151**.

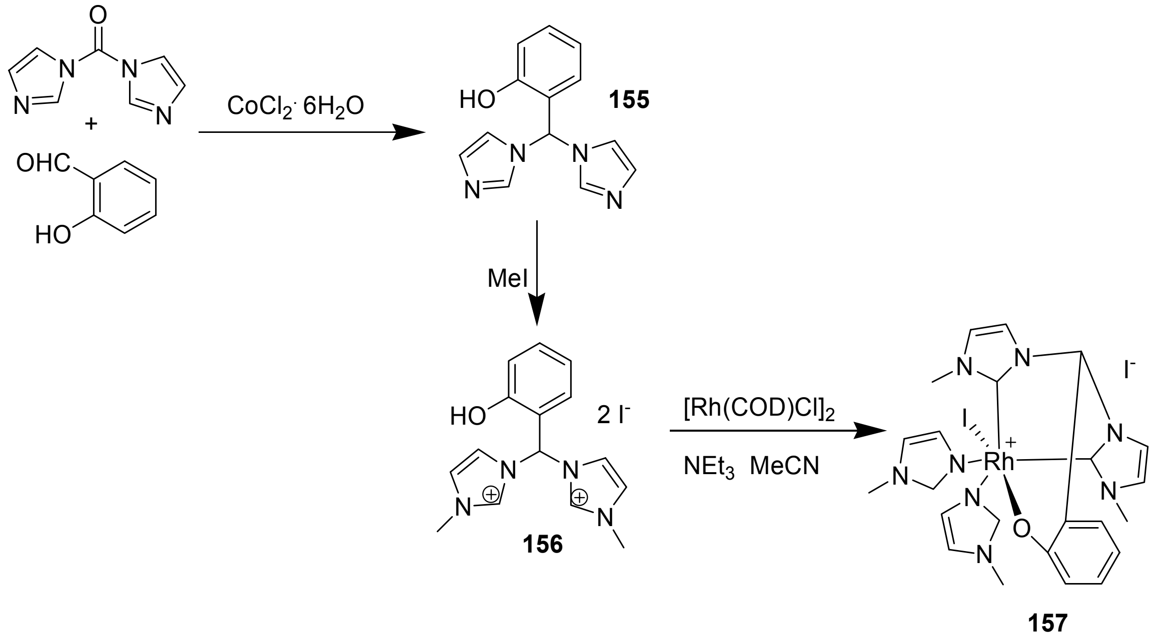
Field *et al* (Equation 1-47)[119] synthesized the bis NHC Rh complexes **153a,b** utilizing a variation of the method introduced by Herrmann *et al.*[102] The bis NHC, **152a** or **152b**, was combined with $[Rh(COD)(OEt]_2$ and sodium ethoxide in methanol at reflux for 15 minutes to yield **153a** as an orange solid in 63% yield or for 3 days to yield **153b** as an orange-red crystalline solid in 67% yield. Passing CO gas through a suspension of

153a or **153b** in methanol and diethylether overnight yielded **154a** as a yellow solid in 88% yield or for three days yielded **154b** as a yellow solid in 46% yield.



Equation 1-47

Peris *et al* also did some work with the tripodal ligand **156** to form the NHC rhodium complex **157** (Scheme 1-12).[120,121] The NHC ligand **156** was synthesized via a reaction between salicylaldehyde and bis(imidazolyl)ketone at 80 °C using $CoCl_2\cdot 6H_2O$ as a catalyst. Reaction with MeI in refluxing methanol overnight afforded **156** as a light yellow solid in 74% yield. Complex **156** was combined with $[Rh(COD)Cl]_2$ and triethylamine in acetonitrile overnight. After workup, **157** was obtained as an orange-yellow powder in 30% yield.



Scheme 1-12 The synthesis of **157.**

CHAPTER II

THE SYNTHESIS OF THE OCTACARBENE TETRAPLATINUM HETEROCYCLYNE

Introduction

There exists much interest in the synthesis and study of macrocycles.[122,123] The synthesis of macrocyclic cyclynes[124] and more recently heterocyclynes[93] has been of great interest to our research group for some time. We are interested in the applications that have been discussed.[125,126,127] The previous squares employed chelating phosphines on the Pt atoms to enforce the required cis geometry needed for the synthesis of the squares.[93] While phosphines are superb ligands for many different metals, they do have their drawbacks. Most phosphines are toxic and have a foul odor, and most are also oxygen-sensitive making them more difficult with which to work. A while before our research group began working with N-heterocyclic carbenes (NHC) Herrmann declared that NHCs were a great substitute for phosphines.[6] At that time, there were no examples of chelating N-heterocyclic carbene (bis NHC) complexes of Pt, so we decided to synthesize a macrocyclic square with butadiyne edges and Pt atoms at the corners held in a *cis* position by bis NHCs.

All previous bis NHC Pt complexes were synthesized via carbene transfer to Pt,[46,47] via the free carbene,[128] or *in situ* in non-aqueous ionic liquids.[51,129] Where the Pd systems were easily synthesized using Pd(II) acetate,[130,131,132,133] the corresponding Pt complexes were unattainable via an analogous route using Pt(II) acetate. Many attempts to synthesize the NHC Pt complex were attempted (Scheme 2-2) before the final route was discovered.

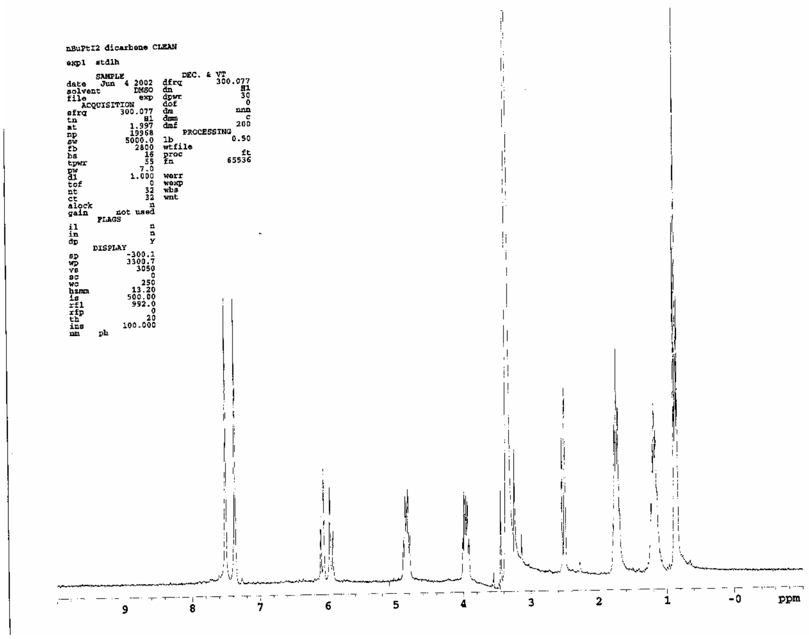
The Synthesis and Characterization of the Bis NHC Pt Complexes

The synthesis of the Pt(II) complexes **2** and **3** is illustrated in Scheme 2-3. The condensation of *n*-butyl imidazole and diiodomethane in THF afforded **1a** as a fine white powder in 83% yield (Scheme 2-1). **1a** was characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, and elemental analysis. The ESI mass spectrum of a DMSO solution of **1a** gave a M$^+$ for $^{12}C_{15}H_{26}I_2N_4$ of 642.9 (calculated 642.91). Deprotonation of **1a** with sodium acetate in DMSO at 90 ^oC in the presence of $PtCl_2$ produced complexes **2** and **3** in 50% and 16% yields respectively. Even when a precise ratio of **1a** to $PtCl_2$ was used, a small amount of the tetracarbene complex, **3**, was produced. A 2:1 reaction resulted in approximately a 50:50 mixture of the two products. Complexes **2** and **3** were characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of a combination of **2** and **3** gave a M$^+$ for $^{12}C_{15}H_{24}IN_4{}^{195}Pt$ of 582.2 (calculated 582.6) and a M$^+$ for $^{12}C_{30}H_{48}IN_8{}^{195}Pt$ of 843.3 (calculated 843.2).

The choice of DMSO as the solvent proved to be problematic. Mass spectrometric analysis revealed the presence of (DMSO)PtI_2 in the sample. This is believed to be the reason for the low yields observed. By diluting the reaction mixture, the synthesis of **3** can be avoided, thereby increasing the yield of **2** to 69.2%. Other solvents were screened, and acetonitrile seemed to be the next best solvent, though, even in dilute reactions, it affords a greater percentage **3**.

The complexes **2** and **3** can be readily separated with acetonitrile. Whereas **3** is very soluble in acetonitrile, **2** is only slightly soluble. Surprisingly, both **2** and **3** were cocrystallized from a solution in acetonitrile. Crystals of **2** alone were obtained by slow evaporation from a concentrated solution in chloroform. Crystals of **3** alone have not been obtained.

The ^{1}H and ^{13}C NMR spectra are in agreement with the solid state structure for **2** and **3** (shown in Figures 2-5 and 2-6). In the ^{1}H and ^{13}C NMR spectra for **1a**, the most notable resonances are the carbonium proton occurring as a singlet at 9.46 ppm (137.40 ppm in the ^{13}C NMR spectrum) and the methylene linker between the imidazolium units occurring as a singlet at 6.63 ppm. In contrast to the ^{1}H NMR spectrum of **1a**, the two protons on the methylene linker are inequivalent and appear as two doublets at 6.05 ppm ($J_{\text{H-H}}$ = 13 Hz) for **2** (Figure 2-1) and at 6.34 ppm ($J_{\text{H-H}}$ = 13 Hz) for **3**. The inequivalency of the protons can be explained by hindered rotation about the methylene linker due to the presence of the Pt. Also the protons of the butyl chain closest to the nitrogen are split into two multiplets. This occurs because the ligand is twisted relative to the Pt and, therefore, the two protons on that particular carbon are no longer equivalent on the NMR time scale. The absence of a resonance at ca. 9 ppm (137 ppm in the the ^{13}C NMR spectrum) is diagnostic for the loss of the carbonium proton. The appearance of a resonance at 149.61 ppm in the the ^{13}C NMR spectrum confirmed the presence of a Pt-carbene bond.



```
nBuPtI2 dicarbene CLEAN

exp1  stdlh

       SAMPLE              DEC. & VT
date    Jun  4 2002  dfrq          300.077
solvent        DMSO  dn                 H1
file            exp  dpwr               30
    ACQUISITION      dof                 0
sfrq        300.077  dm                nnn
tn               H1  dmm                 c
at            1.997  dmf               200
np            19968        PROCESSING
sw           5000.0  lb               0.50
fb             2800  wtfile
bs               16  proc               ft
tpwr             55  fn              65536
pw              7.0
d1            1.000  werr
tof               0  wexp
nt               32  wbs
ct               32  wnt
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp           -300.1
wp           3300.7
vs             3050
sc                0
wc              250
hzmm          13.20
is           500.00
rfl           992.0
rfp               0
th               20
ins         100.000
nm     ph
```

Figure 2-1 The ^{1}H NMR spectrum of **2** in *d*-DMSO

Compound **2** is neutral with two coordinating iodides balancing the charge of the metal. In this complex, Pt(1) is square planar with both the iodide ligands in a *cis* conformation. The C(7)-Pt(1)-I(1) and C(11)-Pt(1)-I(2) bond angles are 174.7(1) and 171.9(1), respectively. The Pt(1)-C(7) and Pt(1)-C(11) carbene distances are 1.983(3) and 1.991(3) Å, which compare well with previously reported Pt-carbene distances.[47,48]

The C(7)-Pt(1)-C(11) bond angle of 84.2(1)^{o} deviates from idealized angles, presumably due to the restraint imposed by the chelating nature of the ligand. The Pt(1)-I(1) and Pt(1)-I(2) distances are 2.6563(3) and 2.6441(3) Å, respectively. The C(22)-Pt(2)-C(27) bond angle is 84.0(1)^{o}, which corresponds well with that of **2**. The alkyl chains of the respective ligands point away from one another in order to minimize the steric interactions.

Because of the problems associated with the formation of the tetracarbene platinum complex, **3**, it was necessary to synthesize **4** in order to proceed with the crucial reactions to form the square. It was essential to use the chloride anion on the ligand, **1b**, in order to avoid halogen scrambling as seen in the previous example. For the synthesis of **1b**, **1a** was dissolved in H_2O and two equivalents of silver nitrate were added along with 2.1 equivalents of saturated brine solution. The bright yellow precipitate that formed was filtered over Celite®, and the volatile compounds were removed *in vacuo*. The synthesis of **4** is outlined in Scheme 2-4. The condensation of **1b**, $PtCl_2$, and two molar equivalents of sodium acetate in DMSO at 90 ^{o}C for 2 h afforded **4** as a white powder in 72% yield after workup. No evidence of a tetracarbene species was observed in this reaction, as had been seen previously observed with the iodide anion. Complex **4** was characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, elemental analysis, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **4** gave a M$^+$ for $^{12}C_{15}H_{24}N_4{}^{95}PtCl_2$ of 491.1 (calculated 489.1).

Notable features in the ^{1}H NMR spectrum for **4** include the absence of a resonance at ca. 9 ppm, suggesting a loss of the carbonium proton. In this complex as well, the presence of the Pt causes the hindered rotation of the two protons on the methylene linker resulting in the appearance of two doublets at 5.96 ppm (J_{H-H} = 13.0 Hz) and at 6.08 ppm (J_{H-H} = 13.1 Hz). Also, the ligand is twisted into a conformation that results in the hindered rotation of the two protons on the carbon atom of the butyl chain closest to the nitrogen atom resulting in the appearance of two multiplets at 3.97 and 4.85 ppm. These features are a common thread in all of the Pt complexes synthesized. In the ^{13}C NMR spectrum, the resonance for the Pt-carbene bond appears at 143.13 ppm.

Crystals of **4**, suitable for crystallographic study, were grown from a concentrated solution of **4** in acetonitrile. The structure of **4** is depicted in Figure 2-7. The platinum atom is bound by two chlorines and two N-heterocyclic carbenes in a square planar fashion. The Pt-carbene bond distances are 1.930(11) and 1.930(8) Å for Pt(1)-C(5) and Pt(1)-C(9), respectively. The bond angle between the bidentate N-heterocyclic carbene rings and the platinum atom (C(5)-Pt(1)-C(9)) is 87.3(4)°. The Pt(1)-Cl(1) and Pt(1)-Cl(2) bond distance is 2.362(3) and 2.370(2) Å, respectively. The Cl(1)-Pt-(Cl(2) bond angle is 87.49(8)°.

The synthesis of **5** is outlined in Scheme 2-4. Under anaerobic conditions, the combination of **4** with lithium acetylide TMEDA complex in THF at rt for 24 h afforded **5** as a fine light tan powder in 86% yield. The synthesis of a tetra platinum square with this complex was attempted, but did not succeed likely due to the strong Pt-C-H interaction with the terminal protons of the acetylides, as can be seen in the very strong Pt-C coupling in the ^{13}C NMR spectrum causing that terminal proton to be less acidic, or simply due to sterics. Complex **5** was characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, elemental analysis, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **5** gave a M$^+$ for $^{12}C_{15}H_{26}N_4{}^{195}Pt$ of 453.2 (calculated 452.2).

Notable features in the ^{1}H NMR spectrum of **5** include the same characteristic resonances as described for **4** as well as the appearance of a singlet at 1.92 ppm with $J_{\text{Pt-H}}$ = 23 Hz for the terminal proton on the acetylide. In the ^{13}C NMR spectrum (Figure 2-2), the C_α has a resonance at 99.99 ppm ($J_{\text{Pt-C}}$ = 1013.2 Hz), and the C_β appears at 93.52 ppm ($J_{\text{Pt-C}}$ = 297.6 Hz). Pt coupling to the carbene carbon is observed at 166.76 ($J_{\text{Pt-C}}$ = 898.7 Hz).

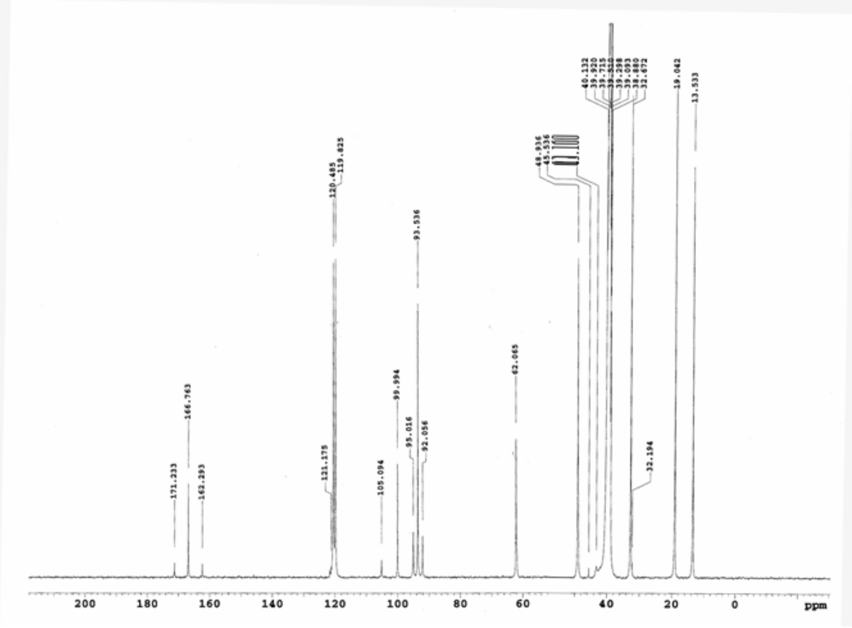


Figure 2-2 The ^{13}C NMR spectrum of **5** in *d*-DMSO

Crystals of **5** were grown from a concentrated solution of acetonitrile. These crystals were suitable for x-ray crystallographic study and the structure of **5** is depicted in Fig. 2-8. The platinum is square planar and bound by two N-heterocyclic carbenes and two acetylides. Pt-carbene distances are 2.013(9) and 2.037(9) Å for Pt-C(5) and Pt-

C(9), respectively. The bond angle between the NHC rings and the platinum atom (C(5)-Pt-C(9)) is 84.9(3)°. The Pt-acetylide distances are 2.022(9) (Pt-C(16)) and 2.013(10) Å (Pt-C(18)) with a bond angle between the acetylides (C(16)-Pt-C(18)) of 88.7(3)°.

The synthesis of **6** is outlined in Scheme 2-4. It is first necessary to prepare trimethylsilylbutadiyde·Li TMEDA by adding dropwise MeLi to a solution containing bis(trimethylsilyl)butadiyde and one molar equivalent of TMEDA in THF. After filtration, the trimethylsilylbutadiyde·Li TMEDA complex is contained in the filtrate. No further steps are required to isolate this product. The filtrate is taken into the dry box, and 0.5 molar equivalent of **4** is added to the solution. After stirring for 18 h at rt, the clear yellow solution is evaporated, and the residue is washed with water yielding **6** as a tan powder in 95.2% yield. Complex **6** was characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, elemental analysis, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **6** gave a M$^+$ for $^{12}C_{29}H_{42}N_4{}^{95}PtSi_2$ of 720.4 (calculated 719.1).

Notable features in the ^{1}H NMR spectrum of **6** include all of the characteristics described for **4** as well as a strong singlet at 0.12 ppm for the methyl groups on Si. In the ^{13}C NMR spectrum, the methyl groups on Si appear as a single resonance at 0.29 ppm. For the butadiyde chain, C_α appears at 103.07 ppm ($J_{Pt\text{-}C}$ = 1013.2 Hz), C_β appears at 93.81 ppm ($J_{Pt\text{-}C}$ = 297.6 Hz), C_γ appears at 93.81, and C_δ appears at 74.92 ppm. No evidence on Pt coupling to C_γ or C_δ is observed.

Crystals of **6**, suitable for crystallographic study, were grown from a concentrated solution of **6** in acetonitrile. The structure of **6** is depicted in Figure 2-9. The asymmetric unit contains two Pt carbene complexes. The platinum atom is bound by two trimethylsilylbutadiydes (TMSB) and two N-heterocyclic carbenes in a square planar fashion. The Pt-carbene bond distances range between 2.017(4)-2.038(4)Å. The bond angle between the bidentate N-heterocyclic carbene rings and the platinum atom range from 85.29(15)-86.13(15)°. The Pt-TMSB bond distances range from 1.983(4)-1.994(4) Å, and the TMSB-Pt-TMSB bond angles range between 86.58(15)-85.46(15)°.

The synthesis of **7** is outlined in Scheme 2-4. To a solution of **6** in DMF is added a solution of four equivalents of KF in H_2O. After stirring for 18 h, crushed ice is added to the solution to precipitate **7** and leave behind any remaining **6**. After filtering the solution and washing the precipitate with Et_2O, **7** is obtained as a light tan powder in 95.4% yield. Complex **7** was characterized by ^1H and $^{13}C\{^1H\}$ NMR, mass spectrometry, elemental analysis, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **7**gave a M^+ for $^{12}C_{23}H_{26}N_4{}^{95}Pt$ of 575.2 (calculated 575.2).

Notable features in the ^1H NMR spectrum of **7** include all of the characteristic features described for **4** as well as the disappearance of the Si-Me resonance at 0.12 ppm and the appearance of a singlet resonance at 2.57 ppm for the terminal proton on the butadiyde chain. In the ^{13}C NMR spectrum (Figure 2-3), there is also a disappearance of the Si-Me resonance at 0.29 ppm. For the butadiyde chain, C_α appears at 103.07 ppm ($J_{Pt\text{-}C}$ = 1013.2 Hz), C_β appears at 93.81 ppm ($J_{Pt\text{-}C}$ = 297.6 Hz), C_γ appears at 93.81, and C_δ appears at 74.92 ppm. No evidence on Pt coupling to C_γ or C_δ is observed.

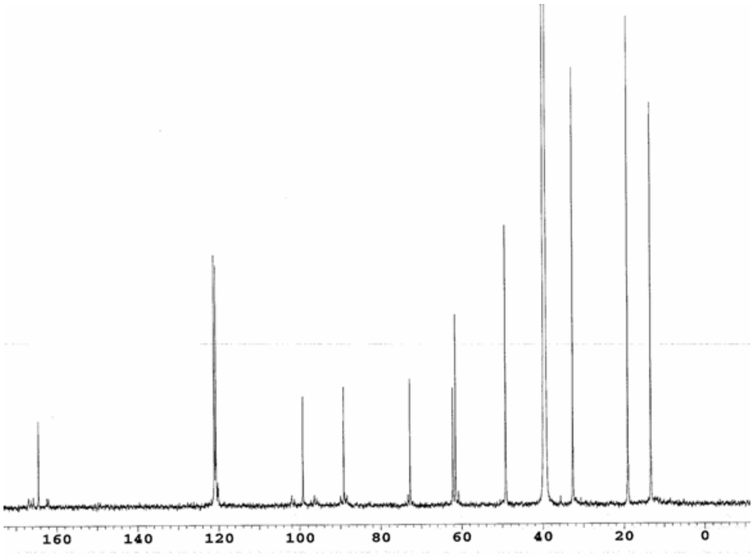


Figure 2-3 The ^{13}C NMR spectrum of **7** in *d*-DMSO

Crystals of **7** were grown from a concentrated solution of acetonitrile. These crystals were suitable for x-ray crystallographic study and the structure of **7** is depicted in Fig. 2-10. The platinum is square planar and bound by two N-heterocyclic carbenes and two butadiydes. The Pt-carbene distances are 2.013(5) and 2.031(5) Å for Pt-C(5) and Pt-C(9), respectively. The bond angle between the NHC rings and the platinum atom (C(5)-Pt-C(9)) is 84.74(19)°. The Pt- butadiyde distances are 1.999(5) (Pt-C(16)) and 1.985(5) Å (Pt-C(20)) with a bond angle between the butadiydes (C(16)-Pt-C(20)) of 88.55(19)°.

The synthesis of the tetraplatinum square **8$^{\cdot}$Et$_2$NH$_2$Cl** is outlined in Scheme 2-5. The square **8$^{\cdot}$Et$_2$NH$_2$Cl** was synthesized by the CuI coupling reaction of **7** with an equimolar amount of **3** in a mixture of THF and diethylamine. After stirring for 10 days at RT and following workup, **8$^{\cdot}$Et$_2$NH$_2$Cl** was recovered in 94% yield. Complex

8·Et$_2$NH$_2$Cl was characterized by ^{1}H and ^{13}C – {^{1}H} NMR and mass spectrometry. No crystals were able to be obtained. The ESI mass spectrum of a DMSO solution of **8·Et$_2$NH$_2$Cl** gave a M$^+$ for $^{12}C_{76}H_{96}N_{16}{}^{195}Pt_4$ of 2015.5(calculated 2014.0).

Notable features in the ^{13}C NMR spectrum of **8·Et$_2$NH$_2$Cl** (Figure 2-4) include the switching of the peak positions for C_α and C_β. A resonance for C_α appears at 91.68 ppm and for C_β at 95.79 ppm. The Pt-carbene resonance appeared at 166.67 ppm. No Pt-C coupling was distinguishable, even in a concentrated solution using the 750 MHz NMR instrument.

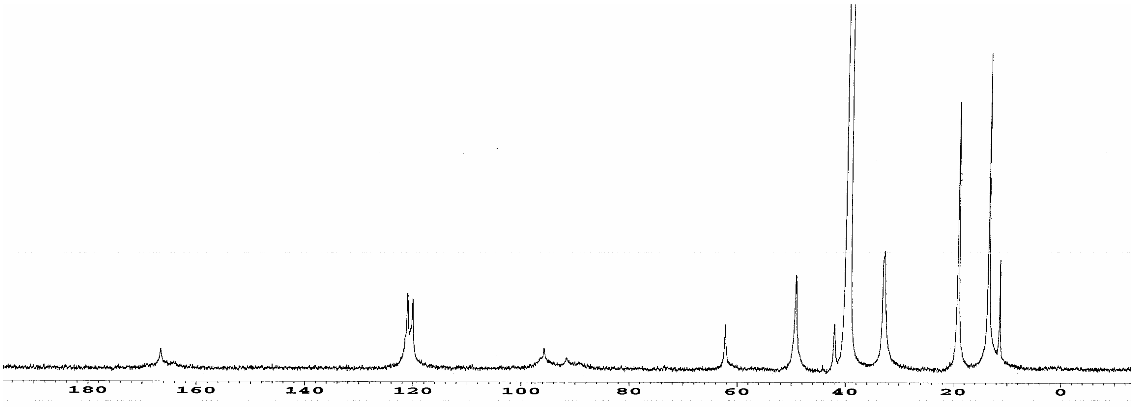
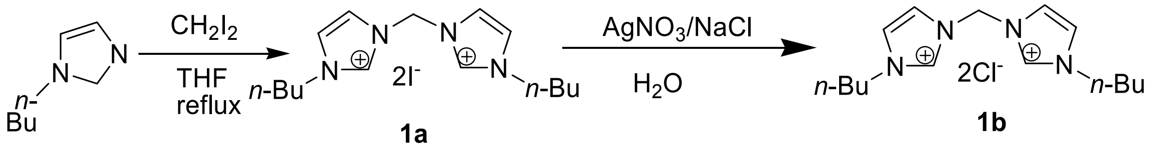
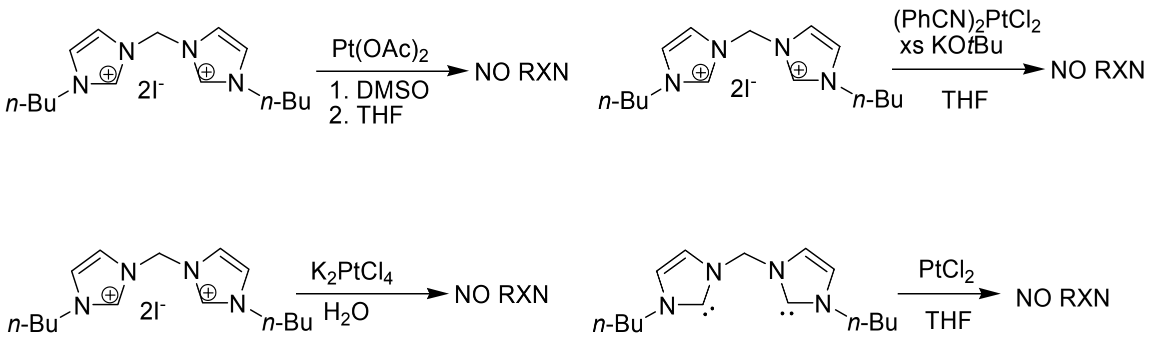


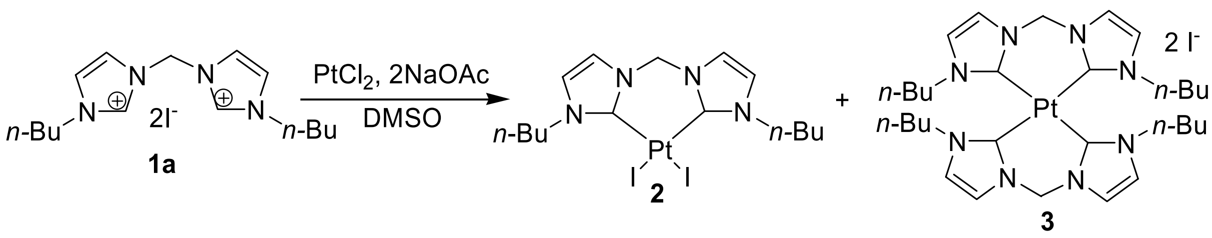
Figure 2-4 The ^{13}C NMR spectrum of **8·Et$_2$NH$_2$Cl** in *d*-DMSO



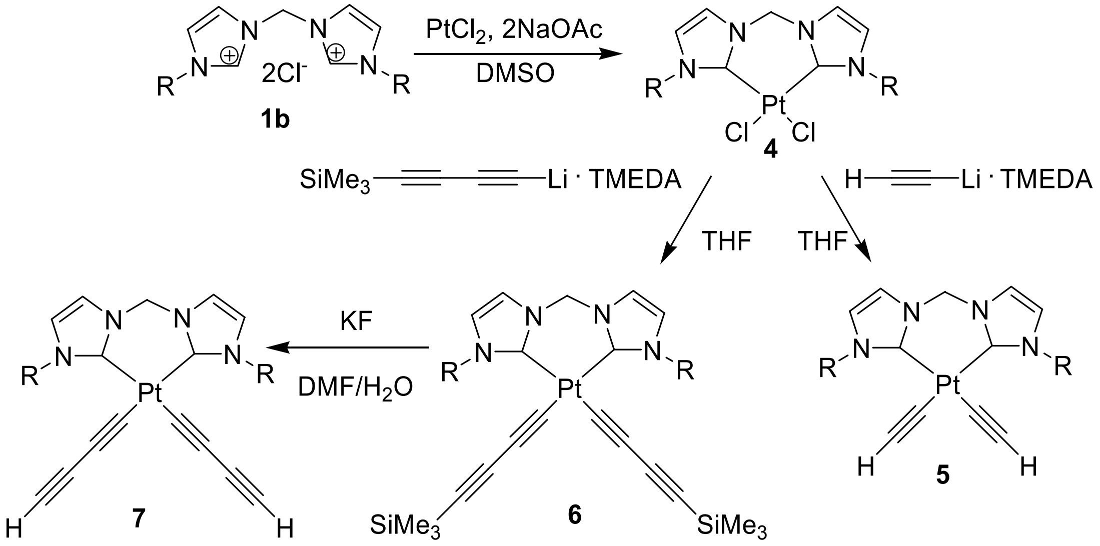
Scheme 2-1 The synthesis of **1a** and **1b**.



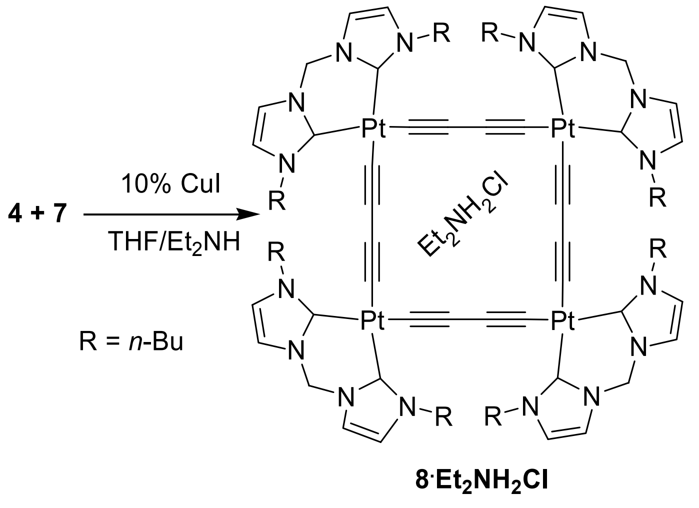
Scheme 2-2 The unsuccessful attempts to synthesize **2**.



Scheme 2-3 The synthesis of **2** and **3**.



Scheme 2-4 The synthesis of **4**, **5**, **6**, and **7**.



Scheme 2-5 The synthesis of $\mathbf{8{\cdot}Et_2NH_2Cl}$

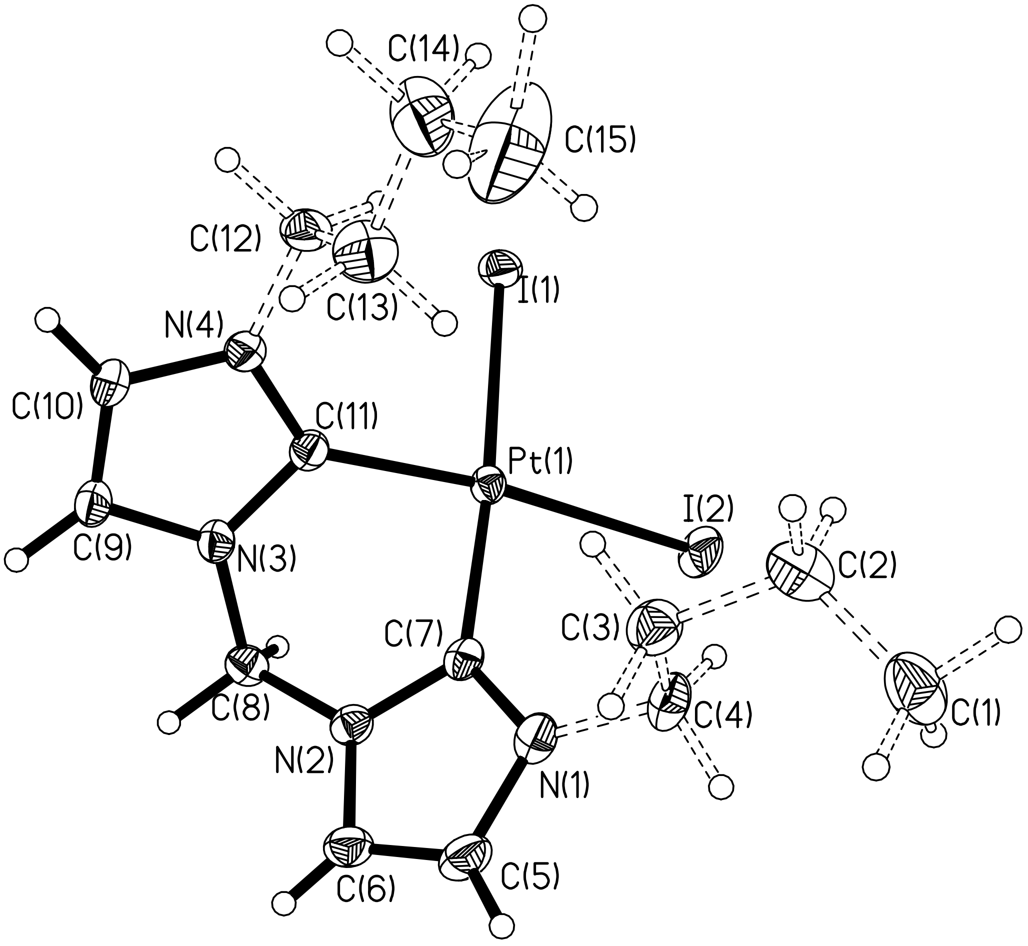


Figure 2-5 Thermal ellipsoid plot of compound **2**. The thermal ellipsoids are drawn at 50% probability.

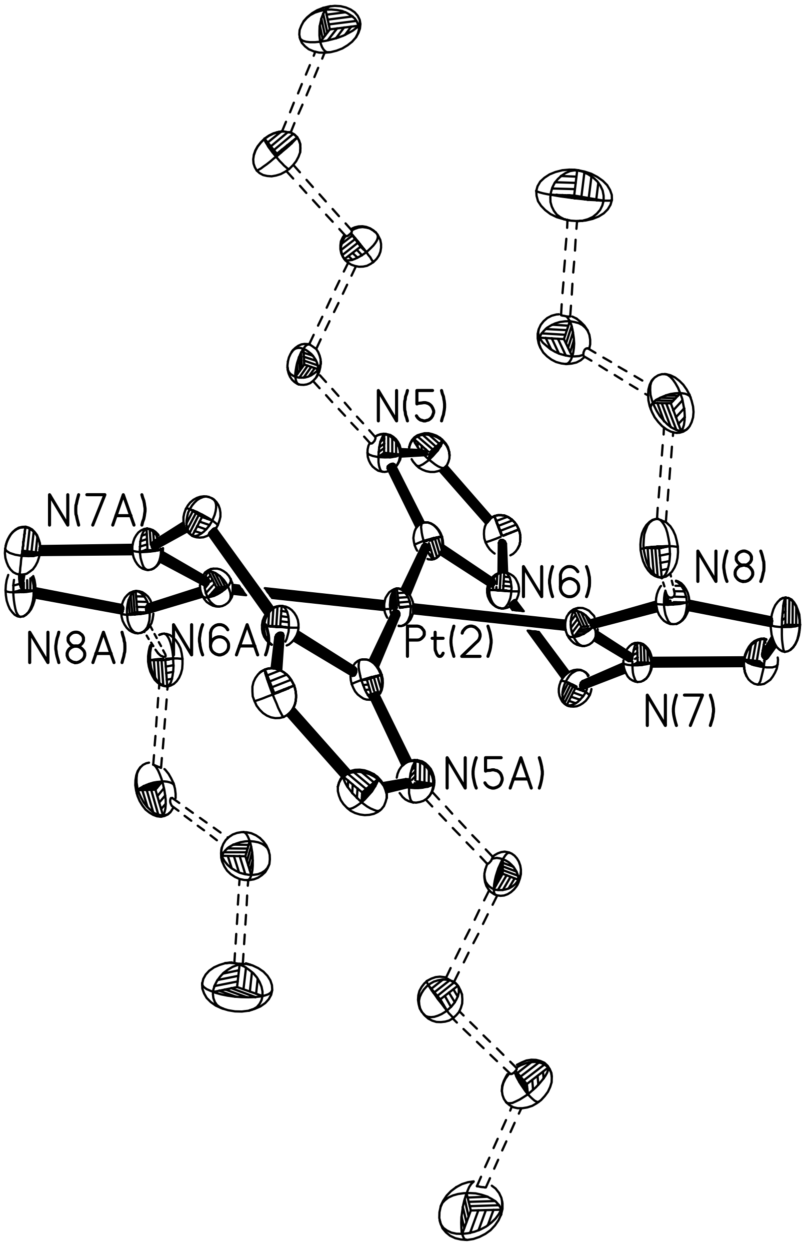


Figure 2-6 Thermal ellipsoid plot of compound **3**. The thermal ellipsoids are drawn at 50% probability. Iodide anions and hydrogen atoms on the alkyl chains have been omitted for clarity. Carbons on the alkyl chains were fixed as isotropic with artificially low displacement parameters for modeling purposes.

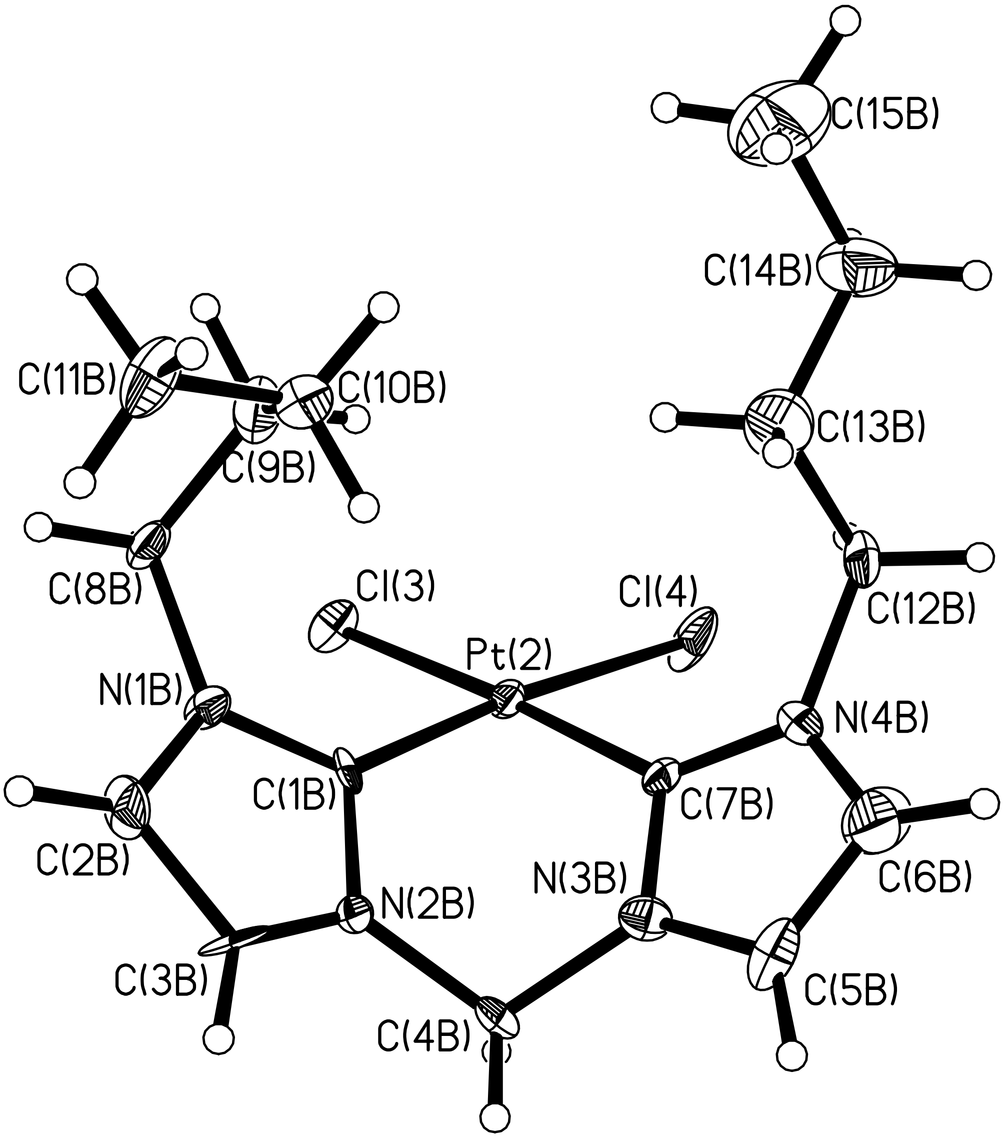


Figure 2-7 Thermal ellipsoid plot of compound **4**. The thermal ellipsoids are drawn at 50% probability.

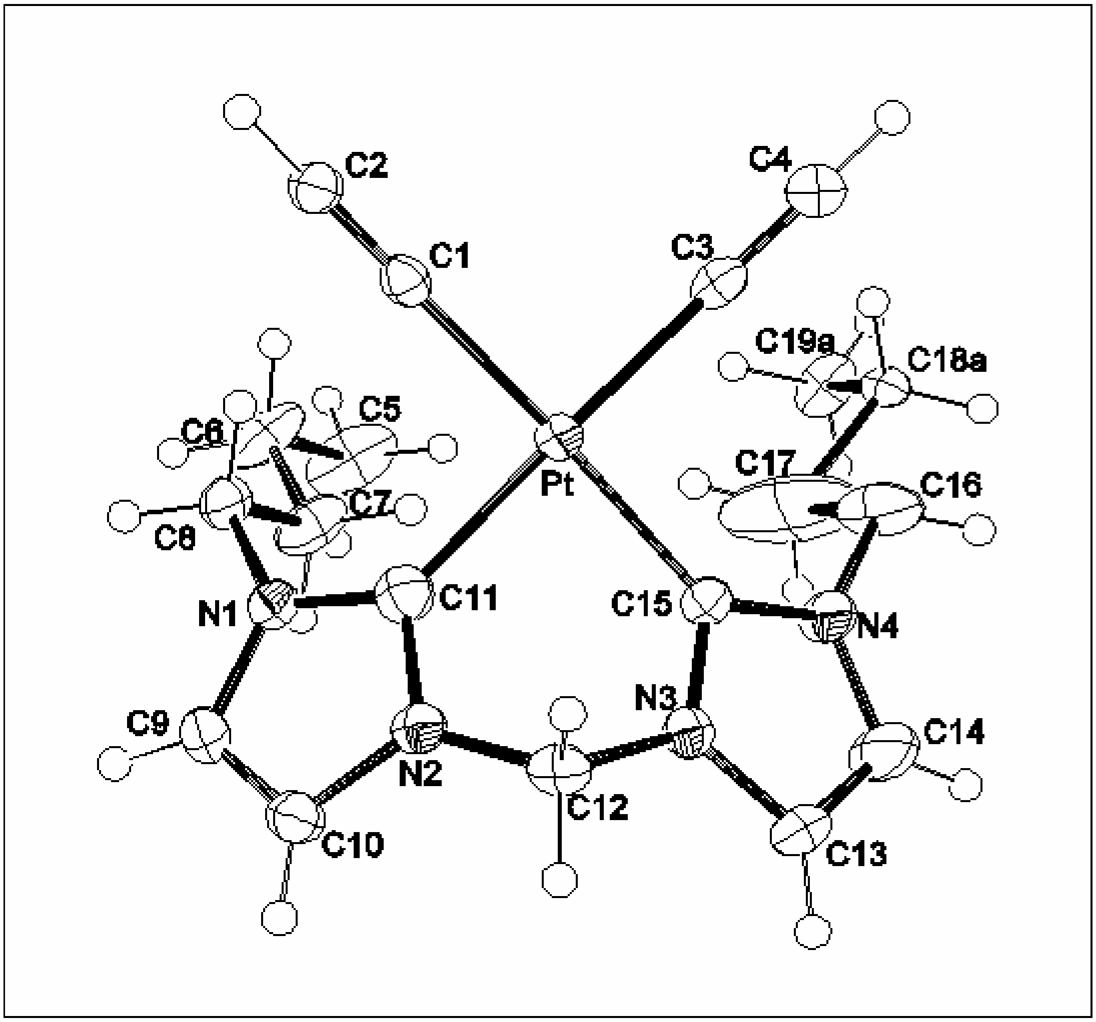


Figure 2-8 Thermal ellipsoid plot of compound **5**. The thermal ellipsoids are drawn at 50% probability.

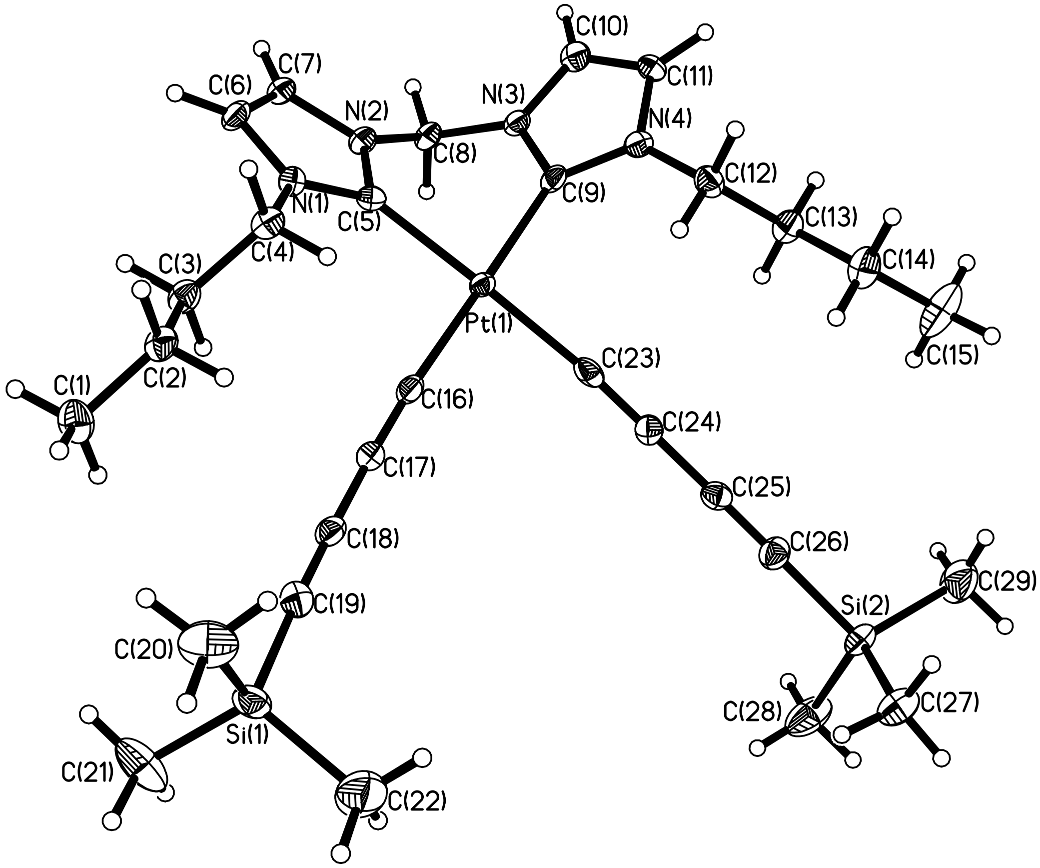


Figure 2-9 Thermal ellipsoid plot of compound **6**. The thermal ellipsoids are drawn at 50% probability.

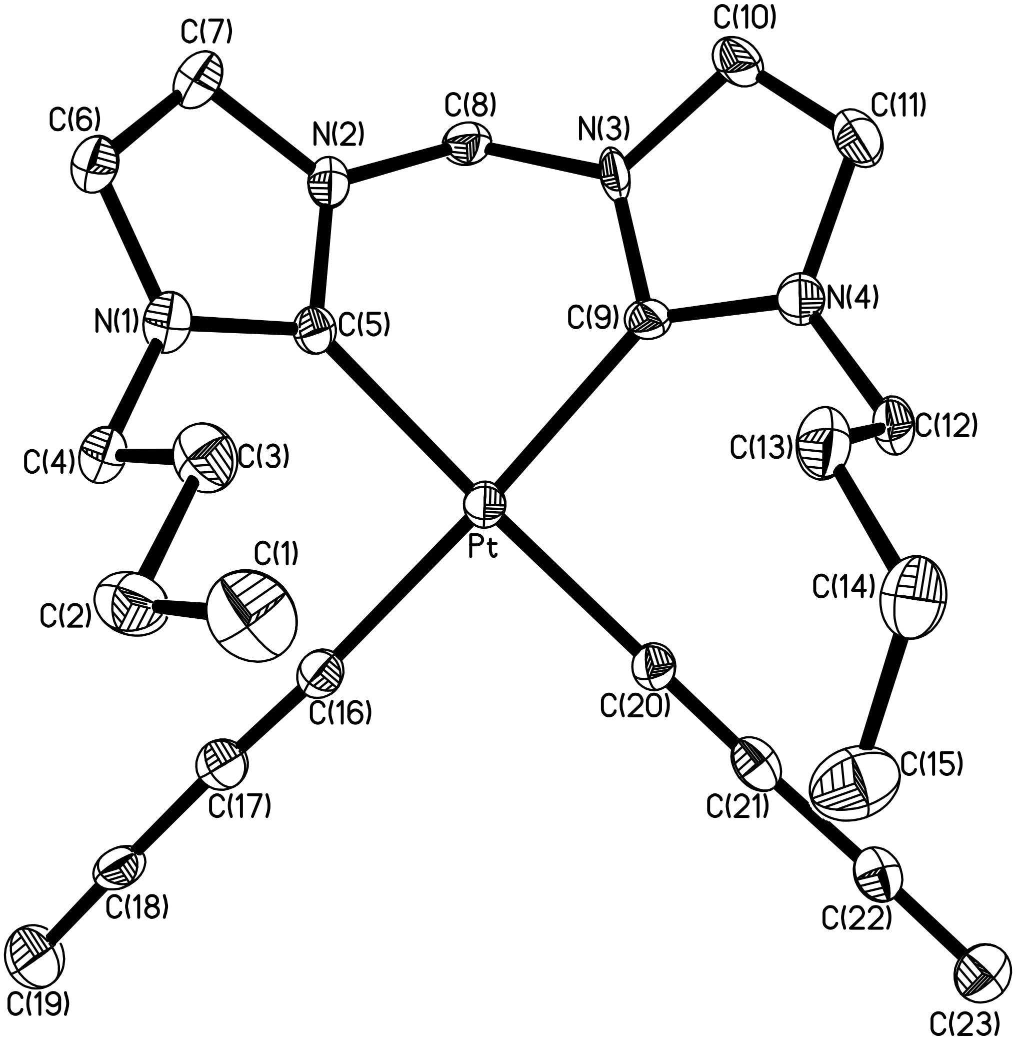


Figure 2-10 Thermal ellipsoid plot of compound **7**. The thermal ellipsoids are drawn at 50% probability.

Experimental Procedure

General Procedures

The *n*-butyl imidazole, CH_2I_2, bis(trimethylsilyl)butadiyde, lithium acetylide TMEDA complex, sodium acetate, and potassium fluoride were purchased from Aldrich and used as received. $PtCl_2$ was purchased from Strem and also used as received. Where applicable, tetrahydrofuran, THF, was predried over potassium hydroxide and distilled from sodium/benzophenone prior to use. Diethyl amine was distilled from a sodium hydroxide. Unless otherwise noted, all reactions were run in an N_2 atmosphere with standard Schlenk techniques.[134,135]

Mass spectrometric analysis was performed by the mass spectrometry facility at The University of Akron. For ^1H and ^{13}C NMR spectra, the residual proton and the carbon in the deuterated solvents were used as references for the chemical shift. ^1H and ^{13}C NMR spectra were obtained on a Varian 300 or 750 MHz instrument. Elemental analyses were performed by E & R Microanalytical Laboratories, Inc. The X-ray analyses were performed in our laboratory by either Jared Garrison or Matthew Panzner.

The full sphere of data was collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The reflections were collected using psi and omega scans. Unit cell determination was achieved by using reflections from three different orientations. Am empirical absorption correction and other corrections were done using multi-scan SADABS. Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package.[136] Hydrogen atoms for the structures of **2**, **4**, **5**, **6**, and **7** were calculated and their β values fixed accordingly. Hydrogen atoms for the co-crystallized structure of **2** and **3** were found from the difference map and their positions refined.

1, 1'-Methylene bis(3-*n*-butylimidazolium)diodide (**1a**) and 1, 1'-Methylene bis(3-*n*-butylimidazolium)dichloride (**1b**): To a solution containing 10.0 g (80.5 mmol) of *n*-butyl imidazole in 150 ml THF was added 10.27 g (38.3 mmol) of CH_2I_2. The solution was stirred at reflux temperature for 72 h. The solution was cooled and filtered to give **1a** as a fine white powder in 83% yield (16.4 g). 5.00 g (9.69 mmol) of **1a** was dissolved in 10 ml H_2O, and 3.29 g (19.37 mmol) of $AgNO_3$ was dissolved in 5 ml H_2O. The two solutions were mixed, and a yellow precipitate emerged immediately. 1.13 g (19.37 mmol) of NaCl was added to the suspension, and it was filtered over Celite®. The H_2O was removed *in vacuo* to give **1b** as a white powder in 98% yield (3.17 g). For **1a**: ^{1}H NMR 300 MHz (Me_2SO-d_6): δ 0.91 (t, 3H, CH_3), 1.29 (sextet, 2H, CH_2), 1.79 (quintet, 2H, CH_2), 4.23 (t, 2H, CH_2), 6.63 (s, 1H, CH_2), 7.92 (d, 1H, CH), 8.00 (d, 1H, CH), 9.46 (s, 1H, CH). ^{13}C NMR 60 MHz (Me_2SO-d_6): δ 13.29 (CH_3), 18.71 (CH_2), 30.97 (CH_2), 49.06 (CH_2), 58.28 (N-CH_2-N), 122.09 (CH), 123.14 (CH), 137.40 (carbonium C). MS m/z$^+$ ESI Calculated: 642.91 Found: 642.9. Anal. Calc. for $C_{15}H_{26}N_4I_2$: C, 34.9; H, 5.08; N, 10.85. Found: C, 34.8; H, 4.98; N, 10.74.

$C_{15}H_{24}N_4PtI_2$ (**2**) and $C_{30}H_{48}N_8PtI_2$ (**3**): To a solution of 1.07 g (2.07 mmol) of **1a** in 50 ml of Me_2SO was added 0.50 g (1.88 mmol) of $PtCl_2$ and 0.57 g (4.14 mmol) of sodium acetate. The solution was stirred at 90 °C for 1.5 h, and the solvent was removed *in vacuo*. The residue was taken up in $CHCl_3$ and washed several times with water. Removal of the solvent *in vacuo* afforded **2** (0.995 g) and **3** (0.637 g) in 50% and 16% yields, respectively. In order to optimize the yield of **2** under the exact same reaction conditions, the volume of solvent was increased to 500 ml. This avoided the synthesis of **3** and afforded 1.250 g (69.2%) of **2**. For **2**: ^{1}H NMR 300 MHz (Me_2SO-*d*$_6$): δ 0.85 (t, 3H, CH_3), 1.15 (sextet, 2H, CH_2), 1.72 (quintet, 2H, CH_2), 3.97 (m, 1H, CH_2), 4.72 (m, 1H, CH_2), 6.05 (2d, 2H, CH_2), 7.39 (d, 1H, CH), 7.53 (d, 1H, CH). ^{13}C NMR 60 MHz (Me_2SO-*d*$_6$): δ 14.16 (CH_3), 19.70 (CH_2), 32.52 (CH_2), 51.13 (CH_2), 62.83 (N-CH_2-N), 121.26 (CH), 122.02 (CH), 149.61 (carbene C). MS m/z$^+$ ESI (-I$^-$) Calculated: 582.6 Found: 582.2. For **3**: ^{1}H NMR 300 MHz (Me_2SO-*d*$_6$): δ 0.85 (t, 3H, CH_3), 1.15 (sextet, 2H, CH_2), 1.72 (quintet, 2H, CH_2), 4.22 (m, 1H, CH_2), 4.48 (m, 1H, CH_2), 6.34 (2d, 1H, CH_2), 7.60 (br. s., 1H, CH), 7.79 (br. s., 1H, CH). MS m/z$^+$ ESI (-I$^-$) Calculated: 842.3 Found: 843.3.

$C_{15}H_{24}N_4PtCl_2$ (**4**): In air, a round bottom reaction flask was charged with 8.1373 g (24.414 mmol) of **1**, 6.4994 g (24.414 mmol) of $PtCl_2$, 6.6444 g (48.820 mmol) of sodium acetate, and 250 ml DMSO. The solution was stirred at 90°C for 2 h. The volume of the solvent was reduced by half, followed by the addition of 300 mL of saturated brine solution. The resulting precipitate was filtered and washed several times with water to yield 9.261 g of a fine white powder in 72.1%. ^{1}H NMR (DMSO-d_6): δ 0.91 (t, 3H, CH_3), 1.29 (sextet, 2H, CH_2), 1.79 (quintet, 2H, CH_2), 3.97 (m, 1H, CH_2), 4.85 (m, 1H, CH_2), 5.96 (d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 6.09 (d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 7.92 (d, 1H, CH_e), 8.00 (d, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 13.47 (CH_3), 19.09 (CH_2), 32.43 (CH_2), 48.71 (CH_2) 61.78 (N-CH_2-N), 120.36 (CH), 121.31 (CH), 143.13 (Pt-carbene). m/z$^+$ ESI Calculated: 489.1. Found: 491.1. Anal. Calc. for $C_{15}H_{24}N_4PtCl_2$: C, 34.2; H 4.60; N, 10.64. Anal. Found: C, 34.5; H, 4.40; N, 10.6.

$C_{19}H_{26}N_4Pt$ (**5**): A Schlenk flask was charged with 1.1975 g (2.275 mmol) of **2**, 0.419 g (4.550 mmol) of lithium acetylide TMEDA complex, and 100 ml THF. The slurry was allowed to stir at rt for 20 h, then opened and filtered. The precipitate was washed 3 times with 50 ml H_2O, yielding 0.9888 g of a light tan powder (86.0%). ^{1}H NMR (DMSO-d_6): δ 0.84 (t, 3H, CH_3), 1.18 (sextet, 2H, CH_2), 1.69 (quintet, 2H, CH_2), 1.92 (s, 1H, C-H, $J_{\text{Pt-H}}$ = 23.0 Hz) 3.99 (m, 1H, CH_2), 5.01 (m, 1H, CH_2), 5.80 (d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 6.06 (d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 7.31 (d, 1H, CH), 7.44 (d, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 13.53 (CH_3), 19.04 (CH_2), 32.67 (CH_2), 48.94 (CH_2) 62.07 (N-CH_2-N), 93.54 (C-C, $J_{\text{Pt-C}}$ = 297.6 Hz), 99.99 (Pt-C, $J_{\text{Pt-C}}$ = 1013.2 Hz), 119.83 (CH), 120.49

(CH), 166.76 (carbene C, $J_{\text{Pt-C}}$ = 898.7 Hz). m/z$^+$ ESI Calculated: 452.2. Found: 453.2. Anal. Calc. for $C_{15}H_{26}N_4Pt$: C, 45.14; H 5.18; N, 11.08. Anal. Found: C, 45.33; H, 5.29; N, 11.17.

$C_{29}H_{42}N_4PtSi_2$ (**6**): A schlenk flask was charged with 3.904 g (20.081 mmol) of bis(trimethylsilyl)butadiyde, 1.30 ml (20.081 mmol) TMEDA, and 225 ml THF. At rt, 12.6 ml (20.081 mmol) methyl lithium was added dropwise to the stirred solution. After stirring at rt for 45 min, 5.033 g (9.563 mmol) of **2** was added to the solution in the dry box. The slurry was stirred at rt for a further 18 h, in which time the solution became a clear yellow. The solvent was removed *in vacuo*, and the resulting tan solid was washed several times with water to give 6.3544 g of a tan powder (95.2%). ^{1}H NMR (DMSO-*d*$_6$): δ 0.12 (s, 9H, Si-CH_3), 0.90 (t, 3H, CH_3), 1.23 (sextet, 2H, CH_2), 1.75 (quintet, 2H, CH_2), 4.24 (m, 1H, CH_2), 4.42 (m, 1H, CH_2), 5.87 (2 d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 6.13 (2 d, 1H, CH_2, $J_{\text{H-H}}$ = 13.0 Hz), 7.41 (d, 1H, CH), 7.52 (d, 1H, CH). ^{13}C NMR (DMSO-*d*$_6$): δ 0.29 (Si-Me), 13.62 (CH_3), 19.21 (CH_2), 32.83 (CH_2), 49.38 (CH_2) 62.23 (N-CH_2-N), 74.92 (C-Si), 90.20 (C-C), 93.81 (C-C, $J_{\text{Pt-C}}$ = 297.6 Hz), 103.07 (Pt-C, $J_{\text{Pt-C}}$ = 1013.2 Hz), 120.79 (CH), 121.04 (CH), 164.07 (carbene C, $J_{\text{Pt-C}}$ = 898.7 Hz). m/z$^+$ ESI Calculated: 719.1. Found: 720.4. Anal. Calc. for $C_{29}H_{42}N_4PtSi_2$: C, 49.91; H 6.07; N, 8.03. Anal. Found: C, 49.74; H, 5.99; N, 7.97

$C_{23}H_{26}N_4Pt$ (**7**): In air, a round bottom reaction flask was charged with 0.7330 g (1.052 mmol) of **4** dissolved in 20 ml DMF. To this solution was added 0.2441 g (4.200 mmol) of KF dissolved in 5 ml H_2O. The solution was allowed to stir at rt for 18 h. Crushed ice was added to the solution, causing the precipitation of a light powder. The solution was filtered, and the precipitate was washed three times with 30 ml Et_2O yielding 0.5544 g of a light tan powder (95.4%). ^{1}H NMR (DMSO-d_6): δ 0.87 (t, 3H, CH_3), 1.22 (sextet, 2H, CH_2), 1.72 (quintet, 2H, CH_2), 2.57 (s, 1H, CH), 4.13 (m, 1H, CH_2), 4.56 (m, 1H, CH_2), 5.87 (d, 1H, CH_2, $J_{H\text{-}H}$ = 12.7 Hz), 6.12 (d, 1H, CH_2, $J_{H\text{-}H}$ = 12.7 Hz), 7.38 (d, 1H, CH), 7.49 (d, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 13.50 (CH_3), 19.17 (CH_2), 32.72 (CH_2), 48.21 (CH_2) 61.68 (N-CH_2-N), 62.17 (CH), 72.77 (CC), 89.15 (CC, $J_{Pt\text{-}C}$ = 303.7 Hz), 99.15 (Pt-C, $J_{Pt\text{-}C}$ = 923.16 Hz), 120.68 (CH), 121.04 (CH), 164.18 (carbene C, $J_{Pt\text{-}C}$ = 898.7 Hz). m/z$^+$ ESI Calculated: 575.2. Found: 575.2. Anal. Calc. for $C_{23}H_{26}N_4Pt$: C, 49.90; H 4.73; N, 10.12. Anal. Found: C, 50.48; H, 4.99; N, 9.87

$C_{76}H_{96}N_{16}Pt_4 \cdot Et_2NH_2Cl$ (**8·Et₂NH₂Cl**): Under N_2, a schlenk flask was charged with 0.5567 g (1.058 mmol) of **4,** 0.5857 g (1.058 mmol) of **7**, and 0.0302 g (0.159 mmol) of CuI. To the flask was added 75 ml of dry THF and 25 ml dry Et_2NH. This suspension was stirred at rt for 10 days. Filtration in air of the resulting suspension yielded 2.1345 g of a brown powder in 95% yield. ^{1}H NMR (DMSO-d_6): δ 0.84 (br. s, 3H, CH_3), 1.14 (br. s, 2H, CH_2), 1.69 (br.s, 2H, CH_2), 4.05 (br. s, 1H, CH_2), 4.68 (br. s, 1H, CH_2), 5.78 (Br. s, 1H, CH_2), 6.10 (br. s, 1H, CH_2), 7.34 (br.s, 1H, CH), 7.46 (br. s, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 11.40 (3H, CH_3 of Et_2NHCl), 13.46 (CH_3), 19.11 (CH_2), 32.88 (CH_2), 42.05 (CH_2 of Et_2NHCl), 49.24 (CH_2), 49.24 (CH_2), 62.28 (CH_2), 91.68 (C_α), 95.79(C_β), 120.16 (CH), 121.12 (CH), 166.67 (C-Pt) m/z$^+$ ESI (M + H$^+$) Calculated: 2014.0. Found: 2015.5.

CHAPTER III

THE SYNTHESIS OF SILVER N-HETEROCYCLIC CARBENE COMPLEXES AND CARBENE TRANSFER TO FORM THE RHODIUM N-HETEROCYCLIC CARBENE COMPLEXES

Introduction

The goal of this part of our research was to evaluate the possibility of using chelated rhodium N-heterocyclic carbene (Rh NHC) complexes as ^{105}Rh radiopharmaceuticals.[137] ^{105}Rh has been identified as a viable nuclide for targeted radiotherapy.[138] The stability of Rh(III) complexes is well recognized and is essential for targeted radionuclide therapy to prevent the dissociation of the targeted ligand *in vivo* from the tissue-destroying effects of ^{105}Rh. ^{105}Rh is an excellent choice for tumor therapy because it emits beta particles in the ratio of 70% 0.560 MeV and 30% 0.250 MeV that are suitable for radiation therapy as well as a 319 keV gamma particle that is suitable for imaging.[139] It has a $t_{1/2}$ of 36.4 hours, which is sufficient time to kill tumor cell lines, but also short enough to avoid significant accumulation of radioactive Rh in the body. There are only a handful of papers published on the synthesis of viable ^{105}Rh complexes for this purpose.[140,141,142,143] Because radioactive ^{105}Rh is available only as $RhCl_3{\cdot}xH_2O$, the challenge exists of making a robust Rh NHC complex starting from this reagent well within the 36.4 hour half life with relatively simple chemistry. This could be done in two ways: (a) by rapidly transforming the $RhCl_3\cdot xH_2O$ into a form that had been previously used to form rhodium carbene complexes[114,115,116,117] or (b) by the direct synthesis of Rh NHC complexes from $RhCl_3\cdot xH_2O$. Both approaches have been accomplished.

The transfer of NHC ligands from Ag to Rh (I) using $[Rh(COD)Cl]_2$ has been reported.[97,98,118] It is the goal of our research to find conditions that would allow the transfer of a carbene from silver to $RhCl_3\cdot xH_2O$ directly in a biologically friendly solvent. DMSO is a medicinally benign solvent and has been approved for use in humans since 1971.[144]

The Synthesis and Characterization of the Silver and Rhodium NHC Complexes

The synthesis of the Rh complex (**9**) is illustrated in Scheme 3-1. $(Rh(OAc)_2)_2\cdot 2MeOH$ was obtained from refluxing $RhCl_3\cdot 3H_2O$ with four equivalents of sodium acetate in 50/50 ethanol/acetic acid.[145] The $(Rh(OAc)_2)_2\cdot 2MeOH$ was combined with **1c**, sodium acetate, and KI in acetonitrile at reflux for 12 hours to give **9** after workup. Complex **9** was characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR, mass spectrometry, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **9** gave a M^+ (M – $C_2H_3O_2$) for ${}^{12}C_{11}H_{156}N_4O_2I_2Rh$ of 532.8 (calculated 532.9).

The major problems with this approach are: (a) the synthesis is performed in acetonitrile, a toxic solvent which is not suitable for medicinal use, and (b) if applied to ^{105}Rh, it would require several synthetic steps with radioactive materials, making this approach impractical.

Notable features in the ^{1}H NMR spectrum for **9** include the absence of a resonance at ca. 9 ppm which is diagnostic for the loss of the carbonium proton as well as the appearance of a resonance at 1.82 ppm for the acetate ligand. In the ^{13}C NMR spectrum, the resonance for the carbonium carbon at ca. 136 ppm is replaced with a doublet at 151.34 ppm that is diagnostic for a Rh-C bond ($J_{\text{Rh-C}}$ = 42.4 Hz).

Crystals of **9** were obtained from a concentrated solution in acetonitrile. The crystal structure of **9** is illustrated in Figure 3-3. The rhodium center is bound by one bidentate carbene ligand, two coordinating iodide anions, and a bidentate coordinating acetate in the classical octahedral fashion. The bond angles around the rhodium center do not deviate significantly from 90^o with the exception of the restriction imposed by the chelating carbene and by the bidentate acetate. The bond angle at C4-Rh-C8 is slightly acute at 86.60(15)^o, while the bond angle at O1-Rh-O2 is very acute at 60.38(9)^o. The Rh-NHC bonds vary from 1.960(4) Å to 1.955(3) Å for C4-Rh and C8-Rh. The bond length of the Rh-I bonds are not exceptional at 2.6442(4) Å and 2.6628(4) Å for Rh-I1 and Rh-I2. The bond lengths of the Rh-O bonds are in the normal regime at 2.189(3) Å and 2.174(2) Å for Rh-O1 and Rh-O2.

The syntheses of the Ag complexes **10a,b** are shown in Scheme 3-1. The addition of Ag_2O to an aqueous solution of **1a** or **1c**[69] in air gives the quantitative formation of silver complexes **10a** and **10b** in 12 min and 2h, respectively. Decomposition of **10a** begins to occur within 15 min as shown at first by the formation of a brown solution and later by the deposition of a silver mirror. Decomposition of **10b** begins to occur in 2.5 h.

Decomposition of **10a** and **10b** occurs rapidly when attempting to remove the solvent by evaporation and, therefore, no crystals were obtained. Addition of NH_4PF_6 to aqueous solutions of **10a** and **10b** yields **11a** and **11b,** respectively. The thermal stability of these complexes seems to be anion dependent, with the hexafluorophosphate salts, **11a** and**11b**, being much more stable than the iodide salts, **10a** and **10b**. Complex **10a** was characterized by ^{1}H and ^{13}C – {^{1}H} NMR and mass spectrometry. The ESI mass spectrum of a DMSO solution of **10a** gave a M$^+$ for $^{12}C_{18}H_{24}N_8Ag_2I_2$ of 693.9 (calculated 692.9). Complex **10b** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectrometry. Complexes **11a** and **11b** were characterized by ^{1}H and ^{13}C – {^{1}H} NMR, mass spectrometry, elemental analysis, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **11a** gave a M$^+$ (M – PF_6) for $^{12}C_{18}H_{24}N_8Ag_2{}^{31}P_2F_{12}$ of 712.5 (calculated 710.97). The ESI mass spectrum of a DMSO solution of **11b** gave a M$^+$ (M – PF_6) for $^{12}C_{30}H_{48}N_8Ag_2{}^{31}P_2F_{12}$ of 880.8 (calculated 883.17).

Notable features in the ^{1}H NMR spectrum for **10a** and **10b** include the absence of a resonance at ca. 9 ppm, which is diagnostic for the loss of the carbonium proton, and the occurrence of only one resonance for the two protons in the backbone of the imidazolium ring at 7.77 ppm for **10a** and 7.56 ppm for **10b**. In the ^{13}C NMR spectrum, the resonance for the carbonium carbon at ca. 136 ppm is absent. However, the peak for the Ag-carbene carbon resonance for **10a** and **10b** could not be detected. The ^{1}H NMR spectra of the hexafluorophosphate salts show distinct resonances for the two C-H bonds in the backbone of the imidazolium ring at 7.24 and 7.48 ppm for **11a** and 7.24 and 7.52

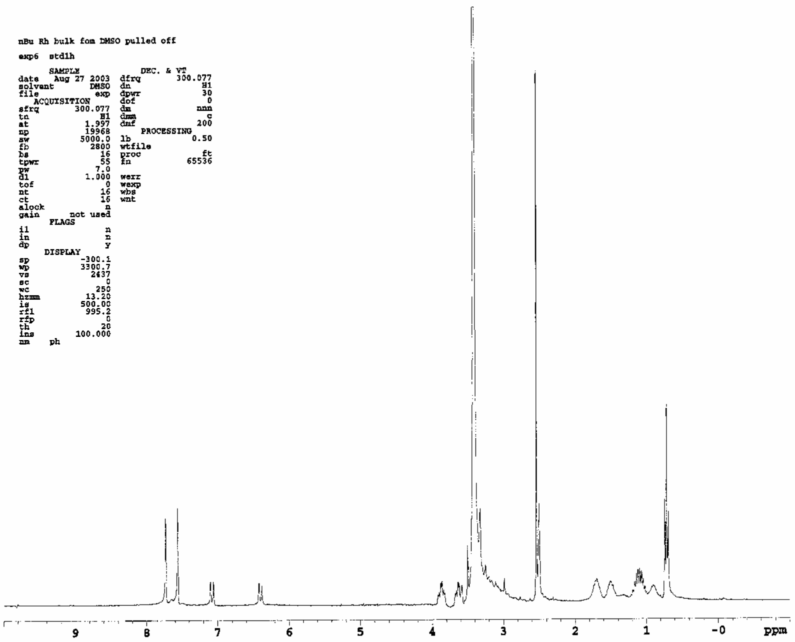
ppm for **11b**. The ^{13}C NMR spectra show the Ag-C peak at 196.01 ppm for **11a** and at 196.27 ppm for **11b**. No coupling of the silver to the carbene carbon is observed.

Single crystals suitable for x-ray diffraction studies of **11b** were grown from a concentrated solution of acetonitrile. The asymmetric unit consists of two dicationic dimers with four hexafluorophosphate anions. Compound **11b**, depicted in Fig. 3-4, forms a "shell-like" structure with the alkyl chains having the same directionality. The asymmetric unit has eight silver-carbene bonds ranging from 2.083(5) – 2.091(5) Å with an average 2.087(5) Å. The C-Ag-C bond angles deviate significantly from linearity with angles ranging from 166.7(2) – 173.4(2)°, with an average of 170.3(2)°. The reason for this deviation is likely due to the restriction imposed by the linking methylene group upon the N-heterocyclic carbene rings. Structural analysis of the methyl analog **11a** (Figure 3-5) was also completed. Structurally the N-heterocyclic carbene rings of both **11a** and **11b** bind to the silver cations in a similar manner.

The syntheses of the Rh complexes, **12a** and **12b**, are outlined in Scheme 3-1. After filtering off any unreacted Ag_2O and any formed AgI, 0.5 molar equivalents of $RhCl_3{\cdot}3H_2O$ was added to the aqueous filtrate containing the solvated Ag NHC complex **10a** or **10b** in air, causing the immediate precipitation of a red powder. Heating this red powder in DMSO at 100°C for 1 h in air, followed by the removal of the solvent *in vacuo* gave **12a** (62%) or **12b** (56%) as fine orange powders. Complexes **12a** and **12b** were characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR, mass spectrometry, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **9** gave a M^+ ($M - C_2H_3O_2$) for $^{12}C_{11}H_{156}N_4O_2I_2Rh$ of 532.8 (calculated 532.9). Complex **12a** was characterized by

^{1}H and ^{13}C{^{1}H} NMR and mass spectrometry. The ESI mass spectrum of a DMSO solution of **12a** gave a M$^+$ (M – Cl) for $^{12}C_{16}H_{24}N_8Cl_3Rh$ of 521.1 (calculated 526.3). Complex **12b** was characterized by ^{1}H and ^{13}C{^{1}H} NMR, mass spectrometry, and x-ray crystallography. The ESI mass spectrum of a DMSO solution of **12b** gave a M$^+$ (M – Cl) for ^{12} $C_{30}H_{48}N_8Cl_3Rh$ of 693.4 (calculated 694.5).

Notable features in the ^{1}H NMR spectrum for **12a** and **12b** (Figure 3-1) include the absence of a resonance at ca. 9 ppm. Due to the conformational rigidity of the ligand, rotation about the methylene linker is hindered, producing two doublets at 6.39 ppm ($J_{H\text{-}H}$ = 12.5 Hz) and 7.02 ppm ($J_{H\text{-}H}$ = 12.5 Hz) for **12a** and at 6.44 ppm ($J_{H\text{-}H}$ = 12.4 Hz) and 7.08 ppm ($J_{H\text{-}H}$ = 12.4 Hz) for **12b** for the two inequivalent protons. In addition, for **12b**, due to the rigidity imposed on the ligand by the metal, the protons on each of the three inner carbon atoms of the butyl chains are diastereotopic, thus producing a relatively complex spectrum. In the ^{13}C NMR, the Rh-carbene resonance occurs as a doublet at 169.82 ppm for **12a** ($J_{Rh\text{-}C}$ = 32.1 Hz) and at 168.05 ppm for **12b** ($J_{Rh\text{-}C}$ = 32.1 Hz) (Figure 3-2). Both complexes **12a** and **12b** are extremely stable with decomposition points of 208-210 °C and 237-238 °C, respectively, in air. They are stable in sodium chloride solution for months.



```
nBu Rh bulk fom DMSO pulled off

exp6  stdlh

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date   Aug 27 2003  dfrq        300.077
solvent       DMSO  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       300.077  dm              nnn
tn              H1  dmm               c
at           1.997  dmf             200
np           19968       PROCESSING
sw          5000.0  lb             0.50
fb            2800  wtfile
bs              16  proc             ft
tpwr            55  fn            65536
pw             7.0
d1           1.000  werr
tof              0  wexp
nt              16  wbs
ct              16  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -300.1
wp          3300.7
vs            2437
sc               0
wc             250
hzmm         13.20
is          500.00
rfl          995.2
rfp              0
th              20
ins        100.000
nm     ph
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Figure 3-1 The ^{1}H NMR spectrum of **12b** in *d*-DMSO.

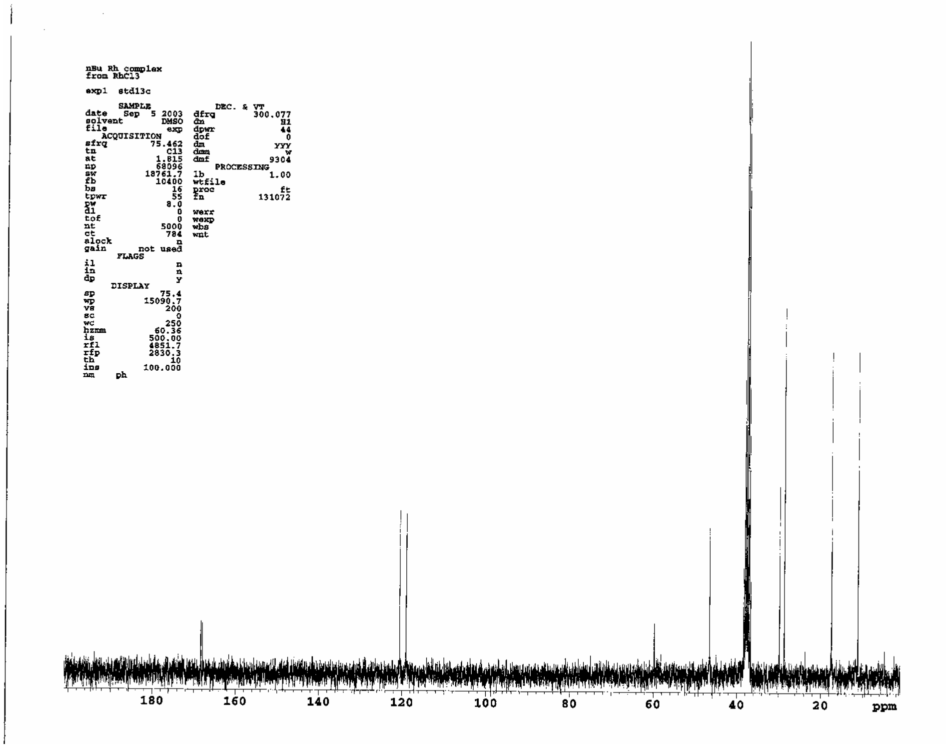
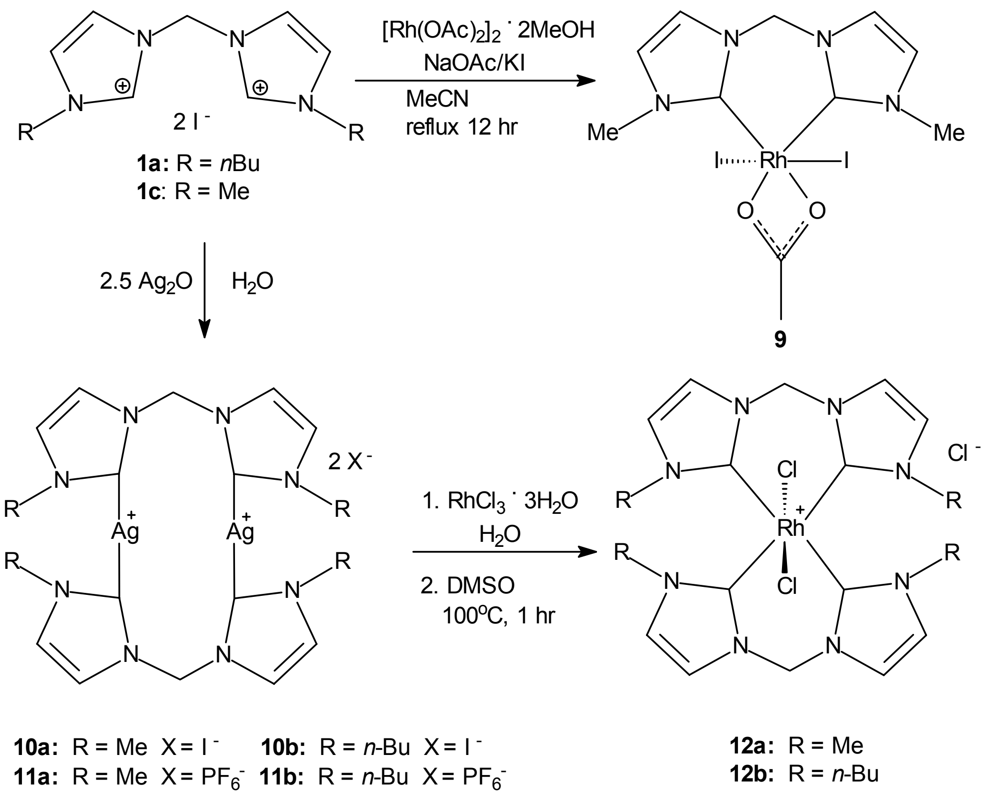


Figure 3-2 The ^{13}C NMR spectrum of **12b** in *d*-DMSO.

Crystals of **12b** suitable for single crystal x-ray diffraction studies were grown from a concentrated acetonitrile solution. The crystal structure of **12b** is shown in Fig. 3-6. Each Rh(III) center is bound to two bidentate carbene ligands and two coordinating chlorides forming a distorted octahedron. The remaining chloride is non-coordinating. Bond angles about the Rh centers deviate significantly from 90°, with C-Rh-C angles to each chelating NHC being acute for C5-Rh-C13A (83.7(2)°) and C20-Rh-C29A (84.1(2)°), and C-Rh-C angles between two NHC ligands being obtuse for C5-Rh-C13 (96.3(2)°) and C20-Rh-C29 (95.9(2)°). The C-Rh-Cl bonds range from 86.6(1)-93.4(1)° with an average of 90.0°. The asymmetric unit contains four rhodium NHC bonds ranging from 2.050(5)-2.067(5) Å with an average of 2.058(5) Å. Crystals of **12a** were not obtained due to its very limited solubility.



Scheme 3-1 The synthesis of **9**, **10a,b**, **11a,b**, and **12a,b**.

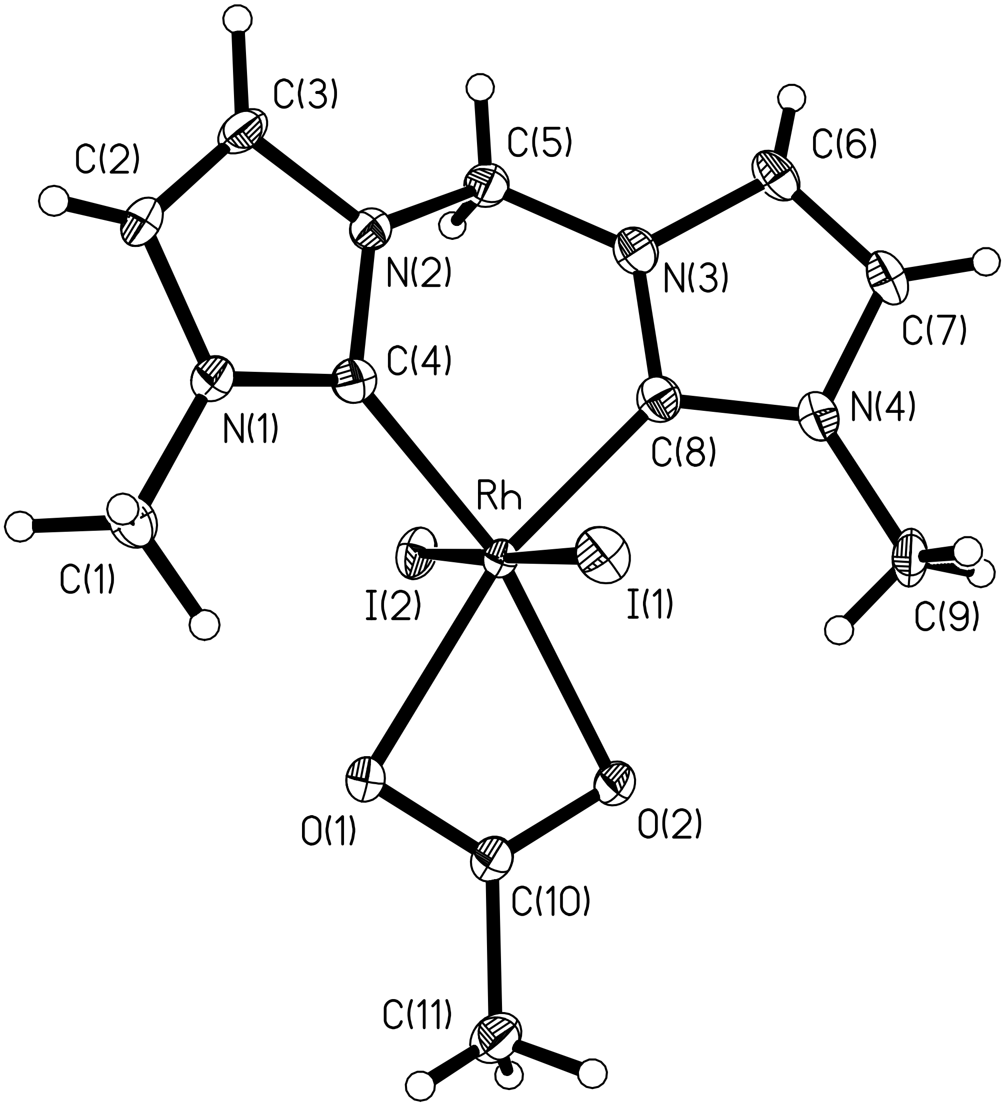


Figure 3-3 Thermal ellipsoid plot of compound **9**. Thermal ellipsoids are drawn at 50% probability.

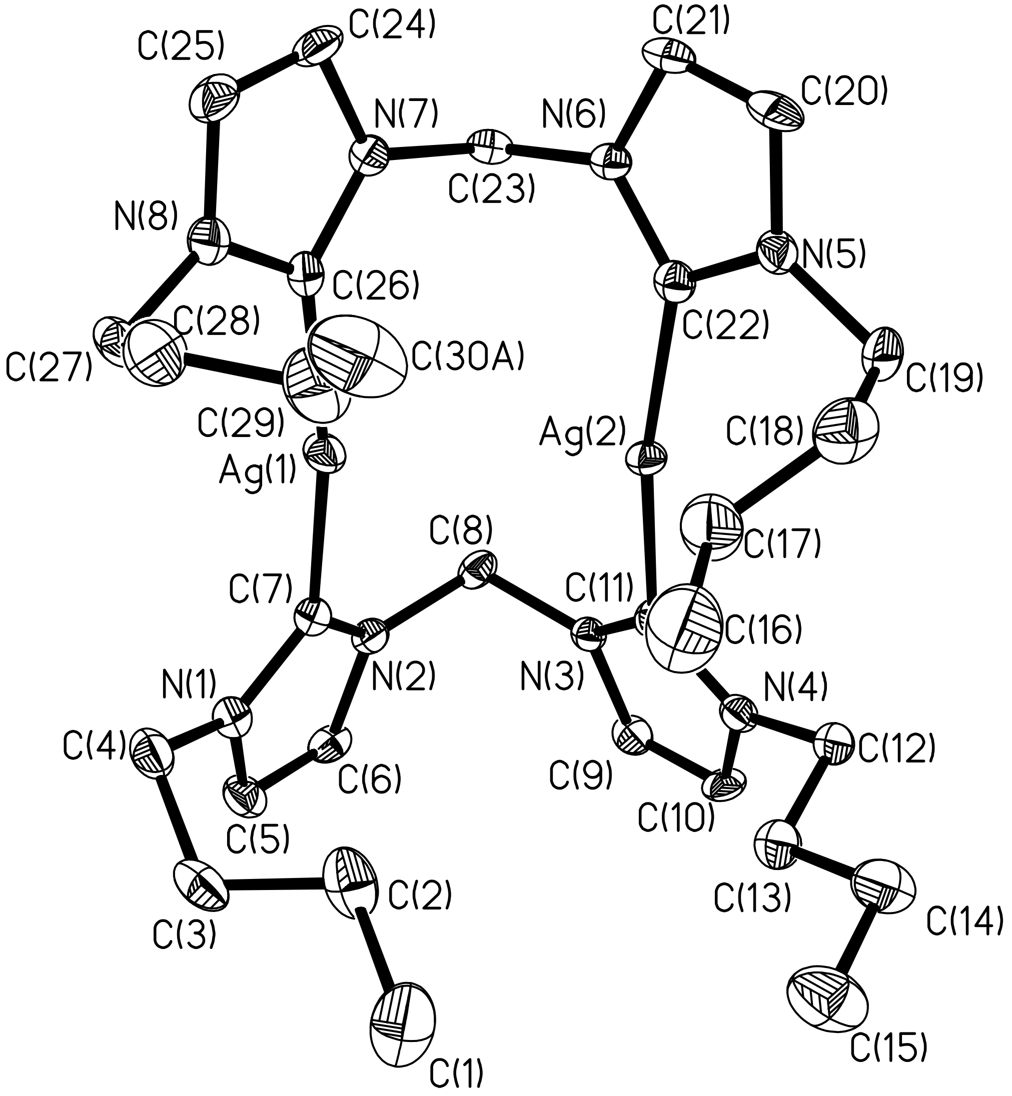


Figure 3-4 Thermal ellipsoid plot of the cationic portion of compound **11b**. The thermal ellipsoids are drawn at 50% probability. The anisotropic parameters for the alkyl chains were artificially fixed, and the hydrogen atoms were omitted for clarity.

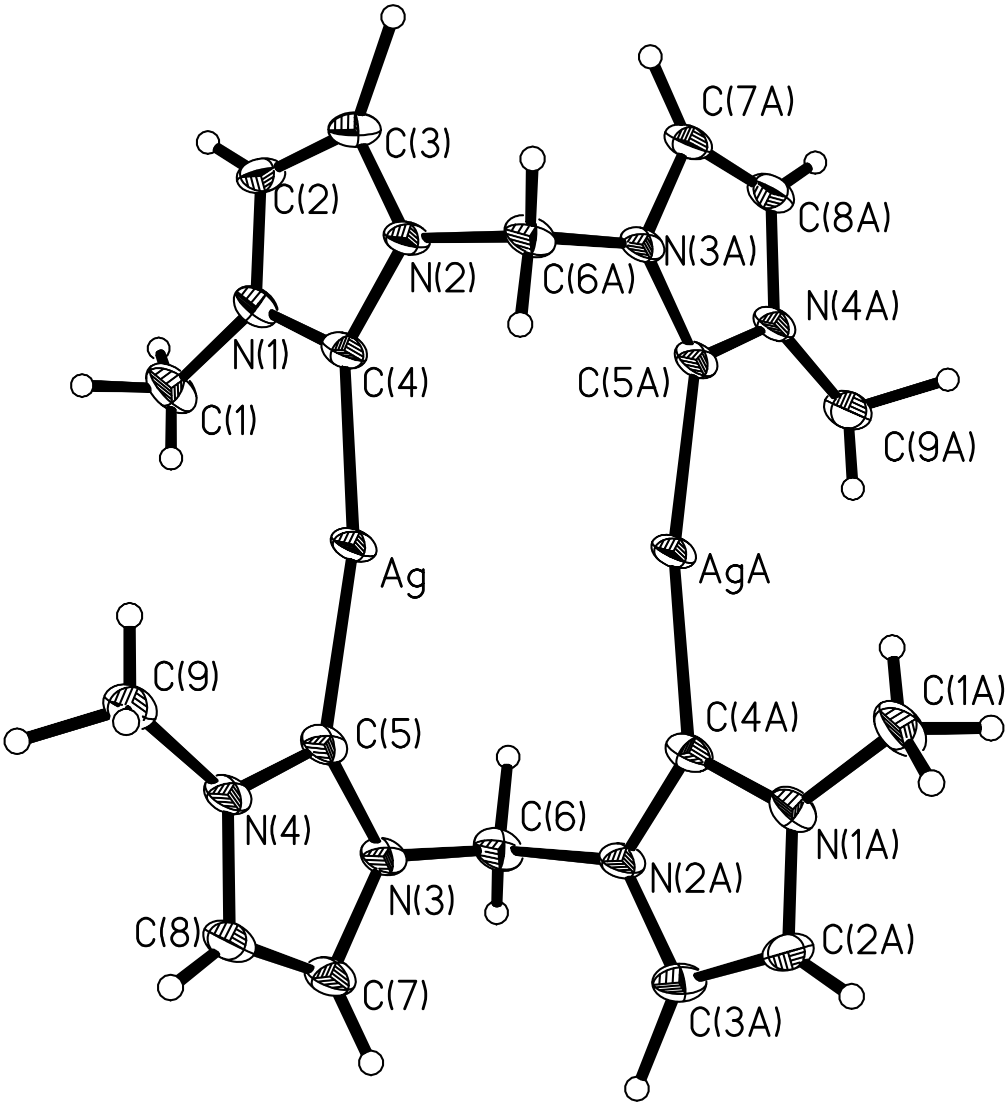


Figure 3-5 Thermal ellipsoid plot of the cationic portion of compound **11a**. Thermal ellipsoids are drawn at 50% probability.

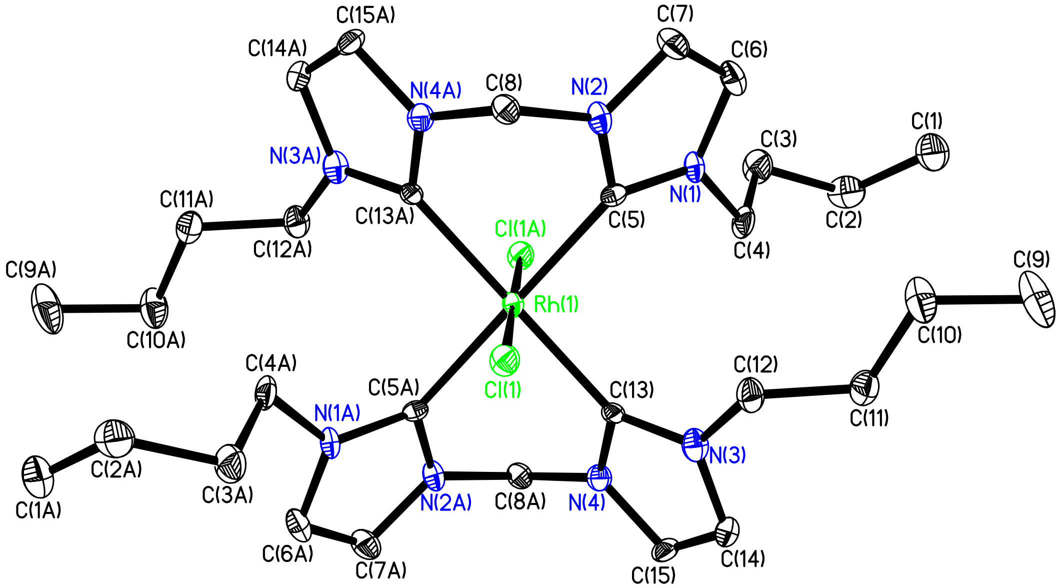


Figure 3-6 Thermal ellipsoid plot the cationic portion of compound **12b**. Thermal ellipsoids are depicted at 50% probability. Hydrogen atoms were omitted for clarity.

Experimental Procedure

General Procedures

Bis(1,1’-methylimidazolium)-3,3’-methylenediiodide and bis(1,1’- *n* -butylimidazolium)-3,3’-methylenediiodide were prepared according to literature procedures.[103,69] All other chemicals were obtained commercially and used without further purification.

Elemental analyses were performed by Complete Analysis Laboratories, Inc. Mass spectrometric analysis was performed by the mass spectrometry facility at The University of Akron. For ^1H and ^{13}C NMR spectra, the residual proton and the carbon in the deuterated solvents were used as references for the chemical shift. ^1H and ^{13}C NMR spectra were obtained on a Varian 300 MHz instrument. The X-ray analyses were performed in our laboratory by either Jared Garrison or Matthew Panzner.

The full sphere of data was collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The reflections were collected using psi and omega scans. Unit cell determination was achieved by using reflections from three different orientations. Am empirical absorption correction and other corrections were done using multi-scan SADABS. Structure solution, refinement, and modeling were accomplished using the Bruker SHELXTL package.[146] Hydrogen atoms for the structures of **9**, **10a,b**, **11a,b**, and **12a,b** were calculated and their β values fixed accordingly.

***The Rh complex* (9):** To a stirring solution of 0.056 g (0.121 mmol) of **1a** in 30 ml acetonitrile was added 0.030 g (0.068 mmol) of $(Rh(OAc)_2)_2{\cdot}2MeOH$, 0.003 g (0.243 mmol) of sodium acetate, and 0.081 g (0.487 mmol) of KI. The initially purple solution became red after refluxing for 10 min. and orange after a further 1.5 h. The solution was allowed to reflux for 10 h more before it was cooled and filtered. The solvent was removed by rotary evaporation leaving an orange residue. The residue was taken up in $CHCl_3$ and washed with 3 x 25 mL H_2O and dried over Na_2SO_4. Removal of the solvent *in vacuo* afforded 0.025 g (68.1%) of a fine orange powder. Single crystals suitable for X-ray analysis were grown by slow evaporation from a concentrated acetonitrile solution. $C_{11}H_{15}N_4O_2I_2Rh$ (**9**): ^1H NMR (DMSO-d_6): δ 1.82 (s, 3H, CH_3), 3.94 (s, 6H, CH_3), 6.08 (s, 2H, CH_2), 7.57 (d, 2H, CH), 7.59 (d, 2H, CH). ^{13}C NMR (DMSO-d_6): δ 24.17 (CH_3), 37.50 (CH_3), 62.04 (CH_2), 121.47 (CH), 125.01 (CH), 151.34 (d, Rh-C, $J_{Rh\text{-}C}$ = 42.39 Hz), 186.52 (O-C-O). Mz^+ ESI (M-$C_2H_3O_2$) Calc: 532.9 Found: 532.8.

***The Ag Complexes* (10a,b; 11a,b):** To a 100 ml round-bottomed flask was added 1.00 g of either **1a** or **1b** and 50 mL deionized H_2O. An excess, 2.5 molar equivalents, of Ag_2O was added to the solution. This suspension was stirred at rt for 15 min for **3a** or for 2 h for **3b**. The solution was filtered over Celite. Monitoring the solution by ^1H NMR showed complete conversion to the Ag complexes. Removal of the volatile components under vacuum caused the decomposition of **3a** and **3b**.

Alternatively, the addition of two molar equivalents of NH_4PF_6 to each solution resulted in precipitation of **4a** 1.77 g (89.3%) and **4b** 1.84g (92.7%) as white powders. Slow evaporation of concentrated acetonitrile solutions gave colorless crystals of **4a** and **4b** suitable for X-ray analysis.

$C_{18}H_{24}N_8Ag_2I_2$ (**10a**): ^{1}H NMR (D_2O): δ 3.96 (s, 3H, CH_3), 6.70 (s, 2H, N-CH_2-N), 7.77 (s, 2H, CH). ^{13}C NMR (D_2O): δ 38.63 (CH_3), 64.32 (N-CH_2-N), 123.84 (2 CH), Ag-C not observed. Mz$^+$ ESI Calc: 692.9 Found: 693.9

$C_{18}H_{24}N_8Ag_2P_2F_{12}$ (**11a**): ^{1}H NMR (DMSO-*d$_6$*) δ 3.83 (s, 3H, CH_3), 6.39 (br. s, 2H, N-CH_2-N), 7.24 (d, 1H, CH), 7.48 (d, 1H, CH). ^{13}C NMR (DMSO-*d$_6$*): δ 39.68 (CH_3), 65.11 (N-CH_2-N), 122.44 (CH), 125.19 (CH), 196.01 (Ag-C). Mz$^+$ ESI ($M - PF_6^-$) Calc: 710.97 Found: 712.5 Anal calc. for $C_{18}H_{24}N_8Ag_2P_2F_{12}$: C 25.14, H 3.05, N 13.03 Found C 24.93, H 2.67, N 12.85.

$C_{30}H_{48}N_8Ag_2I_2$ (**10b**): ^{1}H NMR (D_2O): δ 0.81 (t, 3H, CH_3), 1.24 (sextet, 2H CH_2), 1.79 (q, 2H, CH_2), 4.17 (t, 2H, CH_2), 6.61 (s, 1H, N-CH_2-N), 7.56 (br. s, 2H, 2 CH). ^{13}C NMR (D_2O): δ 12.89 (CH_3), 19.06 (CH_2), 31.17 (CH_2), 50.40 (CH_2), 59.11 (N-CH_2-N), 123.96 (2 CH), Ag-C not observed.

$C_{30}H_{48}N_8Ag_2P_2F_{12}$ (**11b**): ^{1}H NMR (DMSO-*d$_6$*): δ 0.78 (t, 3H, CH_3), 0.98 (sextet, 2H CH_2), 1.67 (q, 2H, CH_2), 4.01 (t, 2H, CH_2), 6.41 (br. s, 1H, N-CH_2-N), 7.24 (d, 1H, CH), 7.52 (d, 1H, CH). ^{13}C NMR (DMSO-*d$_6$*): δ 13.97 (CH_3), 20.44 (CH_2), 34.33 (CH_2), 52.99 (CH_2), 65.33 (N-CH_2-N), 122.56 (CH), 123.89 (CH), 196.27 (Ag-C). Mz$^+$ ESI Calculated: 883.17 Found: 880.8. Anal calc. for $C_{30}H_{48}N_8Ag_2P_2F_{12}$: C 35.11, H 4.71, N 10.92 Found: C 34.25, H 4.25, N 10.63.

The Rh Complexes **(12a,b):** To the aqueous filtrate containing the appropriate Ag salt (**3a** or **3b**) was added 0.5 molar equivalents of $RhCl_3{\cdot}3H_2O$, resulting in the immediate precipitation of brick red powders. The mixtures were stirred at rt for a further 20 min and filtered through a medium frit. The red powders were dried with an aspirator and heated in DMSO at 100 ^{0}C for 1 hour as the DMSO solution turned a bright orange. Removal of the solvent *in vacuo* afforded 0.063 g (62.1%) of **5a** and 0.096 g (56.3%) of **5b**. Crystals of **5b** suitable for X-ray analysis were grown by slow evaporation of a concentrated acetonitrile solution.

$C_{16}H_{24}N_8Cl_3Rh$ (**12a**): ^{1}H NMR (DMSO-d_6): δ 3.39 (s, 3H, CH_3), 6.39 (d, 1H, N-CH_2-N ($J_{H\text{-}H}$ = 12.5 Hz)), 7.02 (d, 1H, N-CH_2-N ($J_{H\text{-}H}$ = 12.5 Hz)), 7.44 (d, 1H, CH), 7.70 (d, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 36.50 (CH_3), 61.86 (N-CH_2-N), 122.32 (CH), 123.25 (CH), 169.82 (d, Rh-C, $J_{Rh\text{-}C}$ = 32.1 Hz). Mz$^+$ ESI (M-Cl) Calc: 526.3 Found: 525.1.

$C_{30}H_{48}N_8Cl_3Rh$ (**12b**): ^{1}H NMR (DMSO-d_6): δ 0.72 (t, 3H, CH_3), 1.10 (m, 2H CH_2), 1.51 (m, 1H, CH_2), 1.70 (m, 1H, CH_2) 3.64 (m, 1H, CH_2), 3.88 (m, 1H, CH_2), 6.44 (d, 1H, N-CH_2-N ($J_{H\text{-}H}$ = 12.4 Hz)), 7.08 (d, 1H, N-CH_2-N($J_{H\text{-}H}$ = 12.4 Hz)), 7.58 (br. s, 1H, CH), 7.75 (br. s, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 11.15 (CH_3), 17.45 (CH_2), 28.68 (CH_2), 46.55 (CH_2), 59.77 (N-CH_2-N), 119.03 (CH), 120.56 (CH), 168.05 (d, Rh-C, $J_{Rh\text{-}C}$ = 32.1 Hz). Mz$^+$ ESI (M-Cl) Calc: 694.5 Found: 693.4.

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APPENDICES

APPENDIX 1

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF THE CO-CRYSTALLIZED $C_{15}H_{24}N_4PtI_2$ (II-**2**) and $C_{30}H_{48}N_8PtI_2$ (II-**3**)

Table 1. Crystal data and structure refinement for $C_{32}H_{51}I_3N_9Pt_{1.50}$.

Identification code	$C_{32}H_{51}I_3N_9Pt_{1.50}$	
Empirical formula	C32 H51 I3 N9 Pt1.50	
Formula weight	1235.15	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1145(6) Å	α= 109.0220(10)°.
	b = 13.1692(8) Å	β= 95.8560(10)°.
	c = 16.5482(10) Å	γ = 92.7960(10)°.
Volume	2065.1(2) $Å^3$	
Z	2	
Density (calculated)	1.986 Mg/m^3	
Absorption coefficient	7.357 mm^{-1}	
F(000)	1164	
Crystal size	0.20 x 0.10 x 0.09 mm^3	
Theta range for data collection	1.64 to 27.49°.	
Index ranges	$-13 \leq h \leq 12$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$	
Reflections collected	25314	
Independent reflections	9127 [R(int) = 0.0272]	
Completeness to theta = 27.49°	96.4 %	
Max. and min. transmission	0.5573 and 0.3208	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9127 / 0 / 565
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0559
R indices (all data)	R1 = 0.0273, wR2 = 0.0569
Largest diff. peak and hole	1.558 and -0.727 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $C_{32}H_{51}I_3N_9Pt_{1.50}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	1755(1)	1433(1)	1337(1)	16(1)
Pt(2)	5000	10000	5000	14(1)
I(1)	3068(1)	-161(1)	1583(1)	23(1)
I(2)	380(1)	1469(1)	2635(1)	28(1)
I(3)	9608(1)	7068(1)	2187(1)	22(1)
N(1)	488(3)	3559(2)	1484(2)	23(1)
N(2)	110(3)	2337(2)	235(2)	19(1)
N(3)	1722(3)	1262(2)	-463(2)	20(1)
N(4)	3776(3)	1309(2)	24(2)	21(1)
N(5)	5596(3)	8032(2)	3462(2)	18(1)
N(6)	3656(3)	8571(2)	3302(2)	16(1)
N(7)	2177(3)	9165(2)	4346(2)	15(1)
N(8)	2468(3)	9305(2)	5683(2)	18(1)
N(9)	3768(4)	6036(3)	636(2)	45(1)
C(1)	2321(6)	6176(4)	3901(3)	40(1)
C(2)	3086(5)	5305(4)	3347(3)	37(1)
C(3)	2419(4)	4760(3)	2423(3)	29(1)
C(4)	1070(4)	4185(3)	2386(2)	27(1)
C(5)	-251(4)	3997(3)	944(3)	27(1)

C(6)	-483(4)	3238(3)	162(3)	24(1)
C(7)	708(3)	2530(3)	1047(2)	17(1)
C(8)	286(4)	1356(3)	-467(2)	20(1)
C(9)	2440(4)	1218(3)	-1141(2)	25(1)
C(10)	3723(4)	1250(3)	-831(2)	28(1)
C(11)	2541(3)	1320(3)	259(2)	18(1)
C(12)	5030(4)	1487(3)	594(3)	26(1)
C(13)	5442(5)	2689(4)	1055(3)	36(1)
C(14)	6784(5)	2914(5)	1576(3)	49(1)
C(15)	7078(8)	4106(7)	2125(5)	89(3)
C(16)	8262(6)	5676(5)	4732(4)	51(1)
C(17)	8221(4)	6736(4)	4554(3)	33(1)
C(18)	6885(4)	6835(3)	4066(3)	27(1)
C(19)	6904(4)	7869(3)	3857(3)	21(1)
C(20)	4979(4)	7396(3)	2655(2)	22(1)
C(21)	3763(4)	7725(3)	2553(2)	20(1)
C(22)	4788(3)	8775(3)	3860(2)	16(1)
C(23)	2484(4)	9172(3)	3506(2)	17(1)
C(24)	973(4)	8782(3)	4525(2)	22(1)
C(25)	1162(4)	8876(3)	5364(2)	23(1)
C(26)	3096(3)	9490(3)	5057(2)	16(1)
C(27)	3068(4)	9459(3)	6568(2)	24(1)
C(28)	3583(4)	8441(4)	6670(3)	30(1)
C(29)	4764(5)	8066(4)	6188(3)	33(1)
C(30)	5308(7)	7087(5)	6359(4)	57(2)
C(31)	3393(4)	5154(4)	334(3)	30(1)
C(32)	2936(5)	4016(4)	-69(3)	38(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{32}H_{51}I_3N_9Pt_{1.50}$.

Pt(1)-C(7)	1.983(3)
Pt(1)-C(11)	1.991(3)

Pt(1)-I(1)	2.6563(3)
Pt(1)-I(2)	2.6641(3)
Pt(2)-C(22)	2.026(3)
Pt(2)-C(22)#1	2.026(3)
Pt(2)-C(26)#1	2.030(3)
Pt(2)-C(26)	2.030(3)
N(1)-C(7)	1.354(4)
N(1)-C(5)	1.389(5)
N(1)-C(4)	1.492(5)
N(2)-C(7)	1.355(4)
N(2)-C(6)	1.389(5)
N(2)-C(8)	1.462(4)
N(3)-C(11)	1.361(4)
N(3)-C(9)	1.384(5)
N(3)-C(8)	1.464(4)
N(4)-C(11)	1.345(4)
N(4)-C(10)	1.387(5)
N(4)-C(12)	1.461(5)
N(5)-C(22)	1.352(4)
N(5)-C(20)	1.387(4)
N(5)-C(19)	1.473(5)
N(6)-C(22)	1.352(4)
N(6)-C(21)	1.390(4)
N(6)-C(23)	1.464(4)
N(7)-C(26)	1.358(4)
N(7)-C(24)	1.392(4)
N(7)-C(23)	1.458(4)
N(8)-C(26)	1.349(4)
N(8)-C(25)	1.390(5)
N(8)-C(27)	1.472(5)
N(9)-C(31)	1.133(5)
C(1)-C(2)	1.516(7)
C(2)-C(3)	1.529(6)
C(3)-C(4)	1.513(6)

C(5)-C(6)	1.343(5)
C(9)-C(10)	1.340(6)
C(12)-C(13)	1.531(6)
C(13)-C(14)	1.493(7)
C(14)-C(15)	1.532(9)
C(16)-C(17)	1.519(7)
C(17)-C(18)	1.536(6)
C(18)-C(19)	1.510(5)
C(20)-C(21)	1.337(5)
C(24)-C(25)	1.347(5)
C(27)-C(28)	1.516(6)
C(28)-C(29)	1.517(6)
C(29)-C(30)	1.523(7)
C(31)-C(32)	1.457(6)
C(7)-Pt(1)-C(11)	84.23(14)
C(7)-Pt(1)-I(1)	174.76(10)
C(11)-Pt(1)-I(1)	92.79(10)
C(7)-Pt(1)-I(2)	92.49(9)
C(11)-Pt(1)-I(2)	171.89(10)
I(1)-Pt(1)-I(2)	89.892(9)
C(22)-Pt(2)-C(22)#1	180.000(1)
C(22)-Pt(2)-C(26)#1	95.98(13)
C(22)#1-Pt(2)-C(26)#1	84.02(13)
C(22)-Pt(2)-C(26)	84.02(13)
C(22)#1-Pt(2)-C(26)	95.98(13)
C(26)#1-Pt(2)-C(26)	180.0
C(7)-N(1)-C(5)	110.3(3)
C(7)-N(1)-C(4)	125.4(3)
C(5)-N(1)-C(4)	123.9(3)
C(7)-N(2)-C(6)	110.9(3)
C(7)-N(2)-C(8)	121.5(3)
C(6)-N(2)-C(8)	126.9(3)
C(11)-N(3)-C(9)	111.4(3)
C(11)-N(3)-C(8)	122.5(3)

C(9)-N(3)-C(8)	125.7(3)
C(11)-N(4)-C(10)	110.4(3)
C(11)-N(4)-C(12)	126.4(3)
C(10)-N(4)-C(12)	122.7(3)
C(22)-N(5)-C(20)	110.6(3)
C(22)-N(5)-C(19)	124.6(3)
C(20)-N(5)-C(19)	124.7(3)
C(22)-N(6)-C(21)	111.3(3)
C(22)-N(6)-C(23)	122.3(3)
C(21)-N(6)-C(23)	126.4(3)
C(26)-N(7)-C(24)	111.1(3)
C(26)-N(7)-C(23)	122.6(3)
C(24)-N(7)-C(23)	126.2(3)
C(26)-N(8)-C(25)	110.3(3)
C(26)-N(8)-C(27)	126.2(3)
C(25)-N(8)-C(27)	123.3(3)
C(1)-C(2)-C(3)	114.6(4)
C(4)-C(3)-C(2)	112.2(4)
N(1)-C(4)-C(3)	112.0(3)
C(6)-C(5)-N(1)	107.4(3)
C(5)-C(6)-N(2)	106.4(3)
N(1)-C(7)-N(2)	105.0(3)
N(1)-C(7)-Pt(1)	134.2(3)
N(2)-C(7)-Pt(1)	120.6(2)
N(2)-C(8)-N(3)	107.2(3)
C(10)-C(9)-N(3)	105.7(3)
C(9)-C(10)-N(4)	107.9(3)
N(4)-C(11)-N(3)	104.5(3)
N(4)-C(11)-Pt(1)	136.1(3)
N(3)-C(11)-Pt(1)	119.3(2)
N(4)-C(12)-C(13)	111.9(3)
C(14)-C(13)-C(12)	113.8(4)
C(13)-C(14)-C(15)	112.1(6)
C(16)-C(17)-C(18)	112.8(4)

C(19)-C(18)-C(17)	111.4(3)
N(5)-C(19)-C(18)	112.5(3)
C(21)-C(20)-N(5)	107.5(3)
C(20)-C(21)-N(6)	106.1(3)
N(5)-C(22)-N(6)	104.6(3)
N(5)-C(22)-Pt(2)	133.8(2)
N(6)-C(22)-Pt(2)	121.6(2)
N(7)-C(23)-N(6)	108.1(3)
C(25)-C(24)-N(7)	105.9(3)
C(24)-C(25)-N(8)	107.6(3)
N(8)-C(26)-N(7)	105.1(3)
N(8)-C(26)-Pt(2)	133.5(3)
N(7)-C(26)-Pt(2)	121.2(2)
N(8)-C(27)-C(28)	112.9(3)
C(27)-C(28)-C(29)	114.2(3)
C(28)-C(29)-C(30)	112.3(4)
N(9)-C(31)-C(32)	178.6(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for $C_{32}H_{51}I_3N_9Pt_{1.50}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	15(1)	18(1)	15(1)	6(1)	3(1)	0(1)
Pt(2)	13(1)	16(1)	12(1)	4(1)	3(1)	-1(1)
I(1)	20(1)	30(1)	25(1)	17(1)	6(1)	6(1)
I(2)	30(1)	34(1)	27(1)	15(1)	16(1)	6(1)
I(3)	24(1)	21(1)	19(1)	6(1)	0(1)	2(1)
N(1)	28(2)	21(2)	21(2)	6(1)	8(1)	4(1)
N(2)	18(2)	19(2)	21(2)	7(1)	5(1)	2(1)

N(3)	23(2)	20(2)	15(1)	4(1)	3(1)	3(1)
N(4)	19(2)	26(2)	20(2)	11(1)	5(1)	5(1)
N(5)	17(2)	18(1)	16(1)	3(1)	3(1)	0(1)
N(6)	16(1)	18(1)	13(1)	5(1)	4(1)	1(1)
N(7)	14(1)	18(1)	14(1)	4(1)	4(1)	-2(1)
N(8)	17(1)	20(2)	15(1)	4(1)	4(1)	-2(1)
N(9)	54(3)	36(2)	37(2)	2(2)	10(2)	-1(2)
C(1)	55(3)	28(2)	31(2)	7(2)	-8(2)	-1(2)
C(2)	35(3)	38(2)	38(2)	16(2)	-3(2)	3(2)
C(3)	25(2)	30(2)	30(2)	6(2)	4(2)	2(2)
C(4)	37(2)	21(2)	21(2)	2(2)	10(2)	5(2)
C(5)	30(2)	21(2)	31(2)	8(2)	10(2)	10(2)
C(6)	25(2)	24(2)	28(2)	13(2)	7(2)	9(2)
C(7)	13(2)	20(2)	19(2)	6(1)	6(1)	-2(1)
C(8)	21(2)	18(2)	21(2)	7(1)	1(2)	1(1)
C(9)	32(2)	28(2)	17(2)	7(2)	8(2)	12(2)
C(10)	26(2)	42(2)	21(2)	14(2)	11(2)	11(2)
C(11)	19(2)	18(2)	18(2)	6(1)	5(1)	3(1)
C(12)	17(2)	36(2)	28(2)	15(2)	3(2)	4(2)
C(13)	32(2)	34(2)	39(2)	11(2)	2(2)	-2(2)
C(14)	36(3)	73(4)	37(3)	21(3)	4(2)	-16(3)
C(15)	56(4)	104(6)	65(4)	-24(4)	25(3)	-42(4)
C(16)	41(3)	63(4)	63(4)	42(3)	2(3)	15(3)
C(17)	24(2)	38(2)	41(3)	16(2)	2(2)	8(2)
C(18)	22(2)	27(2)	34(2)	14(2)	-1(2)	1(2)
C(19)	17(2)	21(2)	25(2)	6(2)	7(2)	1(1)
C(20)	28(2)	17(2)	17(2)	2(1)	6(2)	2(2)
C(21)	24(2)	21(2)	14(2)	3(1)	2(2)	-2(2)
C(22)	16(2)	17(2)	15(2)	6(1)	3(1)	-2(1)
C(23)	15(2)	20(2)	15(2)	5(1)	4(1)	2(1)
C(24)	17(2)	25(2)	22(2)	5(2)	3(2)	-2(2)
C(25)	16(2)	30(2)	21(2)	5(2)	7(2)	-6(2)
C(26)	17(2)	17(2)	15(2)	5(1)	5(1)	0(1)
C(27)	23(2)	33(2)	14(2)	7(2)	5(2)	-6(2)

C(28)	31(2)	38(2)	23(2)	17(2)	-2(2)	-10(2)
C(29)	35(2)	36(2)	33(2)	19(2)	1(2)	1(2)
C(30)	65(4)	48(3)	67(4)	32(3)	8(3)	17(3)
C(31)	26(2)	40(2)	23(2)	10(2)	3(2)	4(2)
C(32)	31(2)	39(3)	38(3)	11(2)	-4(2)	-7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for $C_{32}H_{51}I_3N_9Pt_{1.50}$.

	x	y	z	U(eq)
H(1A)	2900(50)	6420(40)	4480(30)	59
H(1B)	1430(60)	5800(40)	3970(30)	59
H(1C)	2090(50)	6680(40)	3600(30)	59
H(2A)	3200(50)	4790(40)	3590(30)	44
H(2B)	4060(50)	5680(40)	3370(30)	44
H(3A)	2190(40)	5310(40)	2120(30)	35
H(3B)	3020(40)	4230(40)	2130(30)	35
H(4A)	350(40)	4610(30)	2620(30)	33
H(4B)	1020(40)	3710(30)	2690(30)	33
H(5)	-450(40)	4720(40)	1150(30)	32
H(6)	-960(40)	3210(30)	-320(30)	29
H(8A)	-100(40)	1420(30)	-1030(30)	24
H(8B)	-120(40)	700(30)	-350(20)	24
H(9)	1980(40)	1170(30)	-1700(30)	30
H(10)	4540(40)	1260(30)	-1090(30)	33
H(12A)	5740(40)	1180(30)	190(30)	31
H(12B)	4930(40)	1140(30)	1030(30)	31
H(13A)	4810(50)	3090(40)	1450(30)	43
H(13B)	5380(40)	3070(40)	630(30)	43
H(14A)	6960(50)	2390(40)	1930(30)	59
H(14B)	7530(50)	2700(40)	1190(30)	59

H(15A)	6390(80)	4230(70)	2470(50)	133
H(15B)	7280(90)	4590(70)	1860(60)	133
H(15C)	8120(90)	4030(70)	2390(50)	133
H(16A)	9050(60)	5680(50)	5110(40)	76
H(16B)	7580(60)	5580(50)	5000(40)	76
H(16C)	8170(60)	5010(50)	4150(40)	76
H(17A)	8990(50)	6810(40)	4220(30)	40
H(17B)	8370(40)	7440(40)	5110(30)	40
H(18A)	6160(40)	6860(30)	4450(30)	33
H(18B)	6630(40)	6290(40)	3530(30)	33
H(19A)	7110(40)	8460(30)	4390(30)	26
H(19B)	7480(40)	7930(30)	3530(30)	26
H(20)	5370(40)	6860(30)	2310(30)	26
H(21)	3060(40)	7520(30)	2140(30)	24
H(23A)	2620(40)	9870(30)	3510(20)	20
H(23B)	1720(40)	8850(30)	3140(20)	20
H(24)	260(40)	8550(30)	4120(30)	26
H(25)	620(40)	8620(30)	5690(30)	28
H(27A)	3800(40)	10070(30)	6710(30)	29
H(27B)	2430(40)	9740(30)	6960(30)	29
H(28A)	3880(40)	8580(30)	7290(30)	36
H(28B)	2920(50)	7910(40)	6500(30)	36
H(29A)	4510(50)	7940(40)	5600(30)	40
H(29B)	5500(50)	8700(40)	6370(30)	40
H(30A)	6060(60)	6850(50)	6000(40)	85
H(30B)	5570(60)	7210(50)	7030(40)	85
H(30C)	4670(70)	6470(50)	6140(40)	85
H(32A)	3630(50)	3660(40)	-290(30)	56
H(32B)	2770(50)	3670(40)	400(30)	56
H(32C)	2200(50)	3900(40)	-500(30)	56

APPENDIX 2

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF $C_{15}H_{24}N_4PtI_2$ (II-**2**)

Table 1. Crystal data and structure refinement for $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$

Identification code	$C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$	
Empirical formula	C15.50 H24.50 Cl1.50 I2 N4 Pt	
Formula weight	768.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.6139(10) Å	α= 90°.
	b = 15.2592(15) Å	β= 102.937(2)°.
	c = 14.3928(14) Å	γ = 90°.
Volume	2271.9(4) $Å^3$	
Z	4	
Density (calculated)	2.248 Mg/m^3	
Absorption coefficient	9.076 mm^{-1}	
F(000)	1420	
Crystal size	0.06 x 0.03 x 0.02 mm^3	
Theta range for data collection	1.97 to 25.00°.	
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-17 \le l \le 17$	
Reflections collected	15924	
Independent reflections	3998 [R(int) = 0.0567]	
Completeness to theta = 25.00°	100.0 %	

Max. and min. transmission	0.8393 and 0.6120
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3998 / 0 / 228
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0858
R indices (all data)	R1 = 0.0693, wR2 = 0.0918
Largest diff. peak and hole	1.848 and -0.974 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt	9005(1)	2441(1)	2040(1)	21(1)
I(1)	10700(1)	3739(1)	2471(1)	25(1)
I(2)	8369(1)	2632(1)	3709(1)	40(1)
Cl(1)	5502(4)	10721(2)	4542(3)	73(1)
Cl(2)	7197(8)	9541(5)	5738(5)	70(2)
N(1)	10392(7)	2166(5)	402(5)	21(2)
N(2)	8343(7)	2312(4)	-30(5)	17(2)
N(3)	6778(7)	1704(5)	726(6)	24(2)
N(4)	7183(8)	857(5)	1946(6)	29(2)
C(1)	12084(14)	146(11)	368(12)	80(5)
C(2)	11428(12)	413(8)	1228(11)	59(4)
C(3)	11878(14)	1213(11)	1579(16)	118(8)
C(4)	11708(9)	2055(7)	969(7)	28(2)
C(5)	10069(9)	2076(6)	-573(7)	23(2)
C(6)	8758(9)	2171(6)	-849(7)	23(2)
C(7)	9329(8)	2317(5)	752(6)	17(2)
C(8)	6982(8)	2376(6)	54(7)	24(2)
C(9)	5856(10)	1057(7)	563(8)	37(3)
C(10)	6124(10)	524(8)	1323(8)	37(3)

C(11)	7586(9)	1585(7)	1586(7)	27(2)
C(12)	7828(10)	385(7)	2813(7)	32(3)
C(13)	8747(12)	-254(8)	2617(8)	47(3)
C(14)	9331(11)	-818(9)	3514(8)	50(3)
C(15)	10202(18)	-1552(11)	3343(11)	97(6)
C(16)	5800(20)	9607(16)	4917(19)	68(10)

Table 3. Bond lengths [Å] and angles [°] for $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$.

Pt-C(7)	1.969(9)
Pt-C(11)	1.990(10)
Pt-I(2)	2.6521(8)
Pt-I(1)	2.6539(7)
Cl(1)-C(16)	1.79(2)
Cl(1)-C(16)#1	1.80(3)
Cl(2)-C(16)	1.68(2)
N(1)-C(7)	1.354(11)
N(1)-C(5)	1.375(11)
N(1)-C(4)	1.461(12)
N(2)-C(7)	1.355(11)
N(2)-C(6)	1.365(12)
N(2)-C(8)	1.480(11)
N(3)-C(11)	1.351(12)
N(3)-C(9)	1.373(12)
N(3)-C(8)	1.459(12)
N(4)-C(11)	1.337(12)
N(4)-C(10)	1.369(13)
N(4)-C(12)	1.470(12)
C(1)-C(2)	1.602(19)
C(2)-C(3)	1.37(2)
C(3)-C(4)	1.544(19)

C(5)-C(6)	1.366(13)
C(9)-C(10)	1.341(15)
C(12)-C(13)	1.451(15)
C(13)-C(14)	1.560(15)
C(14)-C(15)	1.507(17)
C(16)-Cl(1)#1	1.80(3)
C(7)-Pt-C(11)	84.6(4)
C(7)-Pt-I(2)	175.4(2)
C(11)-Pt-I(2)	92.4(3)
C(7)-Pt-I(1)	92.3(2)
C(11)-Pt-I(1)	171.9(3)
I(2)-Pt-I(1)	90.19(2)
C(16)-Cl(1)-C(16)#1	73.0(17)
C(7)-N(1)-C(5)	111.0(8)
C(7)-N(1)-C(4)	125.7(8)
C(5)-N(1)-C(4)	123.2(8)
C(7)-N(2)-C(6)	112.3(7)
C(7)-N(2)-C(8)	121.2(7)
C(6)-N(2)-C(8)	126.2(8)
C(11)-N(3)-C(9)	110.0(8)
C(11)-N(3)-C(8)	122.9(8)
C(9)-N(3)-C(8)	126.7(8)
C(11)-N(4)-C(10)	109.9(8)
C(11)-N(4)-C(12)	127.4(8)
C(10)-N(4)-C(12)	122.2(9)
C(3)-C(2)-C(1)	109.6(14)
C(2)-C(3)-C(4)	123.2(16)
N(1)-C(4)-C(3)	112.9(9)
C(6)-C(5)-N(1)	106.9(8)
N(2)-C(6)-C(5)	105.7(8)
N(1)-C(7)-N(2)	104.0(8)
N(1)-C(7)-Pt	134.6(7)
N(2)-C(7)-Pt	121.2(6)

N(3)-C(8)-N(2)	107.5(7)
C(10)-C(9)-N(3)	106.5(9)
C(9)-C(10)-N(4)	107.6(9)
N(4)-C(11)-N(3)	105.9(8)
N(4)-C(11)-Pt	134.6(7)
N(3)-C(11)-Pt	119.4(7)
C(13)-C(12)-N(4)	111.7(9)
C(12)-C(13)-C(14)	111.7(10)
C(15)-C(14)-C(13)	114.8(11)
Cl(2)-C(16)-Cl(1)	109.7(12)
Cl(2)-C(16)-Cl(1)#1	108.7(14)
Cl(1)-C(16)-Cl(1)#1	107.0(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt	14(1)	31(1)	17(1)	-4(1)	2(1)	1(1)
I(1)	23(1)	28(1)	22(1)	-5(1)	-1(1)	0(1)
I(2)	24(1)	74(1)	23(1)	-16(1)	9(1)	-7(1)
Cl(1)	106(3)	49(2)	60(2)	-1(2)	13(2)	-6(2)
Cl(2)	79(5)	68(5)	60(5)	-24(4)	7(4)	8(4)
N(1)	14(4)	27(4)	23(4)	-1(3)	8(3)	-2(3)
N(2)	13(4)	13(4)	23(4)	1(3)	2(3)	3(3)
N(3)	20(4)	26(5)	25(5)	1(4)	2(4)	-7(3)
N(4)	25(5)	38(5)	23(5)	11(4)	6(4)	-2(4)
C(1)	50(9)	87(12)	103(13)	-26(10)	19(9)	0(8)
C(2)	36(7)	48(8)	105(12)	40(8)	40(8)	13(6)
C(3)	36(9)	77(12)	210(20)	41(14)	-35(11)	1(9)

C(4)	21(5)	37(6)	25(6)	-6(5)	6(4)	-1(5)
C(5)	27(6)	28(5)	17(5)	-5(4)	9(4)	3(4)
C(6)	24(5)	25(5)	21(5)	-4(4)	4(4)	-12(4)
C(7)	16(5)	11(5)	21(5)	5(4)	-3(4)	-3(4)
C(8)	16(5)	31(6)	23(5)	-3(4)	1(4)	2(4)
C(9)	25(6)	34(6)	47(7)	9(5)	2(5)	-19(5)
C(10)	22(6)	52(7)	39(7)	11(6)	9(5)	-19(5)
C(11)	20(5)	45(7)	17(5)	-5(5)	6(4)	-2(5)
C(12)	34(6)	35(6)	30(6)	18(5)	12(5)	-1(5)
C(13)	56(8)	49(8)	34(7)	15(6)	7(6)	-1(6)
C(14)	39(7)	76(9)	36(7)	10(6)	10(6)	21(7)
C(15)	127(15)	106(14)	60(11)	28(10)	28(10)	72(12)
C(16)	64(18)	51(16)	60(18)	38(14)	-50(15)	-42(14)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{15.5}H_{24.5}Cl_{1.5}I_2N_4Pt$.

	x	y	z	U(eq)
H(1A)	12049	645	-65	120
H(1B)	11618	-351	21	120
H(1C)	12988	-19	624	120
H(2A)	10477	436	997	71
H(2B)	11633	-33	1739	71
H(3A)	12818	1143	1840	142
H(3B)	11485	1332	2128	142
H(4A)	11937	2568	1395	33
H(4B)	12313	2038	537	33
H(5)	10647	1968	-978	28
H(6)	8243	2143	-1480	28
H(8A)	6810	2964	288	28
H(8B)	6391	2281	-575	28
H(9)	5164	998	19	44

H(10)	5662	9	1412	45
H(12A)	8285	811	3290	39
H(12B)	7170	84	3088	39
H(13A)	9453	53	2404	56
H(13B)	8308	-644	2094	56
H(14A)	9828	-429	4014	60
H(14B)	8613	-1072	3762	60
H(15A)	9783	-1876	2769	145
H(15B)	10368	-1949	3892	145
H(15C)	11022	-1308	3257	145
H(16)	5831	9223	4359	82

APPENDIX 3

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF

$C_{15}H_{24}N_4PtCl_2$ (II-**4**)

Table 1. Crystal data and structure refinement for $\mathbf{C_{16}H_{25.50}Cl_2N_{4.50}Pt}$.

Identification code	$\mathbf{C_{16}H_{25.50}Cl_2N_{4.50}Pt}$	
Empirical formula	C16 H25.50 Cl2 N4.50 Pt	
Formula weight	546.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P n	
Unit cell dimensions	a = 10.1753(5) Å	α= 90°.
	b = 14.4941(5) Å	β= 101.8510(10)°.
	c = 13.3930(5) Å	γ = 90°.
Volume	1933.12(14) $Å^3$	
Z	4	
Density (calculated)	1.879 Mg/m^3	
Absorption coefficient	7.541 mm^{-1}	
F(000)	1060	
Crystal size	0.10 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.40 to 27.50°.	
Index ranges	$-13 \leq h \leq 13$, $-18 \leq k \leq 18$, $-17 \leq l \leq 17$	
Reflections collected	23770	
Independent reflections	8621 [R(int) = 0.0366]	
Completeness to theta = 27.50°	99.6 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7043 and 0.5193
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8621 / 657 / 419
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0659
R indices (all data)	R1 = 0.0385, wR2 = 0.0674
Absolute structure parameter	0.478(7)
Extinction coefficient	0.00000(6)
Largest diff. peak and hole	1.974 and -1.288 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{16}H_{25.50}Cl_{2}N_{4.50}Pt}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2423(1)	4767(1)	3242(1)	13(1)
Cl(1)	4176(2)	3665(1)	3582(2)	20(1)
Cl(2)	1851(3)	4315(2)	4791(2)	28(1)
C(1A)	2750(11)	5038(6)	1899(8)	16(1)
N(1A)	3916(10)	5221(4)	1527(8)	17(2)
C(2A)	3578(11)	5406(6)	484(8)	21(2)
C(3A)	2258(11)	5382(6)	165(8)	18(2)
N(2A)	1721(9)	5183(4)	1081(7)	15(2)
C(4A)	321(10)	5137(5)	1142(8)	12(2)
N(3A)	112(8)	5686(4)	1972(7)	16(2)
C(5A)	-883(9)	6375(5)	1944(8)	21(2)
C(6A)	-648(9)	6759(6)	2842(8)	25(2)
N(4A)	489(8)	6315(5)	3495(6)	20(2)
C(7A)	938(9)	5624(5)	2933(7)	13(2)
C(8A)	5245(12)	5288(5)	2129(10)	18(1)
C(9A)	5398(10)	6070(6)	2910(8)	24(2)
C(10A)	4955(10)	6998(6)	2516(8)	27(2)

C(11A)	5690(10)	7359(6)	1684(8)	28(2)
C(12A)	1041(8)	6538(5)	4572(6)	28(2)
C(13A)	1574(7)	7518(5)	4687(6)	26(2)
C(14A)	2769(9)	7661(6)	4223(7)	33(2)
C(15A)	3457(9)	8600(6)	4576(8)	39(2)
Pt(2)	9530(1)	-139(1)	4209(1)	14(1)
Cl(3)	7784(2)	-1240(1)	3775(2)	20(1)
Cl(4)	10109(2)	-393(2)	2621(2)	33(1)
C(1B)	9218(11)	80(6)	5602(8)	16(1)
N(1B)	8095(10)	188(4)	5959(8)	15(2)
C(2B)	8408(12)	338(6)	6999(8)	23(2)
C(3B)	9800(10)	285(5)	7238(9)	19(2)
N(2B)	10210(9)	96(5)	6427(8)	18(2)
C(4B)	11622(10)	0(6)	6317(8)	19(2)
N(3B)	11850(8)	690(4)	5532(6)	16(2)
C(5B)	12792(9)	1341(6)	5645(8)	26(2)
C(6B)	12556(11)	1826(7)	4749(10)	42(3)
N(4B)	11512(8)	1421(5)	4173(6)	21(2)
C(7B)	11038(8)	745(5)	4633(7)	15(2)
C(8B)	6690(12)	291(5)	5335(10)	18(1)
C(9B)	6547(11)	1103(6)	4608(9)	30(2)
C(10B)	7047(10)	2013(6)	5087(8)	25(2)
C(11B)	6324(10)	2342(6)	5911(8)	32(2)
C(12B)	10842(8)	1878(6)	3212(6)	30(2)
C(13B)	9627(9)	2471(6)	3320(8)	35(2)
C(14B)	9104(8)	3009(6)	2409(6)	37(2)
C(15B)	7946(11)	3648(8)	2537(9)	66(4)
N(1S)	1227(9)	3049(5)	545(6)	52(2)
C(1S)	2231(10)	2721(6)	831(7)	40(2)
C(2S)	3571(13)	2335(8)	1214(11)	57(3)

Table 3. Bond lengths [Å] and angles [°] for $\mathbf{C_{16}H_{25.50}Cl_{2}N_{4.50}Pt}$.

Pt(1)-C(7A)	1.934(8)
Pt(1)-C(1A)	1.935(11)
Pt(1)-Cl(2)	2.360(2)
Pt(1)-Cl(1)	2.368(2)
C(1A)-N(2A)	1.367(13)
C(1A)-N(1A)	1.403(13)
N(1A)-C(2A)	1.395(14)
N(1A)-C(8A)	1.429(14)
C(2A)-C(3A)	1.323(14)
C(3A)-N(2A)	1.471(12)
N(2A)-C(4A)	1.445(13)
C(4A)-N(3A)	1.418(12)
N(3A)-C(7A)	1.388(11)
N(3A)-C(5A)	1.417(10)
C(5A)-C(6A)	1.302(13)
C(6A)-N(4A)	1.449(11)
N(4A)-C(7A)	1.386(10)
N(4A)-C(12A)	1.472(10)
C(8A)-C(9A)	1.528(13)
C(9A)-C(10A)	1.481(12)
C(10A)-C(11A)	1.555(12)
C(12A)-C(13A)	1.517(10)
C(13A)-C(14A)	1.490(11)
C(14A)-C(15A)	1.559(12)
Pt(2)-C(1B)	1.981(11)
Pt(2)-C(7B)	1.991(8)
Pt(2)-Cl(4)	2.350(2)
Pt(2)-Cl(3)	2.370(2)
C(1B)-N(2B)	1.335(14)
C(1B)-N(1B)	1.336(13)
N(1B)-C(2B)	1.381(14)
N(1B)-C(8B)	1.508(14)
C(2B)-C(3B)	1.388(15)

C(3B)-N(2B)	1.270(14)
N(2B)-C(4B)	1.481(14)
C(4B)-N(3B)	1.503(11)
N(3B)-C(7B)	1.315(11)
N(3B)-C(5B)	1.331(11)
C(5B)-C(6B)	1.369(14)
C(6B)-N(4B)	1.316(12)
N(4B)-C(7B)	1.302(10)
N(4B)-C(12B)	1.484(10)
C(8B)-C(9B)	1.515(13)
C(9B)-C(10B)	1.509(12)
C(10B)-C(11B)	1.523(13)
C(12B)-C(13B)	1.536(12)
C(13B)-C(14B)	1.454(11)
C(14B)-C(15B)	1.536(12)
N(1S)-C(1S)	1.121(11)
C(1S)-C(2S)	1.465(15)
C(7A)-Pt(1)-C(1A)	86.9(4)
C(7A)-Pt(1)-Cl(2)	92.5(3)
C(1A)-Pt(1)-Cl(2)	173.7(3)
C(7A)-Pt(1)-Cl(1)	177.4(2)
C(1A)-Pt(1)-Cl(1)	92.8(3)
Cl(2)-Pt(1)-Cl(1)	87.46(8)
N(2A)-C(1A)-N(1A)	104.5(10)
N(2A)-C(1A)-Pt(1)	121.7(8)
N(1A)-C(1A)-Pt(1)	133.4(8)
C(2A)-N(1A)-C(1A)	109.9(9)
C(2A)-N(1A)-C(8A)	124.2(10)
C(1A)-N(1A)-C(8A)	125.8(10)
C(3A)-C(2A)-N(1A)	110.1(10)
C(2A)-C(3A)-N(2A)	105.2(10)
C(1A)-N(2A)-C(4A)	123.3(9)
C(1A)-N(2A)-C(3A)	110.1(9)

C(4A)-N(2A)-C(3A)	126.6(9)
N(3A)-C(4A)-N(2A)	109.1(8)
C(7A)-N(3A)-C(5A)	111.3(7)
C(7A)-N(3A)-C(4A)	122.1(7)
C(5A)-N(3A)-C(4A)	126.6(8)
C(6A)-C(5A)-N(3A)	106.4(9)
C(5A)-C(6A)-N(4A)	109.9(8)
C(7A)-N(4A)-C(6A)	107.7(7)
C(7A)-N(4A)-C(12A)	126.0(7)
C(6A)-N(4A)-C(12A)	126.2(7)
N(4A)-C(7A)-N(3A)	104.6(7)
N(4A)-C(7A)-Pt(1)	132.7(7)
N(3A)-C(7A)-Pt(1)	122.5(6)
N(1A)-C(8A)-C(9A)	112.8(8)
C(10A)-C(9A)-C(8A)	116.7(9)
C(9A)-C(10A)-C(11A)	113.8(8)
N(4A)-C(12A)-C(13A)	111.2(7)
C(14A)-C(13A)-C(12A)	113.1(7)
C(13A)-C(14A)-C(15A)	110.4(7)
C(1B)-Pt(2)-C(7B)	83.7(4)
C(1B)-Pt(2)-Cl(4)	174.8(3)
C(7B)-Pt(2)-Cl(4)	92.1(3)
C(1B)-Pt(2)-Cl(3)	94.7(3)
C(7B)-Pt(2)-Cl(3)	177.1(2)
Cl(4)-Pt(2)-Cl(3)	89.26(9)
N(2B)-C(1B)-N(1B)	104.9(10)
N(2B)-C(1B)-Pt(2)	122.9(8)
N(1B)-C(1B)-Pt(2)	132.1(8)
C(1B)-N(1B)-C(2B)	110.0(10)
C(1B)-N(1B)-C(8B)	126.6(10)
C(2B)-N(1B)-C(8B)	122.7(10)
N(1B)-C(2B)-C(3B)	103.7(10)
N(2B)-C(3B)-C(2B)	108.3(10)
C(3B)-N(2B)-C(1B)	112.7(10)

C(3B)-N(2B)-C(4B)	127.0(10)
C(1B)-N(2B)-C(4B)	119.9(10)
N(2B)-C(4B)-N(3B)	107.4(7)
C(7B)-N(3B)-C(5B)	111.3(8)
C(7B)-N(3B)-C(4B)	121.5(8)
C(5B)-N(3B)-C(4B)	127.1(9)
N(3B)-C(5B)-C(6B)	105.9(9)
N(4B)-C(6B)-C(5B)	105.0(9)
C(7B)-N(4B)-C(6B)	113.1(8)
C(7B)-N(4B)-C(12B)	126.7(8)
C(6B)-N(4B)-C(12B)	118.7(8)
N(4B)-C(7B)-N(3B)	104.8(7)
N(4B)-C(7B)-Pt(2)	133.5(7)
N(3B)-C(7B)-Pt(2)	121.7(6)
N(1B)-C(8B)-C(9B)	112.9(9)
C(10B)-C(9B)-C(8B)	115.2(10)
C(9B)-C(10B)-C(11B)	114.3(8)
N(4B)-C(12B)-C(13B)	113.8(7)
C(14B)-C(13B)-C(12B)	112.6(8)
C(13B)-C(14B)-C(15B)	112.8(8)
N(1S)-C(1S)-C(2S)	177.3(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^{3}) for $\mathbf{C_{16}H_{25.50}Cl_{2}N_{4.50}Pt}$. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^{2} a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	12(1)	16(1)	13(1)	1(1)	4(1)	2(1)
Cl(1)	17(1)	22(1)	21(1)	6(1)	5(1)	5(1)
Cl(2)	24(1)	42(1)	21(1)	7(1)	10(1)	6(1)

C(1A)	16(2)	18(2)	15(2)	10(3)	6(1)	-4(3)
N(1A)	18(4)	16(4)	19(4)	-7(3)	11(3)	-5(3)
C(2A)	20(5)	21(4)	24(5)	3(4)	12(4)	-3(4)
C(3A)	22(5)	26(4)	15(4)	13(4)	19(3)	6(4)
N(2A)	16(4)	20(4)	10(4)	8(3)	7(3)	4(2)
C(4A)	9(4)	12(4)	13(4)	5(3)	-2(3)	0(3)
N(3A)	7(4)	16(3)	25(4)	0(3)	4(3)	1(3)
C(5A)	13(5)	13(4)	35(5)	4(3)	2(4)	4(3)
C(6A)	4(4)	30(4)	42(5)	-10(4)	8(3)	2(3)
N(4A)	14(4)	31(4)	16(3)	-11(3)	3(3)	5(3)
C(7A)	9(4)	10(3)	19(4)	1(3)	2(3)	-2(2)
C(8A)	8(2)	22(2)	25(2)	1(3)	4(1)	-1(3)
C(9A)	15(5)	37(4)	17(5)	2(3)	-4(4)	-6(4)
C(10A)	21(5)	25(4)	39(6)	-9(4)	21(4)	-6(3)
C(11A)	32(6)	16(4)	35(6)	3(4)	5(4)	-4(4)
C(12A)	24(4)	37(4)	19(4)	-7(3)	-2(3)	4(3)
C(13A)	16(4)	36(4)	22(4)	-5(3)	-3(3)	10(3)
C(14A)	42(6)	36(5)	27(5)	-1(4)	20(4)	12(4)
C(15A)	31(5)	40(5)	58(7)	4(4)	35(5)	2(4)
Pt(2)	9(1)	20(1)	11(1)	0(1)	3(1)	1(1)
Cl(3)	15(1)	21(1)	24(1)	-8(1)	5(1)	-1(1)
Cl(4)	13(1)	74(2)	14(1)	-11(1)	6(1)	-6(1)
C(1B)	16(2)	18(2)	15(2)	10(3)	6(1)	-4(3)
N(1B)	11(4)	23(4)	10(4)	-5(3)	2(3)	3(2)
C(2B)	24(5)	35(5)	12(4)	-4(4)	8(4)	-3(4)
C(3B)	8(4)	22(4)	22(5)	-7(3)	-8(3)	10(3)
N(2B)	10(4)	21(4)	23(4)	13(3)	4(3)	0(3)
C(4B)	19(4)	21(4)	18(5)	13(4)	4(4)	3(4)
N(3B)	18(4)	16(3)	14(4)	-2(3)	0(3)	0(3)
C(5B)	16(5)	30(4)	34(5)	-7(4)	10(4)	-7(3)
C(6B)	26(6)	26(5)	70(7)	18(5)	1(5)	-5(4)
N(4B)	17(4)	24(3)	22(4)	12(3)	1(3)	-2(3)
C(7B)	7(4)	23(4)	13(4)	3(3)	0(3)	-2(3)
C(8B)	8(2)	22(2)	25(2)	1(3)	4(1)	-1(3)

C(9B)	26(6)	29(4)	41(6)	8(4)	18(5)	1(4)
C(10B)	18(5)	30(4)	27(5)	6(4)	4(4)	2(3)
C(11B)	17(5)	36(5)	43(6)	-6(4)	9(4)	-9(4)
C(12B)	18(4)	50(5)	24(5)	18(4)	8(3)	-4(3)
C(13B)	34(5)	39(5)	31(5)	-1(4)	6(4)	-1(3)
C(14B)	36(5)	43(5)	26(5)	4(4)	-3(4)	7(4)
C(15B)	55(8)	68(8)	80(9)	3(6)	25(7)	29(5)
N(1S)	57(5)	46(5)	52(5)	-16(4)	8(4)	1(4)
C(1S)	54(6)	39(5)	26(5)	-9(4)	5(4)	-1(4)
C(2S)	53(5)	81(9)	36(5)	-31(5)	12(4)	9(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for $\mathbf{C_{16}H_{25.50}Cl_2N_{4.50}Pt}$.

	x	y	z	U(eq)
H(2A)	4204	5531	63	25
H(3A)	1764	5473	-511	22
H(4A)	-245	5365	499	14
H(4B)	67	4489	1243	14
H(5A)	-1582	6527	1381	25
H(6A)	-1148	7255	3040	30
H(8A)	5883	5390	1672	22
H(8B)	5484	4697	2491	22
H(9A)	4886	5902	3437	29
H(9B)	6356	6110	3251	29
H(10A)	5105	7439	3093	32
H(10B)	3978	6980	2228	32
H(11A)	5187	7877	1322	42
H(11B)	5752	6862	1200	42
H(11C)	6596	7565	2007	42
H(12A)	1777	6103	4846	33

H(12B)	331	6463	4972	33
H(13A)	853	7946	4363	31
H(13B)	1817	7673	5422	31
H(14A)	2490	7654	3470	40
H(14B)	3417	7152	4428	40
H(15A)	4217	8697	4242	59
H(15B)	3780	8592	5318	59
H(15C)	2807	9102	4391	59
H(2B)	7812	450	7447	27
H(3B)	10351	375	7894	23
H(4C)	11787	-633	6094	23
H(4D)	12240	121	6977	23
H(5B)	13484	1447	6227	31
H(6B)	13041	2344	4580	51
H(8C)	6059	370	5800	22
H(8D)	6439	-281	4938	22
H(9C)	7042	962	4063	37
H(9D)	5587	1171	4282	37
H(10C)	6945	2488	4546	30
H(10D)	8017	1956	5389	30
H(11D)	6604	2974	6110	48
H(11E)	6551	1936	6507	48
H(11F)	5352	2328	5647	48
H(12C)	10542	1399	2687	36
H(12D)	11504	2274	2968	36
H(13C)	8908	2064	3465	42
H(13D)	9894	2894	3906	42
H(14C)	8784	2584	1832	44
H(14D)	9838	3386	2238	44
H(15D)	7692	4038	1930	99
H(15E)	8234	4038	3140	99
H(15F)	7173	3276	2622	99
H(2SA)	4211	2838	1429	85

H(2SB)	3851	1978	672	85
H(2SC)	3548	1932	1798	85

APPENDIX 4

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF $C_{19}H_{26}N_4Pt$ (II-**5**)

Table 1. Crystal data and structure refinement for **$C_{19}H_{26}N_4Pt$**.

Identification code	**$C_{19}H_{26}N_4Pt$**	
Empirical formula	C19 H26 N4 Pt	
Formula weight	505.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P bca	
Unit cell dimensions	a = 13.6204(18) Å	α= 90°.
	b = 14.941(2) Å	β= 90°.
	c = 18.810(3) Å	γ = 90°.
Volume	3827.9(9) $Å^3$	
Z	8	
Density (calculated)	1.754 Mg/m^3	
Absorption coefficient	7.338 mm^{-1}	
F(000)	1968	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.17 to 27.65°.	
Index ranges	$-17 \leq h \leq 17$, $-19 \leq k \leq 19$, $-24 \leq l \leq 24$	
Reflections collected	30057	
Independent reflections	4363 [R(int) = 0.0506]	
Completeness to theta = 27.65°	97.6 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7105 and 0.3215
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4363 / 0 / 237
Goodness-of-fit on F^2	1.256
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1108
R indices (all data)	R1 = 0.0700, wR2 = 0.1207
Largest diff. peak and hole	2.877 and -1.002 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **$C_{19}H_{26}N_4Pt$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt	7616(1)	60(1)	3238(1)	18(1)
N(1)	9864(6)	-227(5)	3069(4)	26(2)
N(2)	9031(6)	-1437(5)	2982(4)	23(2)
N(3)	7611(6)	-1857(5)	3651(4)	24(2)
N(4)	6826(7)	-1159(6)	4471(5)	38(2)
C(1)	7905(7)	1018(6)	2509(5)	22(2)
C(2)	8029(7)	1530(6)	2035(5)	25(2)
C(3)	6286(7)	617(6)	3388(4)	22(2)
C(4)	5478(8)	937(7)	3458(6)	33(2)
C(5)	10374(11)	1739(8)	5170(6)	57(4)
C(6)	10453(10)	1683(8)	4355(6)	45(3)
C(7)	10123(9)	762(7)	4091(6)	40(3)
C(8)	10154(7)	685(6)	3282(6)	31(2)
C(9)	10522(8)	-913(7)	2938(6)	36(2)
C(10)	10005(8)	-1676(7)	2893(5)	32(2)
C(11)	8927(6)	-534(6)	3089(4)	17(2)
C(12)	8181(7)	-2030(6)	3006(5)	24(2)
C(13)	7342(8)	-2510(6)	4153(6)	39(3)
C(14)	6849(10)	-2055(8)	4652(8)	59(4)

C(15)	7305(7)	-1029(6)	3850(5)	24(2)
C(16)	6410(13)	-429(9)	4909(8)	76(6)
C(17)	7198(19)	57(10)	5347(11)	115(8)
C(18A)	6381(16)	767(13)	5689(9)	21(6)
C(19A)	7030(20)	1252(15)	6210(11)	34(7)
C(18B)	7050(20)	1047(15)	5690(12)	40(7)
C(19B)	6290(20)	968(14)	6242(11)	39(7)

Table 3. Bond lengths [Å] and angles [°] for $\mathbf{C_{19}H_{26}N_4Pt}$.

Pt-C(3)	2.013(9)
Pt-C(11)	2.014(9)
Pt-C(1)	2.022(9)
Pt-C(15)	2.037(9)
N(1)-C(11)	1.357(12)
N(1)-C(9)	1.383(12)
N(1)-C(8)	1.474(12)
N(2)-C(11)	1.372(11)
N(2)-C(10)	1.384(12)
N(2)-C(12)	1.459(12)
N(3)-C(15)	1.357(11)
N(3)-C(13)	1.407(12)
N(3)-C(12)	1.464(11)
N(4)-C(15)	1.352(12)
N(4)-C(14)	1.381(14)
N(4)-C(16)	1.481(14)
C(1)-C(2)	1.186(13)
C(3)-C(4)	1.208(14)
C(5)-C(6)	1.539(16)
C(6)-C(7)	1.530(14)
C(7)-C(8)	1.525(15)
C(9)-C(10)	1.344(15)
C(13)-C(14)	1.339(16)

C(16)-C(17)	1.54(3)
C(17)-C(18B)	1.63(3)
C(17)-C(18A)	1.67(3)
C(18A)-C(19A)	1.51(3)
C(18B)-C(19B)	1.47(4)
C(3)-Pt-C(11)	178.3(3)
C(3)-Pt-C(1)	88.7(3)
C(11)-Pt-C(1)	92.5(3)
C(3)-Pt-C(15)	93.7(3)
C(11)-Pt-C(15)	84.9(3)
C(1)-Pt-C(15)	171.6(3)
C(11)-N(1)-C(9)	111.3(8)
C(11)-N(1)-C(8)	123.8(8)
C(9)-N(1)-C(8)	124.1(8)
C(11)-N(2)-C(10)	111.8(8)
C(11)-N(2)-C(12)	120.7(8)
C(10)-N(2)-C(12)	127.4(8)
C(15)-N(3)-C(13)	111.6(8)
C(15)-N(3)-C(12)	123.5(7)
C(13)-N(3)-C(12)	124.9(8)
C(15)-N(4)-C(14)	109.9(8)
C(15)-N(4)-C(16)	124.1(8)
C(14)-N(4)-C(16)	125.9(9)
C(2)-C(1)-Pt	173.7(8)
C(4)-C(3)-Pt	177.9(9)
C(7)-C(6)-C(5)	110.7(9)
C(8)-C(7)-C(6)	112.6(9)
N(1)-C(8)-C(7)	109.5(8)
C(10)-C(9)-N(1)	107.5(9)
C(9)-C(10)-N(2)	105.9(9)
N(1)-C(11)-N(2)	103.3(7)
N(1)-C(11)-Pt	133.6(7)
N(2)-C(11)-Pt	123.0(7)

N(2)-C(12)-N(3)	109.9(7)
C(14)-C(13)-N(3)	104.3(9)
C(13)-C(14)-N(4)	109.4(10)
N(4)-C(15)-N(3)	104.8(7)
N(4)-C(15)-Pt	134.7(7)
N(3)-C(15)-Pt	120.6(6)
N(4)-C(16)-C(17)	112.3(13)
C(16)-C(17)-C(18B)	123.8(18)
C(16)-C(17)-C(18A)	92.3(16)
C(18B)-C(17)-C(18A)	35.5(11)
C(19A)-C(18A)-C(17)	99.4(17)
C(19B)-C(18B)-C(17)	107.1(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$C_{19}H_{26}N_4Pt$**. The anisotropic displacement factor exponent takes the form: $-2\square^{2}[h^{2} a^{*2}U^{11} + ... + 2 h k a^{*} b^{*} U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt	20(1)	19(1)	16(1)	-1(1)	-1(1)	0(1)
N(1)	25(4)	26(4)	26(4)	7(3)	3(3)	1(3)
N(2)	31(4)	23(4)	15(4)	0(3)	3(3)	2(3)
N(3)	25(4)	24(4)	23(4)	1(3)	4(3)	1(3)
N(4)	50(6)	30(5)	34(5)	12(4)	29(4)	12(4)
C(1)	21(4)	21(4)	25(5)	-5(4)	2(4)	1(3)
C(2)	29(5)	28(5)	19(4)	3(4)	4(4)	7(4)
C(3)	37(5)	18(4)	10(4)	-2(3)	2(3)	-3(4)
C(4)	31(6)	29(5)	40(6)	8(4)	3(5)	5(4)
C(5)	92(11)	43(7)	37(7)	1(6)	-37(7)	-22(7)
C(6)	64(8)	36(6)	35(6)	13(5)	-21(6)	-25(6)
C(7)	48(7)	32(6)	40(6)	10(5)	-18(5)	-14(5)

C(8)	18(5)	29(5)	45(6)	10(5)	-5(5)	-5(3)
C(9)	24(5)	39(6)	44(7)	12(5)	10(5)	6(4)
C(10)	38(6)	33(5)	26(5)	9(4)	11(4)	14(4)
C(11)	26(4)	26(4)	0(4)	3(3)	1(3)	4(3)
C(12)	32(5)	21(4)	17(4)	-5(3)	-2(4)	3(4)
C(13)	40(7)	22(5)	54(7)	10(4)	12(5)	1(5)
C(14)	77(10)	37(6)	64(9)	20(6)	46(8)	16(6)
C(15)	24(5)	23(4)	24(5)	4(4)	1(4)	0(3)
C(16)	113(13)	49(8)	66(10)	26(7)	71(10)	49(8)
C(17)	220(30)	40(8)	88(14)	-18(9)	0(16)	43(12)
C(18A)	27(13)	25(10)	9(10)	3(7)	1(7)	7(8)
C(19A)	59(17)	35(12)	8(11)	-9(8)	7(9)	-10(11)
C(18B)	49(16)	37(12)	34(14)	5(9)	1(10)	-7(11)
C(19B)	65(18)	30(11)	24(12)	-6(9)	-3(10)	-1(10)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)
for **$C_{19}H_{26}N_4Pt$**.

	x	y	z	U(eq)
H(2)	8129	1940	1656	30
H(4)	4842	1190	3513	40
H(5A)	9704	1587	5317	86
H(5B)	10530	2349	5325	86
H(5C)	10837	1318	5386	86
H(6A)	10037	2152	4137	54
H(6B)	11141	1791	4209	54
H(7A)	10554	298	4300	48
H(7B)	9445	647	4257	48
H(8A)	9700	1127	3068	37

H(8B)	10825	815	3109	37
H(9)	11213	-854	2888	43
H(10)	10257	-2261	2815	39
H(12A)	8401	-2661	3001	28
H(12B)	7764	-1929	2582	28
H(13)	7479	-3133	4142	46
H(14)	6561	-2308	5065	71
H(16A)	5910	-680	5235	91
H(16B)	6078	8	4595	91
H(17A)	7702	355	5050	138
H(17B)	7511	-329	5709	138
H(18A)	6112	1176	5323	25
H(18B)	5836	451	5929	25
H(19A)	6645	1699	6468	51
H(19B)	7565	1550	5953	51
H(19C)	7309	821	6548	51
H(18C)	7674	1260	5902	48
H(18D)	6844	1477	5319	48
H(19D)	6179	1553	6463	59
H(19E)	6502	539	6605	59
H(19F)	5675	758	6025	59

APPENDIX 5

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF $C_{29}H_{42}N_4PtSi_2$ (II-**6**)

Table 1. Crystal data and structure refinement for $\mathbf{C_{29}H_{42}N_4PtSi_2}$.

Identification code	$\mathbf{C_{29}H_{42}N_4PtSi_2}$	
Empirical formula	C29 H42 N4 Pt Si2	
Formula weight	697.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.469(3) Å	α= 90°.
	b = 15.045(3) Å	β= 96.841(4)°.
	c = 26.564(5) Å	γ = 90°.
Volume	6535(2) Å^3	
Z	8	
Density (calculated)	1.419 Mg/m^3	
Absorption coefficient	4.390 mm^{-1}	
F(000)	2800	
Crystal size	0.43 x 0.25 x 0.14 mm^3	
Theta range for data collection	1.25 to 28.30°.	
Index ranges	$-21 \leq h \leq 21$, $-19 \leq k \leq 19$, $-34 \leq l \leq 34$	
Reflections collected	57230	
Independent reflections	15623 [R(int) = 0.0610]	
Completeness to theta = 28.30°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	15623 / 0 / 665
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0703
R indices (all data)	R1 = 0.0513, wR2 = 0.0744
Largest diff. peak and hole	2.175 and -1.371 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **$C_{29}H_{42}N_4PtSi_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	4858(1)	7929(1)	1888(1)	14(1)
Pt(2)	-260(1)	7418(1)	6820(1)	15(1)
Si(1)	8666(1)	9269(1)	3582(1)	24(1)
Si(2)	7913(1)	4823(1)	845(1)	22(1)
Si(3)	3600(1)	8587(1)	8541(1)	30(1)
Si(4)	2914(1)	4389(1)	5870(1)	30(1)
N(1)	4043(2)	9317(2)	2545(1)	16(1)
N(2)	3218(2)	8328(2)	2202(1)	16(1)
N(3)	3144(2)	7630(2)	1401(1)	16(1)
N(4)	3913(2)	7793(2)	809(1)	18(1)
N(5)	-1033(2)	8820(2)	7492(1)	17(1)
N(6)	-1856(2)	7790(2)	7203(1)	15(1)
N(7)	-1987(2)	7017(2)	6417(1)	18(1)
N(8)	-1307(2)	7111(2)	5781(1)	19(1)
C(1)	6282(3)	10377(3)	3865(2)	28(1)
C(2)	5872(2)	10424(3)	3321(2)	21(1)
C(3)	5126(2)	9821(3)	3224(2)	21(1)
C(4)	4757(2)	9903(3)	2671(2)	19(1)
C(5)	4019(2)	8596(3)	2241(1)	16(1)
C(6)	3282(2)	9479(3)	2702(2)	20(1)
C(7)	2766(2)	8875(3)	2486(1)	18(1)

C(8)	2904(2)	7563(3)	1908(2)	18(1)
C(9)	3938(2)	7756(3)	1319(2)	17(1)
C(10)	2632(2)	7588(3)	952(2)	20(1)
C(11)	3111(2)	7692(3)	579(2)	21(1)
C(12)	4619(2)	7931(3)	534(2)	21(1)
C(13)	4841(2)	7104(3)	254(2)	23(1)
C(14)	5579(3)	7256(3)	-29(2)	29(1)
C(15)	5792(3)	6431(3)	-313(2)	49(2)
C(16)	5764(2)	8151(3)	2435(2)	19(1)
C(17)	6367(2)	8330(3)	2734(1)	19(1)
C(18)	7067(2)	8579(3)	3031(2)	19(1)
C(19)	7701(2)	8827(3)	3275(2)	24(1)
C(20)	8651(3)	10492(3)	3513(2)	41(1)
C(21)	8764(3)	8976(4)	4266(2)	44(1)
C(22)	9503(3)	8761(4)	3268(2)	49(2)
C(23)	5644(2)	7172(3)	1566(1)	19(1)
C(24)	6133(2)	6676(3)	1404(1)	18(1)
C(25)	6689(2)	6097(3)	1224(2)	19(1)
C(26)	7179(2)	5594(3)	1070(2)	23(1)
C(27)	8877(2)	5439(3)	781(2)	31(1)
C(28)	8114(3)	3907(3)	1315(2)	42(1)
C(29)	7474(3)	4377(4)	218(2)	44(1)
C(30)	1283(2)	9776(3)	8770(2)	29(1)
C(31)	855(2)	9873(3)	8231(2)	24(1)
C(32)	86(2)	9297(3)	8140(1)	20(1)
C(33)	-317(2)	9404(3)	7602(2)	20(1)
C(34)	-1074(2)	8086(3)	7201(1)	16(1)
C(35)	-1771(2)	8978(3)	7678(2)	20(1)
C(36)	-2285(2)	8338(3)	7496(2)	20(1)
C(37)	-2172(2)	6996(3)	6934(1)	17(1)
C(38)	-1219(2)	7157(3)	6295(2)	16(1)
C(39)	-2546(2)	6897(3)	5991(2)	22(1)
C(40)	-2122(2)	6960(3)	5590(2)	25(1)

C(41)	-666(3)	7225(3)	5449(2)	23(1)
C(42)	-461(3)	6365(3)	5191(2)	29(1)
C(43)	49(3)	6521(4)	4753(2)	44(1)
C(44)	871(3)	6888(4)	4923(2)	57(2)
C(45)	692(2)	7680(3)	7335(2)	18(1)
C(46)	1306(2)	7836(3)	7615(2)	20(1)
C(47)	2016(2)	8073(3)	7910(2)	20(1)
C(48)	2647(2)	8285(3)	8157(2)	22(1)
C(49)	3764(3)	9794(4)	8466(2)	59(2)
C(50)	3466(4)	8344(4)	9212(2)	62(2)
C(51)	4423(3)	7883(4)	8331(3)	72(2)
C(52)	518(2)	6669(3)	6488(1)	18(1)
C(53)	1011(2)	6167(3)	6340(2)	20(1)
C(54)	1590(2)	5592(3)	6182(2)	20(1)
C(55)	2103(2)	5094(3)	6054(2)	24(1)
C(56)	3829(3)	4549(5)	6347(3)	93(3)
C(57)	2566(3)	3223(3)	5868(2)	39(1)
C(58)	3139(3)	4749(3)	5233(2)	57(2)

Table 3. Bond lengths [Å] and angles [°] for **$C_{29}H_{42}N_4PtSi_2$**.

Pt(1)-C(16)	1.983(4)
Pt(1)-C(23)	1.992(4)
Pt(1)-C(9)	2.025(4)
Pt(1)-C(5)	2.026(4)
Pt(2)-C(52)	1.989(4)
Pt(2)-C(45)	1.994(4)
Pt(2)-C(38)	2.017(4)
Pt(2)-C(34)	2.038(4)
Si(1)-C(19)	1.823(4)
Si(1)-C(20)	1.850(5)
Si(1)-C(21)	1.856(5)

Si(1)-C(22)	1.858(5)
Si(2)-C(26)	1.828(4)
Si(2)-C(29)	1.860(5)
Si(2)-C(28)	1.863(5)
Si(2)-C(27)	1.863(4)
Si(3)-C(48)	1.825(4)
Si(3)-C(49)	1.851(6)
Si(3)-C(51)	1.857(5)
Si(3)-C(50)	1.857(6)
Si(4)-C(55)	1.817(4)
Si(4)-C(57)	1.846(5)
Si(4)-C(58)	1.855(5)
Si(4)-C(56)	1.865(5)
N(1)-C(5)	1.350(5)
N(1)-C(6)	1.389(4)
N(1)-C(4)	1.476(5)
N(2)-C(5)	1.371(4)
N(2)-C(7)	1.391(5)
N(2)-C(8)	1.451(5)
N(3)-C(9)	1.365(5)
N(3)-C(10)	1.377(5)
N(3)-C(8)	1.451(5)
N(4)-C(9)	1.352(5)
N(4)-C(11)	1.395(5)
N(4)-C(12)	1.461(5)
N(5)-C(34)	1.345(5)
N(5)-C(35)	1.386(5)
N(5)-C(33)	1.471(5)
N(6)-C(34)	1.364(4)
N(6)-C(36)	1.384(5)
N(6)-C(37)	1.457(5)
N(7)-C(38)	1.359(5)
N(7)-C(39)	1.383(5)
N(7)-C(37)	1.444(5)

N(8)-C(38)	1.358(5)
N(8)-C(40)	1.396(5)
N(8)-C(41)	1.464(5)
C(1)-C(2)	1.522(5)
C(2)-C(3)	1.524(5)
C(3)-C(4)	1.526(5)
C(6)-C(7)	1.327(5)
C(10)-C(11)	1.348(6)
C(12)-C(13)	1.516(5)
C(13)-C(14)	1.522(5)
C(14)-C(15)	1.514(6)
C(16)-C(17)	1.226(5)
C(17)-C(18)	1.370(5)
C(18)-C(19)	1.221(5)
C(23)-C(24)	1.214(5)
C(24)-C(25)	1.390(5)
C(25)-C(26)	1.211(5)
C(30)-C(31)	1.527(5)
C(31)-C(32)	1.531(5)
C(32)-C(33)	1.511(5)
C(35)-C(36)	1.334(5)
C(39)-C(40)	1.345(6)
C(41)-C(42)	1.521(6)
C(42)-C(43)	1.533(6)
C(43)-C(44)	1.482(7)
C(45)-C(46)	1.205(5)
C(46)-C(47)	1.375(5)
C(47)-C(48)	1.205(5)
C(52)-C(53)	1.209(5)
C(53)-C(54)	1.388(5)
C(54)-C(55)	1.208(5)
C(16)-Pt(1)-C(23)	86.58(15)
C(16)-Pt(1)-C(9)	177.60(16)

C(23)-Pt(1)-C(9)	94.19(15)
C(16)-Pt(1)-C(5)	94.14(15)
C(23)-Pt(1)-C(5)	174.72(16)
C(9)-Pt(1)-C(5)	85.29(15)
C(52)-Pt(2)-C(45)	85.46(15)
C(52)-Pt(2)-C(38)	94.35(15)
C(45)-Pt(2)-C(38)	179.64(16)
C(52)-Pt(2)-C(34)	174.58(16)
C(45)-Pt(2)-C(34)	94.09(15)
C(38)-Pt(2)-C(34)	86.13(15)
C(19)-Si(1)-C(20)	108.5(2)
C(19)-Si(1)-C(21)	108.7(2)
C(20)-Si(1)-C(21)	109.4(2)
C(19)-Si(1)-C(22)	107.6(2)
C(20)-Si(1)-C(22)	111.5(2)
C(21)-Si(1)-C(22)	111.1(3)
C(26)-Si(2)-C(29)	108.7(2)
C(26)-Si(2)-C(28)	108.7(2)
C(29)-Si(2)-C(28)	110.7(3)
C(26)-Si(2)-C(27)	108.5(2)
C(29)-Si(2)-C(27)	110.0(2)
C(28)-Si(2)-C(27)	110.1(2)
C(48)-Si(3)-C(49)	108.1(2)
C(48)-Si(3)-C(51)	107.5(2)
C(49)-Si(3)-C(51)	114.0(3)
C(48)-Si(3)-C(50)	107.1(2)
C(49)-Si(3)-C(50)	109.4(3)
C(51)-Si(3)-C(50)	110.5(3)
C(55)-Si(4)-C(57)	108.6(2)
C(55)-Si(4)-C(58)	108.0(2)
C(57)-Si(4)-C(58)	111.7(2)
C(55)-Si(4)-C(56)	107.6(2)
C(57)-Si(4)-C(56)	110.5(3)
C(58)-Si(4)-C(56)	110.3(3)

C(5)-N(1)-C(6)	111.0(3)
C(5)-N(1)-C(4)	125.6(3)
C(6)-N(1)-C(4)	123.3(3)
C(5)-N(2)-C(7)	111.0(3)
C(5)-N(2)-C(8)	123.5(3)
C(7)-N(2)-C(8)	125.5(3)
C(9)-N(3)-C(10)	111.5(3)
C(9)-N(3)-C(8)	122.0(3)
C(10)-N(3)-C(8)	126.5(3)
C(9)-N(4)-C(11)	110.5(3)
C(9)-N(4)-C(12)	125.2(3)
C(11)-N(4)-C(12)	124.3(3)
C(34)-N(5)-C(35)	111.1(3)
C(34)-N(5)-C(33)	126.1(3)
C(35)-N(5)-C(33)	122.8(3)
C(34)-N(6)-C(36)	110.8(3)
C(34)-N(6)-C(37)	123.2(3)
C(36)-N(6)-C(37)	126.0(3)
C(38)-N(7)-C(39)	112.0(3)
C(38)-N(7)-C(37)	122.6(3)
C(39)-N(7)-C(37)	125.4(3)
C(38)-N(8)-C(40)	110.9(3)
C(38)-N(8)-C(41)	126.9(3)
C(40)-N(8)-C(41)	122.1(3)
C(1)-C(2)-C(3)	112.9(3)
C(2)-C(3)-C(4)	109.6(3)
N(1)-C(4)-C(3)	112.7(3)
N(1)-C(5)-N(2)	103.9(3)
N(1)-C(5)-Pt(1)	134.6(3)
N(2)-C(5)-Pt(1)	121.5(3)
C(7)-C(6)-N(1)	107.7(3)
C(6)-C(7)-N(2)	106.4(3)
N(2)-C(8)-N(3)	109.0(3)
N(4)-C(9)-N(3)	104.5(3)

N(4)-C(9)-Pt(1)	132.3(3)
N(3)-C(9)-Pt(1)	123.0(3)
C(11)-C(10)-N(3)	106.3(3)
C(10)-C(11)-N(4)	107.2(3)
N(4)-C(12)-C(13)	112.4(3)
C(12)-C(13)-C(14)	111.9(3)
C(15)-C(14)-C(13)	111.7(4)
C(17)-C(16)-Pt(1)	173.1(4)
C(16)-C(17)-C(18)	174.4(4)
C(19)-C(18)-C(17)	176.6(5)
C(18)-C(19)-Si(1)	174.0(4)
C(24)-C(23)-Pt(1)	175.1(4)
C(23)-C(24)-C(25)	179.1(5)
C(26)-C(25)-C(24)	179.4(5)
C(25)-C(26)-Si(2)	179.2(4)
C(30)-C(31)-C(32)	111.9(3)
C(33)-C(32)-C(31)	110.5(3)
N(5)-C(33)-C(32)	112.1(3)
N(5)-C(34)-N(6)	104.3(3)
N(5)-C(34)-Pt(2)	134.4(3)
N(6)-C(34)-Pt(2)	121.3(3)
C(36)-C(35)-N(5)	107.0(3)
C(35)-C(36)-N(6)	106.8(3)
N(7)-C(37)-N(6)	110.2(3)
N(8)-C(38)-N(7)	103.9(3)
N(8)-C(38)-Pt(2)	133.4(3)
N(7)-C(38)-Pt(2)	122.7(3)
C(40)-C(39)-N(7)	106.3(3)
C(39)-C(40)-N(8)	106.9(4)
N(8)-C(41)-C(42)	112.7(3)
C(41)-C(42)-C(43)	112.5(4)
C(44)-C(43)-C(42)	113.0(4)
C(46)-C(45)-Pt(2)	174.6(3)
C(45)-C(46)-C(47)	175.4(5)

C(48)-C(47)-C(46)	178.3(4)
C(47)-C(48)-Si(3)	178.8(4)
C(53)-C(52)-Pt(2)	172.6(4)
C(52)-C(53)-C(54)	178.5(5)
C(55)-C(54)-C(53)	178.6(5)
C(54)-C(55)-Si(4)	177.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **$C_{29}H_{42}N_4PtSi_2$**. The anisotropic displacement factor exponent takes the form: $-2\square^{2}[\, h^{2} a^{*2}U^{11} + ... + 2 h k a^{*} b^{*} U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	11(1)	16(1)	15(1)	-1(1)	2(1)	1(1)
Pt(2)	12(1)	16(1)	16(1)	0(1)	3(1)	1(1)
Si(1)	18(1)	30(1)	23(1)	-1(1)	-3(1)	-3(1)
Si(2)	20(1)	19(1)	27(1)	-1(1)	9(1)	3(1)
Si(3)	19(1)	35(1)	35(1)	-16(1)	-4(1)	2(1)
Si(4)	20(1)	28(1)	40(1)	-16(1)	3(1)	6(1)
N(1)	17(2)	16(2)	16(2)	-1(1)	3(1)	-1(1)
N(2)	14(2)	16(2)	19(2)	-1(1)	4(1)	0(1)
N(3)	12(2)	17(2)	19(2)	-4(1)	2(1)	1(1)
N(4)	16(2)	20(2)	19(2)	-1(2)	2(1)	3(1)
N(5)	16(2)	15(2)	19(2)	-1(1)	1(1)	0(1)
N(6)	13(2)	17(2)	17(2)	0(1)	3(1)	0(1)
N(7)	15(2)	18(2)	19(2)	-4(2)	0(1)	1(1)
N(8)	22(2)	17(2)	18(2)	-3(2)	1(1)	4(1)
C(1)	31(2)	27(3)	27(2)	-7(2)	1(2)	-7(2)
C(2)	24(2)	12(2)	25(2)	-5(2)	2(2)	0(2)
C(3)	20(2)	17(2)	25(2)	-4(2)	4(2)	-1(2)

C(4)	18(2)	16(2)	24(2)	-2(2)	3(2)	-1(2)
C(5)	16(2)	15(2)	17(2)	2(2)	1(2)	2(2)
C(6)	16(2)	22(2)	23(2)	-4(2)	6(2)	5(2)
C(7)	14(2)	21(2)	20(2)	0(2)	4(2)	3(2)
C(8)	15(2)	19(2)	21(2)	-2(2)	6(2)	1(2)
C(9)	17(2)	14(2)	20(2)	-5(2)	4(2)	3(2)
C(10)	19(2)	18(2)	23(2)	-6(2)	0(2)	-1(2)
C(11)	17(2)	28(3)	16(2)	-4(2)	-4(2)	3(2)
C(12)	20(2)	24(2)	17(2)	-1(2)	0(2)	-2(2)
C(13)	22(2)	23(2)	24(2)	-3(2)	5(2)	1(2)
C(14)	29(2)	31(3)	28(3)	-5(2)	11(2)	-4(2)
C(15)	47(3)	41(3)	65(4)	-13(3)	34(3)	2(3)
C(16)	20(2)	18(2)	18(2)	0(2)	6(2)	7(2)
C(17)	19(2)	20(2)	17(2)	-1(2)	2(2)	4(2)
C(18)	20(2)	17(2)	21(2)	1(2)	5(2)	5(2)
C(19)	25(2)	26(3)	21(2)	-2(2)	2(2)	0(2)
C(20)	28(2)	40(3)	55(3)	5(3)	1(2)	-10(2)
C(21)	48(3)	52(4)	28(3)	7(2)	-10(2)	-24(3)
C(22)	26(3)	65(4)	56(4)	-16(3)	3(2)	-4(3)
C(23)	13(2)	30(3)	14(2)	1(2)	-2(2)	-7(2)
C(24)	17(2)	19(2)	17(2)	-2(2)	3(2)	-3(2)
C(25)	19(2)	19(2)	19(2)	3(2)	1(2)	-1(2)
C(26)	25(2)	22(2)	23(2)	3(2)	7(2)	3(2)
C(27)	23(2)	27(3)	44(3)	0(2)	10(2)	1(2)
C(28)	37(3)	31(3)	61(4)	17(3)	23(3)	12(2)
C(29)	37(3)	54(4)	42(3)	-23(3)	5(2)	3(3)
C(30)	26(2)	31(3)	29(3)	-8(2)	3(2)	-5(2)
C(31)	20(2)	19(2)	32(2)	-3(2)	6(2)	-4(2)
C(32)	19(2)	20(2)	22(2)	-6(2)	7(2)	-2(2)
C(33)	15(2)	20(2)	24(2)	-3(2)	3(2)	-4(2)
C(34)	12(2)	18(2)	17(2)	1(2)	2(2)	2(2)
C(35)	20(2)	17(2)	22(2)	-4(2)	4(2)	2(2)
C(36)	15(2)	25(2)	20(2)	-1(2)	5(2)	5(2)
C(37)	16(2)	18(2)	17(2)	-3(2)	4(2)	0(2)

C(38)	18(2)	10(2)	19(2)	-2(2)	4(2)	5(2)
C(39)	19(2)	23(2)	22(2)	-5(2)	-2(2)	6(2)
C(40)	25(2)	26(3)	21(2)	-4(2)	-5(2)	6(2)
C(41)	29(2)	22(2)	17(2)	1(2)	5(2)	3(2)
C(42)	33(2)	29(3)	27(2)	-3(2)	8(2)	2(2)
C(43)	43(3)	50(4)	42(3)	-14(3)	16(2)	6(3)
C(44)	49(3)	74(5)	50(4)	-12(3)	18(3)	4(3)
C(45)	18(2)	14(2)	23(2)	0(2)	7(2)	3(2)
C(46)	19(2)	21(2)	22(2)	-2(2)	5(2)	3(2)
C(47)	22(2)	19(2)	19(2)	-3(2)	2(2)	3(2)
C(48)	21(2)	22(3)	23(2)	-2(2)	8(2)	3(2)
C(49)	37(3)	56(4)	87(5)	-21(3)	23(3)	-15(3)
C(50)	81(4)	65(4)	33(3)	-7(3)	-24(3)	17(4)
C(51)	23(3)	78(5)	110(6)	-62(4)	-11(3)	9(3)
C(52)	15(2)	22(2)	17(2)	-2(2)	2(2)	-3(2)
C(53)	15(2)	22(2)	23(2)	0(2)	5(2)	-1(2)
C(54)	21(2)	21(2)	19(2)	1(2)	5(2)	-1(2)
C(55)	25(2)	20(2)	29(2)	3(2)	8(2)	4(2)
C(56)	39(3)	88(5)	139(7)	-74(5)	-47(4)	38(3)
C(57)	57(3)	25(3)	35(3)	0(2)	8(2)	13(2)
C(58)	73(4)	30(3)	78(4)	-17(3)	54(3)	-17(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **$C_{29}H_{42}N_4PtSi_2$**.

	x	y	z	U(eq)
H(1A)	5884	10530	4097	42
H(1B)	6739	10798	3910	42
H(1C)	6486	9773	3937	42
H(2A)	6273	10254	3088	25

H(2B)	5702	11045	3242	25
H(3A)	4715	9992	3449	25
H(3B)	5289	9197	3299	25
H(4A)	4588	10527	2602	23
H(4B)	5179	9753	2449	23
H(6)	3154	9940	2924	24
H(7)	2200	8825	2520	22
H(8A)	2300	7545	1890	22
H(8B)	3125	7010	2072	22
H(10)	2056	7503	913	24
H(11)	2936	7695	225	25
H(12A)	5093	8113	776	25
H(12B)	4498	8420	287	25
H(13A)	4368	6923	10	27
H(13B)	4961	6614	500	27
H(14A)	5462	7751	-273	34
H(14B)	6054	7429	215	34
H(15A)	5931	5946	-71	73
H(15B)	6262	6556	-496	73
H(15C)	5323	6257	-554	73
H(20A)	8535	10647	3153	62
H(20B)	9184	10735	3649	62
H(20C)	8225	10742	3699	62
H(21A)	8294	9213	4417	66
H(21B)	9269	9233	4438	66
H(21C)	8780	8329	4303	66
H(22A)	9501	8116	3317	74
H(22B)	10030	9005	3417	74
H(22C)	9420	8896	2905	74
H(27A)	8772	5895	518	46
H(27B)	9292	5024	687	46
H(27C)	9074	5723	1105	46
H(28A)	8357	4153	1641	63

H(28B)	8492	3478	1193	63
H(28C)	7598	3610	1361	63
H(29A)	6972	4048	256	66
H(29B)	7871	3979	87	66
H(29C)	7349	4871	-20	66
H(30A)	911	9963	9012	43
H(30B)	1774	10150	8812	43
H(30C)	1439	9154	8833	43
H(31A)	1238	9701	7987	28
H(31B)	704	10504	8168	28
H(32A)	234	8665	8204	24
H(32B)	-303	9472	8380	24
H(33A)	-490	10030	7546	24
H(33B)	85	9266	7364	24
H(35)	-1888	9452	7894	23
H(36)	-2839	8270	7557	24
H(37A)	-1923	6461	7107	20
H(37B)	-2772	6962	6938	20
H(39)	-3116	6791	5983	26
H(40)	-2337	6912	5243	30
H(41A)	-167	7455	5651	27
H(41B)	-847	7673	5186	27
H(42A)	-976	6059	5060	35
H(42B)	-155	5970	5444	35
H(43A)	111	5951	4575	53
H(43B)	-247	6938	4508	53
H(44A)	815	7461	5090	85
H(44B)	1171	6971	4629	85
H(44C)	1172	6474	5162	85
H(49A)	3740	9938	8105	88
H(49B)	4302	9959	8640	88
H(49C)	3338	10124	8615	88
H(50A)	2968	8635	9298	94

H(50B)	3939	8569	9434	94
H(50C)	3420	7701	9258	94
H(51A)	4234	7266	8297	108
H(51B)	4909	7914	8583	108
H(51C)	4560	8097	8003	108
H(56A)	3946	5185	6387	140
H(56B)	4300	4248	6230	140
H(56C)	3721	4298	6672	140
H(57A)	2475	3048	6212	58
H(57B)	2983	2838	5749	58
H(57C)	2054	3163	5641	58
H(58A)	2637	4728	4995	85
H(58B)	3549	4352	5115	85
H(58C)	3351	5359	5253	85

APPENDIX 6

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF $C_{23}H_{26}N_4Pt$ (II-**7**)

Table 1. Crystal data and structure refinement for **$C_{23}H_{26}N_4Pt$**.

Identification code	**$C_{23}H_{26}N_4Pt$**	
Empirical formula	C23 H26 N4 Pt	
Formula weight	553.57	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.587(5) Å	α= 90°.
	b = 22.148(13) Å	β= 91.762(10)°.
	c = 11.267(6) Å	γ = 90°.
Volume	2142(2) $Å^3$	
Z	4	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	6.566 mm^{-1}	
F(000)	1080	
Crystal size	0.19 x 0.11 x 0.05 mm^3	
Theta range for data collection	1.84 to 25.00°.	
Index ranges	$-10 \leq h \leq 10$, $-26 \leq k \leq 26$, $-13 \leq l \leq 13$	
Reflections collected	14625	
Independent reflections	3678 [R(int) = 0.0511]	
Completeness to theta = 25.00°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3678 / 0 / 357
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0629
R indices (all data)	R1 = 0.0357, wR2 = 0.0654
Largest diff. peak and hole	1.646 and -1.245 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{23}H_{26}N_4Pt}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt	5699(1)	1577(1)	7434(1)	14(1)
N(1)	4637(5)	266(2)	6868(3)	20(1)
N(2)	2797(5)	920(2)	6748(3)	16(1)
N(3)	2382(5)	1771(2)	7984(3)	17(1)
N(4)	3708(5)	2081(2)	9492(3)	17(1)
C(1)	8065(8)	-380(3)	10258(5)	35(2)
C(2)	7833(7)	-379(3)	8917(5)	26(1)
C(3)	6347(7)	-52(2)	8537(5)	24(1)
C(4)	6112(6)	-22(2)	7191(4)	21(1)
C(5)	4342(6)	867(2)	6980(4)	15(1)
C(6)	3268(6)	-41(2)	6577(4)	22(1)
C(7)	2117(7)	366(2)	6493(5)	23(1)
C(8)	2000(7)	1501(2)	6839(5)	18(1)
C(9)	3858(6)	1843(2)	8397(4)	16(1)
C(10)	1303(7)	1953(2)	8801(5)	21(1)
C(11)	2143(6)	2152(2)	9744(5)	22(1)
C(12)	4986(7)	2192(2)	10349(5)	22(1)
C(13)	5580(7)	1606(2)	10898(5)	26(1)
C(14)	6986(8)	1689(3)	11724(5)	30(1)
C(15)	8482(8)	1817(3)	11114(6)	36(2)

C(16)	7378(6)	1336(2)	6339(4)	17(1)
C(17)	8280(6)	1219(2)	5569(4)	19(1)
C(18)	9316(6)	1124(2)	4667(4)	20(1)
C(19)	10234(7)	1043(3)	3912(5)	33(1)
C(20)	6967(6)	2294(2)	7895(4)	16(1)
C(21)	7753(6)	2719(2)	8217(4)	17(1)
C(22)	8677(6)	3159(2)	8739(4)	18(1)
C(23)	9515(7)	3519(2)	9226(5)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **$C_{23}H_{26}N_4Pt$**.

Pt-C(20)	1.985(5)
Pt-C(16)	1.999(5)
Pt-C(5)	2.013(5)
Pt-C(9)	2.031(5)
N(1)-C(5)	1.362(6)
N(1)-C(6)	1.389(6)
N(1)-C(4)	1.455(7)
N(2)-C(5)	1.350(6)
N(2)-C(7)	1.386(6)
N(2)-C(8)	1.462(6)
N(3)-C(9)	1.346(6)
N(3)-C(10)	1.385(6)
N(3)-C(8)	1.451(6)
N(4)-C(9)	1.353(6)
N(4)-C(11)	1.391(6)
N(4)-C(12)	1.460(7)
C(1)-C(2)	1.518(8)
C(2)-C(3)	1.516(7)
C(3)-C(4)	1.525(7)
C(6)-C(7)	1.338(8)
C(10)-C(11)	1.342(7)

C(12)-C(13)	1.519(8)
C(13)-C(14)	1.513(8)
C(14)-C(15)	1.503(9)
C(16)-C(17)	1.209(6)
C(17)-C(18)	1.386(7)
C(18)-C(19)	1.192(7)
C(20)-C(21)	1.207(7)
C(21)-C(22)	1.378(7)
C(22)-C(23)	1.196(8)
C(20)-Pt-C(16)	88.55(19)
C(20)-Pt-C(5)	177.90(18)
C(16)-Pt-C(5)	93.29(19)
C(20)-Pt-C(9)	93.34(19)
C(16)-Pt-C(9)	174.14(19)
C(5)-Pt-C(9)	84.74(19)
C(5)-N(1)-C(6)	110.0(4)
C(5)-N(1)-C(4)	124.7(4)
C(6)-N(1)-C(4)	124.6(4)
C(5)-N(2)-C(7)	111.6(4)
C(5)-N(2)-C(8)	121.5(4)
C(7)-N(2)-C(8)	126.8(4)
C(9)-N(3)-C(10)	112.3(4)
C(9)-N(3)-C(8)	122.7(4)
C(10)-N(3)-C(8)	124.9(5)
C(9)-N(4)-C(11)	110.5(4)
C(9)-N(4)-C(12)	125.3(4)
C(11)-N(4)-C(12)	123.9(4)
C(3)-C(2)-C(1)	111.4(5)
C(2)-C(3)-C(4)	112.7(4)
N(1)-C(4)-C(3)	110.8(4)
N(2)-C(5)-N(1)	104.6(4)
N(2)-C(5)-Pt	122.6(3)
N(1)-C(5)-Pt	132.8(4)
C(7)-C(6)-N(1)	107.8(5)

C(6)-C(7)-N(2)	106.0(5)
N(3)-C(8)-N(2)	109.4(4)
N(3)-C(9)-N(4)	104.2(4)
N(3)-C(9)-Pt	121.5(3)
N(4)-C(9)-Pt	134.3(4)
C(11)-C(10)-N(3)	105.5(5)
C(10)-C(11)-N(4)	107.5(5)
N(4)-C(12)-C(13)	111.2(4)
C(14)-C(13)-C(12)	113.5(5)
C(15)-C(14)-C(13)	114.8(5)
C(17)-C(16)-Pt	172.1(4)
C(16)-C(17)-C(18)	176.3(5)
C(19)-C(18)-C(17)	178.4(6)
C(21)-C(20)-Pt	177.4(4)
C(20)-C(21)-C(22)	171.7(5)
C(23)-C(22)-C(21)	176.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$C_{23}H_{26}N_4Pt$**. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt	16(1)	13(1)	14(1)	-2(1)	2(1)	-1(1)
N(1)	24(3)	16(2)	19(2)	-2(2)	-1(2)	1(2)
N(2)	19(2)	14(2)	16(2)	-2(2)	1(2)	1(2)
N(3)	21(3)	13(2)	17(2)	-7(2)	5(2)	3(2)
N(4)	19(2)	16(2)	17(2)	-1(2)	2(2)	-1(2)
C(1)	37(4)	37(4)	30(3)	7(3)	-3(3)	9(3)
C(2)	20(3)	27(3)	32(3)	2(3)	2(3)	3(2)
C(3)	27(3)	21(3)	25(3)	3(2)	2(3)	3(2)

C(4)	22(3)	17(2)	24(3)	-6(2)	3(2)	-3(2)
C(5)	17(3)	17(2)	11(2)	-2(2)	1(2)	-1(2)
C(6)	24(3)	20(3)	22(3)	-7(2)	2(2)	-4(2)
C(7)	24(3)	20(3)	25(3)	-6(2)	-1(3)	-5(2)
C(8)	13(3)	17(3)	25(3)	-2(2)	-1(2)	0(2)
C(9)	13(3)	12(2)	24(3)	-1(2)	5(2)	-2(2)
C(10)	16(3)	16(3)	30(3)	-3(2)	6(2)	5(2)
C(11)	23(3)	21(3)	22(3)	-3(2)	7(2)	3(2)
C(12)	25(3)	22(3)	18(3)	-9(2)	7(3)	-4(2)
C(13)	31(4)	21(3)	28(3)	-7(2)	1(3)	1(2)
C(14)	37(4)	30(3)	23(3)	-3(3)	-2(3)	0(3)
C(15)	33(4)	42(4)	33(4)	7(3)	-5(3)	-6(3)
C(16)	17(3)	15(2)	19(3)	-1(2)	-3(2)	0(2)
C(17)	19(3)	17(2)	21(3)	1(2)	-1(2)	1(2)
C(18)	16(3)	26(3)	19(3)	-5(2)	-2(2)	-6(2)
C(19)	33(4)	40(3)	26(3)	-8(3)	10(3)	-4(3)
C(20)	17(3)	16(2)	15(2)	-2(2)	2(2)	-1(2)
C(21)	20(3)	19(3)	13(2)	3(2)	4(2)	5(2)
C(22)	23(3)	16(2)	14(2)	3(2)	5(2)	0(2)
C(23)	25(3)	24(3)	18(3)	3(2)	-2(3)	-1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for $\mathbf{C_{23}H_{26}N_4Pt}$.

	x	y	z	U(eq)
H(1A)	9030(60)	-570(20)	10490(40)	21(14)
H(1B)	7220(60)	-620(20)	10740(50)	36(16)
H(1C)	8130(90)	20(40)	10550(60)	80(30)
H(2A)	7780(60)	-800(20)	8640(40)	24(14)

H(2B)	8750(70)	-240(20)	8520(50)	39(16)
H(3A)	5430(60)	-260(20)	8880(40)	16(13)
H(3B)	6420(60)	360(20)	8860(40)	31(15)
H(4A)	6100(60)	-440(20)	6860(40)	24(13)
H(4B)	7020(50)	199(17)	6770(30)	0(10)
H(6)	3170(60)	-450(20)	6420(40)	20(14)
H(7)	1110(70)	330(30)	6360(50)	50(20)
H(8A)	950(60)	1461(17)	6830(40)	0(11)
H(8B)	2370(70)	1770(20)	6170(50)	36(16)
H(10)	220(60)	1960(20)	8620(40)	20(14)
H(11)	1790(60)	2290(20)	10450(40)	22(14)
H(12A)	4550(50)	2452(18)	10970(40)	2(10)
H(12B)	5640(60)	2360(20)	9980(40)	13(14)
H(13A)	4580(70)	1410(20)	11290(50)	42(17)
H(13B)	5910(60)	1370(20)	10290(50)	25(15)
H(14A)	7240(70)	1350(30)	12190(50)	36(16)
H(14B)	6790(70)	1950(30)	12380(60)	60(20)
H(15A)	9460(80)	1820(30)	11680(60)	60(20)
H(15B)	8670(70)	1430(30)	10660(50)	42(18)
H(15C)	8490(60)	2150(20)	10590(50)	25(14)
H(19)	11030(70)	990(20)	3330(50)	46(18)
H(23)	10230(70)	3750(30)	9660(50)	48(19)

APPENDIX 7

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF

$C_{18}H_{24}N_8Ag_2P_2F_{12}$ (III-**11a**)

Table 1. Crystal data and structure refinement for **$C_{11}H_{15}AgF_6N_5P$**.

Identification code	**$C_{11}H_{15}AgF_6N_5P$**	
Empirical formula	C11 H15 Ag F6 N5 P	
Formula weight	470.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8875(13) Å	α= 97.346(2)°.
	b = 9.0090(14) Å	β= 98.840(2)°.
	c = 11.0816(17) Å	γ = 107.896(2)°.
Volume	819.7(2) $Å^3$	
Z	2	
Density (calculated)	1.905 Mg/m^3	
Absorption coefficient	1.394 mm^{-1}	
F(000)	464	
Crystal size	0.30 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.89 to 27.50°.	
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 11, -14 \leq l \leq 14$	
Reflections collected	6898	
Independent reflections	3567 [R(int) = 0.0426]	
Completeness to theta = 27.50°	94.5 %	
Max. and min. transmission	0.8967 and 0.6799	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3567 / 0 / 265
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1634
R indices (all data)	R1 = 0.0662, wR2 = 0.1661
Largest diff. peak and hole	3.776 and -2.217 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{11}H_{15}AgF_6N_5P}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag	1433(1)	9381(1)	5560(1)	19(1)
P	6552(2)	8075(1)	7288(1)	21(1)
F(1)	6286(4)	6347(4)	6525(3)	31(1)
F(2)	6472(4)	8718(4)	6013(3)	37(1)
F(3)	4622(4)	7607(4)	7125(4)	38(1)
F(4)	6790(4)	9792(4)	8031(3)	41(1)
F(5)	6642(5)	7425(5)	8558(3)	49(1)
F(6)	8453(4)	8514(4)	7419(4)	40(1)
N(1)	3261(5)	11394(5)	8133(4)	22(1)
N(2)	2951(5)	12960(5)	6898(4)	19(1)
N(3)	-801(5)	6138(5)	3900(3)	18(1)
N(4)	1652(5)	6579(5)	3733(4)	19(1)
N(5)	2080(6)	6647(6)	-24(5)	34(1)
C(1)	3134(8)	9963(7)	8663(5)	30(1)
C(2)	4113(6)	12912(6)	8764(5)	22(1)
C(3)	3918(6)	13902(6)	8002(5)	22(1)
C(4)	2532(6)	11392(6)	6964(5)	20(1)
C(5)	694(6)	7238(6)	4287(4)	19(1)
C(6)	-2258(6)	6440(6)	4132(4)	22(1)
C(7)	-777(6)	4824(6)	3107(5)	23(1)

C(8)	769(6)	5091(6)	3001(5)	24(1)
C(9)	3393(6)	7335(6)	3847(5)	25(1)
C(10)	1117(6)	7042(6)	328(5)	26(1)
C(11)	-171(7)	7520(7)	766(5)	33(1)

Table 3. Bond lengths [Å] and angles [°] for **$C_{11}H_{15}AgF_6N_5P$**.

Ag-C(4)	2.094(5)
Ag-C(5)	2.094(5)
Ag-Ag#1	3.2258(7)
P-F(6)	1.591(3)
P-F(4)	1.592(3)
P-F(5)	1.592(3)
P-F(2)	1.594(3)
P-F(1)	1.603(3)
P-F(3)	1.611(3)
N(1)-C(4)	1.356(6)
N(1)-C(2)	1.374(6)
N(1)-C(1)	1.464(6)
N(2)-C(4)	1.360(6)
N(2)-C(3)	1.385(6)
N(2)-C(6)#1	1.457(6)
N(3)-C(5)	1.356(6)
N(3)-C(7)	1.389(6)
N(3)-C(6)	1.455(6)
N(4)-C(5)	1.354(6)
N(4)-C(8)	1.396(6)
N(4)-C(9)	1.465(6)
N(5)-C(10)	1.125(7)
C(2)-C(3)	1.336(7)
C(6)-N(2)#1	1.457(6)
C(7)-C(8)	1.347(7)
C(10)-C(11)	1.467(8)
C(4)-Ag-C(5)	169.37(18)
C(4)-Ag-Ag#1	93.83(13)

C(5)-Ag-Ag#1	96.79(13)
F(6)-P-F(4)	90.67(19)
F(6)-P-F(5)	90.6(2)
F(4)-P-F(5)	90.0(2)
F(6)-P-F(2)	89.1(2)
F(4)-P-F(2)	90.3(2)
F(5)-P-F(2)	179.5(2)
F(6)-P-F(1)	90.09(18)
F(4)-P-F(1)	179.0(2)
F(5)-P-F(1)	90.5(2)
F(2)-P-F(1)	89.13(18)
F(6)-P-F(3)	178.7(2)
F(4)-P-F(3)	90.39(18)
F(5)-P-F(3)	90.2(2)
F(2)-P-F(3)	90.1(2)
F(1)-P-F(3)	88.84(17)
C(4)-N(1)-C(2)	111.4(4)
C(4)-N(1)-C(1)	124.3(4)
C(2)-N(1)-C(1)	124.3(4)
C(4)-N(2)-C(3)	111.4(4)
C(4)-N(2)-C(6)#1	123.5(4)
C(3)-N(2)-C(6)#1	124.5(4)
C(5)-N(3)-C(7)	111.5(4)
C(5)-N(3)-C(6)	122.9(4)
C(7)-N(3)-C(6)	124.9(4)
C(5)-N(4)-C(8)	111.7(4)
C(5)-N(4)-C(9)	124.8(4)
C(8)-N(4)-C(9)	123.5(4)
C(3)-C(2)-N(1)	107.4(4)
C(2)-C(3)-N(2)	106.3(4)
N(1)-C(4)-N(2)	103.6(4)
N(1)-C(4)-Ag	125.3(3)
N(2)-C(4)-Ag	130.1(4)
N(4)-C(5)-N(3)	104.0(4)

N(4)-C(5)-Ag	126.9(4)
N(3)-C(5)-Ag	129.0(3)
N(3)-C(6)-N(2)#1	110.3(4)
C(8)-C(7)-N(3)	106.8(4)
C(7)-C(8)-N(4)	106.1(4)
N(5)-C(10)-C(11)	178.5(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{11}H_{15}AgF_6N_5P}$. The anisotropic displacement factor exponent takes the form: $-2\square^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag	25(1)	9(1)	21(1)	4(1)	4(1)	3(1)
P	25(1)	12(1)	23(1)	5(1)	7(1)	0(1)
F(1)	41(2)	14(1)	40(2)	6(1)	17(1)	7(1)
F(2)	50(2)	23(2)	36(2)	18(1)	6(2)	4(1)
F(3)	26(2)	19(2)	62(2)	-2(2)	17(2)	-1(1)
F(4)	47(2)	16(2)	50(2)	-7(1)	23(2)	-4(1)
F(5)	72(3)	32(2)	26(2)	13(2)	3(2)	-8(2)
F(6)	25(2)	25(2)	68(2)	14(2)	8(2)	2(1)
N(1)	27(2)	15(2)	24(2)	7(2)	7(2)	8(2)
N(2)	22(2)	11(2)	21(2)	4(2)	4(2)	2(1)
N(3)	24(2)	10(2)	19(2)	7(2)	5(2)	3(2)
N(4)	25(2)	10(2)	23(2)	6(2)	4(2)	4(2)
N(5)	32(2)	28(3)	40(3)	2(2)	6(2)	7(2)
C(1)	48(3)	22(3)	25(3)	8(2)	6(2)	18(2)
C(2)	23(2)	17(2)	19(2)	-1(2)	-2(2)	1(2)
C(3)	23(2)	15(2)	24(2)	2(2)	5(2)	-1(2)
C(4)	22(2)	12(2)	25(2)	4(2)	7(2)	4(2)

C(5)	26(2)	11(2)	19(2)	7(2)	4(2)	5(2)
C(6)	28(2)	14(2)	23(2)	10(2)	8(2)	4(2)
C(7)	29(2)	11(2)	27(2)	4(2)	3(2)	4(2)
C(8)	33(3)	14(2)	23(2)	1(2)	4(2)	9(2)
C(9)	26(2)	16(2)	33(3)	3(2)	7(2)	6(2)
C(10)	29(2)	14(2)	25(2)	5(2)	-1(2)	-4(2)
C(11)	33(3)	25(3)	40(3)	7(2)	8(2)	8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **$C_{11}H_{15}AgF_6N_5P$**.

	x	y	z	U(eq)
H(1A)	3230(90)	10250(100)	9500(70)	50(20)
H(1B)	4110(80)	9660(80)	8750(60)	32(16)
H(1C)	2800(100)	9220(110)	8040(80)	60(20)
H(2)	4690(60)	13030(60)	9390(50)	3(11)
H(3)	4500(110)	15340(120)	8080(80)	80(30)
H(6A)	-2060(60)	7370(70)	4950(50)	23(14)
H(6B)	-3010(80)	5560(80)	4230(60)	30(16)
H(7)	-1750(90)	4020(100)	2660(70)	50(20)
H(8)	1220(90)	4560(100)	2650(70)	50(20)
H(9A)	4050(70)	6520(80)	4150(60)	32(16)
H(9B)	3860(90)	8210(100)	4420(70)	50(20)
H(9C)	3780(70)	7440(80)	3090(60)	27(15)

APPENDIX 8

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF

$C_{30}H_{48}N_8Ag_2P_2F_{12}$ (III-**11b**)

Table 1. Crystal data and structure refinement for $\mathbf{C_{30}H_{48}Ag_2F_{12}N_8P_2}$.

Identification code	$\mathbf{C_{30}H_{48}Ag_2F_{12}N_8P_2}$	
Empirical formula	$C_{30}\ H_{48}\ Ag_2\ F_{12}\ N_8\ P_2$	
Formula weight	1026.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.1948(8) Å	α= 90°.
	b = 29.1373(17) Å	β= 107.7960(10)°.
	c = 21.1562(12) Å	γ = 90°.
Volume	8331.5(8) $Å^3$	
Z	8	
Density (calculated)	1.637 Mg/m^3	
Absorption coefficient	1.103 mm^{-1}	
F(000)	4128	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.40 to 27.51°.	
Index ranges	$-18 \leq h \leq 18, -37 \leq k \leq 37, -27 \leq l \leq 27$	
Reflections collected	72179	
Independent reflections	18930 [R(int) = 0.0617]	
Completeness to theta = 27.51°	98.8 %	
Max. and min. transmission	0.8977 and 0.8095	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18930 / 0 / 1014
Goodness-of-fit on F^2	1.143
Final R indices [I>2sigma(I)]	R1 = 0.0615, wR2 = 0.1110
R indices (all data)	R1 = 0.0847, wR2 = 0.1184
Largest diff. peak and hole	1.054 and -1.035 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{30}H_{48}Ag_2F_{12}N_8P_2}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	1910(1)	7767(1)	1068(1)	21(1)
Ag(2)	133(1)	7383(1)	1606(1)	16(1)
Ag(3)	3775(1)	8671(1)	2071(1)	19(1)
Ag(4)	5648(1)	9086(1)	1623(1)	18(1)
P(1)	6780(1)	6421(1)	1749(1)	53(1)
P(2)	8915(1)	37(1)	1278(1)	19(1)
P(3)	1196(1)	8270(1)	3309(1)	20(1)
P(4)	4492(1)	8280(1)	9732(1)	23(1)
F(1)	8193(2)	454(1)	949(1)	25(1)
F(2)	8602(2)	89(1)	1936(1)	26(1)
F(3)	8015(2)	-318(1)	989(2)	37(1)
F(4)	9630(2)	-384(1)	1602(1)	26(1)
F(5)	9220(3)	-15(1)	614(2)	42(1)
F(6)	9801(2)	389(1)	1566(2)	28(1)
F(7)	6130(3)	6862(1)	1436(2)	57(1)
F(8)	6464(3)	6491(1)	2405(2)	70(1)
F(9)	5835(3)	6107(1)	1451(3)	76(2)
F(10)	7433(3)	5992(1)	2066(3)	85(2)
F(11)	7086(3)	6371(1)	1094(2)	76(1)

F(12)	7717(3)	6749(1)	2048(2)	59(1)
F(13)	3778(2)	8712(1)	9478(1)	32(1)
F(14)	5314(2)	8619(1)	10177(2)	46(1)
F(15)	4043(3)	8213(1)	10331(2)	42(1)
F(16)	5210(2)	7852(1)	9983(2)	47(1)
F(17)	3671(2)	7948(1)	9282(2)	38(1)
F(18)	4928(3)	8353(1)	9129(2)	53(1)
F(19)	591(2)	8300(1)	3827(2)	37(1)
F(20)	460(2)	8634(1)	2837(1)	32(1)
F(21)	1908(2)	8676(1)	3674(1)	33(1)
F(22)	1801(2)	8243(1)	2770(1)	27(1)
F(23)	1934(2)	7902(1)	3762(2)	35(1)
F(24)	492(2)	7864(1)	2925(2)	35(1)
N(1)	3492(3)	7006(1)	1296(2)	21(1)
N(2)	3158(3)	7125(1)	2202(2)	18(1)
N(3)	1879(3)	6865(1)	2611(2)	15(1)
N(4)	635(3)	6420(1)	2224(2)	18(1)
N(5)	-1844(3)	7856(1)	861(2)	19(1)
N(6)	-707(3)	8359(1)	1165(2)	16(1)
N(7)	608(3)	8647(1)	798(2)	18(1)
N(8)	1119(3)	8499(1)	-27(2)	25(1)
N(9)	4636(3)	7987(1)	3214(2)	22(1)
N(10)	5219(3)	7827(1)	2425(2)	21(1)
N(11)	6495(3)	8095(1)	2003(2)	18(1)
N(12)	7622(3)	8605(1)	2313(2)	19(1)
N(13)	5264(3)	10069(1)	1062(2)	22(1)
N(14)	3993(3)	9654(1)	619(2)	20(1)
N(15)	2693(3)	9418(1)	1026(2)	19(1)
N(16)	2315(3)	9474(1)	1928(2)	22(1)
C(1)	1854(5)	5852(2)	168(3)	54(2)
C(2)	2129(4)	6343(2)	414(3)	36(1)
C(3)	3088(4)	6499(2)	313(3)	30(1)
C(4)	3412(4)	6977(2)	582(2)	26(1)

C(5)	4104(4)	6720(2)	1768(2)	23(1)
C(6)	3893(3)	6796(2)	2334(2)	19(1)
C(7)	2893(3)	7253(2)	1553(2)	18(1)
C(8)	2579(4)	7231(2)	2640(2)	18(1)
C(9)	2115(4)	6451(2)	2947(2)	20(1)
C(10)	1339(4)	6174(2)	2703(2)	20(1)
C(11)	964(4)	6848(2)	2162(2)	17(1)
C(12)	-303(4)	6226(2)	1815(2)	22(1)
C(13)	-177(4)	5983(2)	1211(2)	25(1)
C(14)	-1144(4)	5770(2)	780(3)	35(1)
C(15)	-1030(5)	5521(2)	178(3)	47(2)
C(16)	-1669(6)	6797(3)	-666(4)	63(2)
C(17)	-1520(4)	7065(2)	-28(3)	40(2)
C(18)	-2488(4)	7211(2)	73(3)	35(1)
C(19)	-2378(4)	7417(2)	747(3)	26(1)
C(20)	-2290(4)	8277(2)	680(2)	23(1)
C(21)	-1585(4)	8592(2)	868(2)	22(1)
C(22)	-862(3)	7899(2)	1158(2)	17(1)
C(23)	260(3)	8576(2)	1371(2)	18(1)
C(24)	289(4)	9003(2)	352(2)	24(1)
C(25)	613(4)	8909(2)	-164(3)	25(1)
C(26)	1120(4)	8330(2)	570(2)	21(1)
C(27)	1471(4)	8256(2)	-511(3)	31(1)
C(28)	618(5)	8132(2)	-1122(3)	49(2)
C(29)	-221(5)	7869(3)	-1004(4)	54(2)
C(30A)	-1078(8)	7871(5)	-1568(7)	58(4)
C(30B)	-1187(15)	8090(7)	-943(11)	59(7)
C(31)	6110(6)	9166(2)	4403(4)	65(2)
C(32)	5450(5)	8859(2)	3880(3)	42(2)
C(33)	4892(4)	8508(2)	4170(3)	34(1)
C(34)	4154(4)	8227(2)	3640(2)	28(1)
C(35)	5264(4)	7619(2)	3427(3)	26(1)
C(36)	5635(4)	7517(2)	2930(3)	26(1)

C(37)	4608(4)	8125(2)	2598(2)	20(1)
C(38)	5534(3)	7872(2)	1834(2)	19(1)
C(39)	7381(4)	7861(2)	2258(2)	24(1)
C(40)	8088(4)	8184(2)	2452(2)	22(1)
C(41)	6635(4)	8554(2)	2032(2)	18(1)
C(42)	8126(3)	9047(2)	2471(2)	20(1)
C(43)	8252(5)	9191(2)	3180(3)	35(1)
C(44)	8777(5)	9651(2)	3364(3)	34(1)
C(45)	9844(4)	9645(2)	3380(3)	41(2)
C(48)	6048(7)	10508(3)	2082(4)	67(3)
C(46A)	5794(11)	10376(5)	3198(7)	63(5)
C(47A)	5813(10)	10140(4)	2583(7)	40(4)
C(46B)	5895(13)	10066(7)	2966(9)	49(5)
C(47B)	5292(12)	10416(6)	2441(7)	35(5)
C(49)	6196(4)	10239(2)	1513(3)	32(1)
C(50)	4618(4)	10335(2)	584(3)	27(1)
C(51)	3823(4)	10081(2)	311(3)	28(1)
C(52)	4891(4)	9649(2)	1094(2)	21(1)
C(53)	3246(3)	9311(2)	570(2)	20(1)
C(54)	2054(4)	9787(2)	950(3)	26(1)
C(55)	1815(4)	9818(2)	1512(3)	26(1)
C(56)	2870(3)	9223(2)	1635(2)	19(1)
C(57)	2292(4)	9411(2)	2608(2)	25(1)
C(58)	2976(4)	9749(2)	3079(3)	32(1)
C(59)	2969(5)	9680(2)	3789(3)	38(1)
C(60)	3642(5)	10012(2)	4268(3)	54(2)

Table 3. Bond lengths [Å] and angles [°] for $\mathbf{C_{30}H_{48}Ag_2F_{12}N_8P_2}$.

Ag(1)-C(26)	2.083(5)
Ag(1)-C(7)	2.089(5)
Ag(2)-C(22)	2.084(5)
Ag(2)-C(11)	2.086(5)

Ag(3)-C(37)	2.088(5)
Ag(3)-C(56)	2.090(5)
Ag(4)-C(52)	2.089(5)
Ag(4)-C(41)	2.090(5)
P(1)-F(10)	1.579(4)
P(1)-F(11)	1.581(4)
P(1)-F(9)	1.587(4)
P(1)-F(8)	1.596(4)
P(1)-F(12)	1.602(4)
P(1)-F(7)	1.603(4)
P(2)-F(2)	1.591(3)
P(2)-F(6)	1.592(3)
P(2)-F(5)	1.599(3)
P(2)-F(1)	1.604(3)
P(2)-F(4)	1.606(3)
P(2)-F(3)	1.613(3)
P(3)-F(19)	1.587(3)
P(3)-F(21)	1.593(3)
P(3)-F(23)	1.598(3)
P(3)-F(24)	1.601(3)
P(3)-F(20)	1.605(3)
P(3)-F(22)	1.625(3)
P(4)-F(17)	1.588(3)
P(4)-F(18)	1.593(3)
P(4)-F(16)	1.594(3)
P(4)-F(15)	1.595(3)
P(4)-F(14)	1.598(3)
P(4)-F(13)	1.604(3)
N(1)-C(7)	1.349(6)
N(1)-C(5)	1.383(6)
N(1)-C(4)	1.481(6)
N(2)-C(7)	1.361(6)
N(2)-C(6)	1.380(6)
N(2)-C(8)	1.447(6)

N(3)-C(11)	1.356(6)
N(3)-C(9)	1.390(6)
N(3)-C(8)	1.445(6)
N(4)-C(11)	1.351(6)
N(4)-C(10)	1.386(6)
N(4)-C(12)	1.463(6)
N(5)-C(22)	1.349(6)
N(5)-C(20)	1.381(6)
N(5)-C(19)	1.467(6)
N(6)-C(22)	1.358(6)
N(6)-C(21)	1.390(6)
N(6)-C(23)	1.452(6)
N(7)-C(26)	1.353(6)
N(7)-C(24)	1.383(6)
N(7)-C(23)	1.455(6)
N(8)-C(26)	1.354(6)
N(8)-C(25)	1.379(6)
N(8)-C(27)	1.454(6)
N(9)-C(37)	1.353(6)
N(9)-C(35)	1.379(6)
N(9)-C(34)	1.465(6)
N(10)-C(37)	1.354(6)
N(10)-C(36)	1.388(6)
N(10)-C(38)	1.456(6)
N(11)-C(41)	1.351(6)
N(11)-C(39)	1.387(6)
N(11)-C(38)	1.454(6)
N(12)-C(41)	1.353(6)
N(12)-C(40)	1.380(6)
N(12)-C(42)	1.461(6)
N(13)-C(52)	1.344(6)
N(13)-C(50)	1.378(6)
N(13)-C(49)	1.461(7)
N(14)-C(52)	1.362(6)

N(14)-C(51)	1.391(6)
N(14)-C(53)	1.439(6)
N(15)-C(56)	1.358(6)
N(15)-C(54)	1.384(6)
N(15)-C(53)	1.452(6)
N(16)-C(56)	1.355(6)
N(16)-C(55)	1.378(6)
N(16)-C(57)	1.460(6)
C(1)-C(2)	1.532(8)
C(2)-C(3)	1.510(7)
C(3)-C(4)	1.522(7)
C(5)-C(6)	1.340(7)
C(9)-C(10)	1.334(7)
C(12)-C(13)	1.518(7)
C(13)-C(14)	1.528(7)
C(14)-C(15)	1.518(8)
C(16)-C(17)	1.518(8)
C(17)-C(18)	1.515(8)
C(18)-C(19)	1.510(7)
C(20)-C(21)	1.327(7)
C(24)-C(25)	1.336(7)
C(27)-C(28)	1.520(9)
C(28)-C(29)	1.498(9)
C(29)-C(30A)	1.420(14)
C(29)-C(30B)	1.56(2)
C(31)-C(32)	1.505(8)
C(32)-C(33)	1.532(8)
C(33)-C(34)	1.517(7)
C(35)-C(36)	1.345(7)
C(39)-C(40)	1.346(7)
C(42)-C(43)	1.516(7)
C(43)-C(44)	1.526(7)
C(44)-C(45)	1.506(8)
C(48)-C(49)	1.504(11)

C(48)-C(47B)	1.517(15)
C(48)-C(47A)	1.615(14)
C(46A)-C(47A)	1.48(2)
C(46B)-C(47B)	1.56(3)
C(50)-C(51)	1.326(7)
C(54)-C(55)	1.335(7)
C(57)-C(58)	1.522(7)
C(58)-C(59)	1.518(7)
C(59)-C(60)	1.513(8)
C(26)-Ag(1)-C(7)	171.24(18)
C(22)-Ag(2)-C(11)	169.67(17)
C(37)-Ag(3)-C(56)	173.33(18)
C(52)-Ag(4)-C(41)	166.74(18)
F(10)-P(1)-F(11)	90.9(3)
F(10)-P(1)-F(9)	91.5(2)
F(11)-P(1)-F(9)	91.3(3)
F(10)-P(1)-F(8)	91.0(3)
F(11)-P(1)-F(8)	177.9(3)
F(9)-P(1)-F(8)	89.5(2)
F(10)-P(1)-F(12)	89.8(2)
F(11)-P(1)-F(12)	89.0(2)
F(9)-P(1)-F(12)	178.6(2)
F(8)-P(1)-F(12)	90.1(2)
F(10)-P(1)-F(7)	179.1(3)
F(11)-P(1)-F(7)	89.4(2)
F(9)-P(1)-F(7)	89.3(2)
F(8)-P(1)-F(7)	88.7(2)
F(12)-P(1)-F(7)	89.3(2)
F(2)-P(2)-F(6)	90.20(16)
F(2)-P(2)-F(5)	179.6(2)
F(6)-P(2)-F(5)	90.14(18)
F(2)-P(2)-F(1)	89.81(15)
F(6)-P(2)-F(1)	90.23(16)

F(5)-P(2)-F(1)	89.91(16)
F(2)-P(2)-F(4)	90.51(15)
F(6)-P(2)-F(4)	90.37(16)
F(5)-P(2)-F(4)	89.77(16)
F(1)-P(2)-F(4)	179.32(19)
F(2)-P(2)-F(3)	89.59(17)
F(6)-P(2)-F(3)	179.8(2)
F(5)-P(2)-F(3)	90.07(19)
F(1)-P(2)-F(3)	89.69(16)
F(4)-P(2)-F(3)	89.71(16)
F(19)-P(3)-F(21)	91.19(17)
F(19)-P(3)-F(23)	90.92(17)
F(21)-P(3)-F(23)	90.25(17)
F(19)-P(3)-F(24)	90.35(18)
F(21)-P(3)-F(24)	178.44(18)
F(23)-P(3)-F(24)	90.02(17)
F(19)-P(3)-F(20)	90.42(17)
F(21)-P(3)-F(20)	90.40(17)
F(23)-P(3)-F(20)	178.49(18)
F(24)-P(3)-F(20)	89.29(17)
F(19)-P(3)-F(22)	179.17(19)
F(21)-P(3)-F(22)	89.06(16)
F(23)-P(3)-F(22)	89.87(16)
F(24)-P(3)-F(22)	89.40(17)
F(20)-P(3)-F(22)	88.78(15)
F(17)-P(4)-F(18)	89.72(19)
F(17)-P(4)-F(16)	90.07(19)
F(18)-P(4)-F(16)	90.4(2)
F(17)-P(4)-F(15)	90.16(19)
F(18)-P(4)-F(15)	179.1(2)
F(16)-P(4)-F(15)	90.5(2)
F(17)-P(4)-F(14)	179.2(2)
F(18)-P(4)-F(14)	89.8(2)
F(16)-P(4)-F(14)	90.58(19)

F(15)-P(4)-F(14)	90.3(2)
F(17)-P(4)-F(13)	90.22(17)
F(18)-P(4)-F(13)	89.27(19)
F(16)-P(4)-F(13)	179.5(2)
F(15)-P(4)-F(13)	89.80(17)
F(14)-P(4)-F(13)	89.12(18)
C(7)-N(1)-C(5)	111.4(4)
C(7)-N(1)-C(4)	125.4(4)
C(5)-N(1)-C(4)	122.5(4)
C(7)-N(2)-C(6)	110.7(4)
C(7)-N(2)-C(8)	123.5(4)
C(6)-N(2)-C(8)	124.1(4)
C(11)-N(3)-C(9)	110.8(4)
C(11)-N(3)-C(8)	123.8(4)
C(9)-N(3)-C(8)	124.4(4)
C(11)-N(4)-C(10)	110.8(4)
C(11)-N(4)-C(12)	125.4(4)
C(10)-N(4)-C(12)	123.7(4)
C(22)-N(5)-C(20)	111.5(4)
C(22)-N(5)-C(19)	124.5(4)
C(20)-N(5)-C(19)	124.0(4)
C(22)-N(6)-C(21)	110.9(4)
C(22)-N(6)-C(23)	124.6(4)
C(21)-N(6)-C(23)	123.9(4)
C(26)-N(7)-C(24)	111.5(4)
C(26)-N(7)-C(23)	123.9(4)
C(24)-N(7)-C(23)	123.4(4)
C(26)-N(8)-C(25)	111.3(4)
C(26)-N(8)-C(27)	125.2(4)
C(25)-N(8)-C(27)	122.9(4)
C(37)-N(9)-C(35)	111.8(4)
C(37)-N(9)-C(34)	124.7(4)
C(35)-N(9)-C(34)	123.1(4)
C(37)-N(10)-C(36)	111.5(4)

C(37)-N(10)-C(38)	124.4(4)
C(36)-N(10)-C(38)	123.4(4)
C(41)-N(11)-C(39)	111.5(4)
C(41)-N(11)-C(38)	124.6(4)
C(39)-N(11)-C(38)	123.2(4)
C(41)-N(12)-C(40)	111.2(4)
C(41)-N(12)-C(42)	124.4(4)
C(40)-N(12)-C(42)	124.3(4)
C(52)-N(13)-C(50)	111.5(4)
C(52)-N(13)-C(49)	124.7(4)
C(50)-N(13)-C(49)	123.7(4)
C(52)-N(14)-C(51)	110.2(4)
C(52)-N(14)-C(53)	123.2(4)
C(51)-N(14)-C(53)	124.8(4)
C(56)-N(15)-C(54)	111.1(4)
C(56)-N(15)-C(53)	123.9(4)
C(54)-N(15)-C(53)	124.0(4)
C(56)-N(16)-C(55)	110.9(4)
C(56)-N(16)-C(57)	125.1(4)
C(55)-N(16)-C(57)	123.8(4)
C(3)-C(2)-C(1)	112.3(5)
C(2)-C(3)-C(4)	113.9(4)
N(1)-C(4)-C(3)	110.6(4)
C(6)-C(5)-N(1)	106.5(4)
C(5)-C(6)-N(2)	107.2(4)
N(1)-C(7)-N(2)	104.2(4)
N(1)-C(7)-Ag(1)	126.4(3)
N(2)-C(7)-Ag(1)	129.0(3)
N(3)-C(8)-N(2)	109.5(4)
C(10)-C(9)-N(3)	106.6(4)
C(9)-C(10)-N(4)	107.2(4)
N(4)-C(11)-N(3)	104.6(4)
N(4)-C(11)-Ag(2)	126.2(3)
N(3)-C(11)-Ag(2)	128.5(3)

N(4)-C(12)-C(13)	110.9(4)
C(12)-C(13)-C(14)	112.1(4)
C(15)-C(14)-C(13)	112.9(5)
C(18)-C(17)-C(16)	112.6(5)
C(19)-C(18)-C(17)	114.1(5)
N(5)-C(19)-C(18)	113.7(4)
C(21)-C(20)-N(5)	107.0(4)
C(20)-C(21)-N(6)	106.7(4)
N(5)-C(22)-N(6)	103.8(4)
N(5)-C(22)-Ag(2)	127.2(3)
N(6)-C(22)-Ag(2)	128.5(3)
N(6)-C(23)-N(7)	110.0(4)
C(25)-C(24)-N(7)	106.3(4)
C(24)-C(25)-N(8)	107.1(4)
N(7)-C(26)-N(8)	103.8(4)
N(7)-C(26)-Ag(1)	128.4(3)
N(8)-C(26)-Ag(1)	127.2(3)
N(8)-C(27)-C(28)	111.0(4)
C(29)-C(28)-C(27)	116.5(5)
C(30A)-C(29)-C(28)	112.3(8)
C(30A)-C(29)-C(30B)	61.1(9)
C(28)-C(29)-C(30B)	124.6(10)
C(31)-C(32)-C(33)	112.7(5)
C(34)-C(33)-C(32)	112.9(5)
N(9)-C(34)-C(33)	111.4(4)
C(36)-C(35)-N(9)	106.6(4)
C(35)-C(36)-N(10)	106.3(4)
N(9)-C(37)-N(10)	103.7(4)
N(9)-C(37)-Ag(3)	125.8(4)
N(10)-C(37)-Ag(3)	130.4(3)
N(11)-C(38)-N(10)	109.9(4)
C(40)-C(39)-N(11)	106.0(4)
C(39)-C(40)-N(12)	107.0(4)
N(11)-C(41)-N(12)	104.2(4)

N(11)-C(41)-Ag(4)	130.1(3)
N(12)-C(41)-Ag(4)	125.1(3)
N(12)-C(42)-C(43)	111.8(4)
C(42)-C(43)-C(44)	113.4(4)
C(45)-C(44)-C(43)	113.9(5)
C(49)-C(48)-C(47B)	126.9(8)
C(49)-C(48)-C(47A)	106.6(7)
C(47B)-C(48)-C(47A)	39.9(7)
C(46A)-C(47A)-C(48)	109.3(10)
C(48)-C(47B)-C(46B)	98.9(12)
N(13)-C(49)-C(48)	112.3(5)
C(51)-C(50)-N(13)	107.0(5)
C(50)-C(51)-N(14)	107.0(5)
N(13)-C(52)-N(14)	104.2(4)
N(13)-C(52)-Ag(4)	126.7(4)
N(14)-C(52)-Ag(4)	128.1(4)
N(14)-C(53)-N(15)	109.8(4)
C(55)-C(54)-N(15)	106.5(5)
C(54)-C(55)-N(16)	107.4(4)
N(16)-C(56)-N(15)	104.1(4)
N(16)-C(56)-Ag(3)	125.3(3)
N(15)-C(56)-Ag(3)	130.6(3)
N(16)-C(57)-C(58)	111.3(4)
C(59)-C(58)-C(57)	111.5(4)
C(60)-C(59)-C(58)	112.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$C_{30}H_{48}Ag_2F_{12}N_8P_2$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	23(1)	21(1)	21(1)	6(1)	11(1)	7(1)
Ag(2)	17(1)	13(1)	18(1)	2(1)	5(1)	2(1)
Ag(3)	19(1)	20(1)	20(1)	2(1)	7(1)	3(1)
Ag(4)	16(1)	17(1)	21(1)	3(1)	4(1)	2(1)
P(1)	48(1)	19(1)	115(2)	-3(1)	58(1)	2(1)
P(2)	24(1)	14(1)	18(1)	2(1)	7(1)	5(1)
P(3)	19(1)	21(1)	19(1)	-1(1)	4(1)	1(1)
P(4)	20(1)	25(1)	21(1)	-5(1)	4(1)	3(1)
F(1)	27(2)	18(2)	28(2)	8(1)	5(1)	10(1)
F(2)	30(2)	24(2)	28(2)	7(1)	15(1)	6(1)
F(3)	36(2)	16(2)	46(2)	-6(1)	-8(2)	-4(1)
F(4)	28(2)	18(2)	32(2)	5(1)	9(1)	12(1)
F(5)	70(2)	39(2)	26(2)	9(2)	27(2)	24(2)
F(6)	23(2)	20(2)	43(2)	1(1)	13(1)	-2(1)
F(7)	56(2)	27(2)	105(3)	6(2)	50(2)	7(2)
F(8)	65(3)	66(3)	102(3)	14(3)	58(3)	15(2)
F(9)	54(3)	28(2)	168(5)	-18(3)	67(3)	-8(2)
F(10)	56(3)	30(2)	189(5)	19(3)	68(3)	12(2)
F(11)	70(3)	60(3)	127(4)	-32(3)	75(3)	-10(2)
F(12)	51(2)	30(2)	109(3)	-6(2)	46(2)	-3(2)
F(13)	36(2)	29(2)	27(2)	0(1)	5(1)	10(1)
F(14)	30(2)	35(2)	59(2)	-11(2)	-5(2)	-2(2)
F(15)	54(2)	49(2)	26(2)	6(2)	19(2)	7(2)
F(16)	36(2)	36(2)	61(2)	-4(2)	2(2)	17(2)
F(17)	38(2)	36(2)	33(2)	-12(2)	-1(2)	-9(2)
F(18)	71(3)	47(2)	60(2)	-5(2)	51(2)	1(2)
F(19)	39(2)	44(2)	36(2)	0(2)	23(2)	-4(2)
F(20)	29(2)	34(2)	31(2)	4(1)	9(1)	15(1)

F(21)	41(2)	32(2)	25(2)	-5(1)	10(1)	-14(2)
F(22)	25(2)	34(2)	23(2)	0(1)	11(1)	8(1)
F(23)	29(2)	35(2)	36(2)	11(2)	5(1)	5(2)
F(24)	31(2)	29(2)	40(2)	-11(1)	4(2)	-7(1)
N(1)	20(2)	20(2)	24(2)	1(2)	10(2)	1(2)
N(2)	17(2)	14(2)	24(2)	2(2)	7(2)	0(2)
N(3)	17(2)	15(2)	14(2)	2(2)	7(2)	2(2)
N(4)	17(2)	18(2)	20(2)	2(2)	8(2)	4(2)
N(5)	15(2)	20(2)	21(2)	4(2)	6(2)	2(2)
N(6)	17(2)	15(2)	16(2)	1(2)	5(2)	2(2)
N(7)	17(2)	17(2)	20(2)	1(2)	6(2)	0(2)
N(8)	29(2)	23(2)	27(2)	6(2)	17(2)	4(2)
N(9)	19(2)	24(2)	21(2)	3(2)	5(2)	-2(2)
N(10)	17(2)	17(2)	30(2)	1(2)	8(2)	1(2)
N(11)	16(2)	20(2)	20(2)	0(2)	8(2)	4(2)
N(12)	17(2)	19(2)	20(2)	2(2)	8(2)	1(2)
N(13)	19(2)	23(2)	25(2)	4(2)	9(2)	1(2)
N(14)	19(2)	21(2)	21(2)	5(2)	7(2)	5(2)
N(15)	15(2)	20(2)	23(2)	-1(2)	7(2)	2(2)
N(16)	16(2)	19(2)	29(2)	-2(2)	6(2)	1(2)
C(1)	61(5)	67(5)	36(4)	-18(3)	20(3)	-28(4)
C(2)	32(3)	56(4)	20(3)	-8(3)	10(2)	-6(3)
C(3)	32(3)	36(3)	25(3)	-2(2)	14(2)	10(3)
C(4)	27(3)	30(3)	27(3)	6(2)	15(2)	7(2)
C(5)	17(3)	25(3)	27(3)	-2(2)	7(2)	3(2)
C(6)	12(2)	15(2)	25(2)	5(2)	-3(2)	1(2)
C(7)	18(3)	16(2)	22(2)	2(2)	8(2)	0(2)
C(8)	22(3)	15(2)	17(2)	-2(2)	6(2)	-5(2)
C(9)	22(3)	21(3)	18(2)	6(2)	8(2)	6(2)
C(10)	28(3)	12(2)	21(2)	5(2)	9(2)	3(2)
C(11)	22(3)	15(2)	17(2)	2(2)	9(2)	-1(2)
C(12)	18(3)	19(3)	30(3)	-4(2)	9(2)	-2(2)
C(13)	21(3)	25(3)	29(3)	-2(2)	8(2)	-2(2)
C(14)	32(3)	34(3)	37(3)	-7(3)	8(3)	5(3)

C(15)	39(4)	53(4)	43(4)	-20(3)	4(3)	5(3)
C(16)	83(6)	62(5)	59(5)	-28(4)	44(4)	-25(4)
C(17)	42(4)	39(4)	44(4)	-15(3)	21(3)	-8(3)
C(18)	34(3)	35(3)	33(3)	-8(3)	4(3)	-8(3)
C(19)	17(3)	24(3)	38(3)	1(2)	9(2)	-5(2)
C(20)	21(3)	23(3)	24(3)	4(2)	5(2)	12(2)
C(21)	22(3)	17(3)	26(3)	1(2)	7(2)	9(2)
C(22)	19(3)	19(3)	14(2)	0(2)	7(2)	1(2)
C(23)	18(3)	15(2)	19(2)	-1(2)	4(2)	4(2)
C(24)	29(3)	14(3)	30(3)	8(2)	8(2)	1(2)
C(25)	24(3)	22(3)	29(3)	11(2)	7(2)	3(2)
C(26)	18(3)	21(3)	27(3)	3(2)	12(2)	0(2)
C(27)	40(3)	32(3)	31(3)	15(2)	25(3)	18(3)
C(28)	75(5)	37(4)	54(4)	-4(3)	47(4)	1(3)
C(29)	63(5)	52(4)	60(5)	4(4)	40(4)	7(4)
C(30A)	40(7)	61(9)	64(8)	-23(6)	2(6)	4(6)
C(30B)	43(13)	62(15)	70(15)	-13(12)	15(11)	-4(11)
C(31)	64(5)	50(5)	67(5)	-26(4)	-2(4)	-7(4)
C(32)	39(4)	45(4)	43(4)	-13(3)	13(3)	-8(3)
C(33)	25(3)	46(4)	30(3)	-13(3)	7(2)	3(3)
C(34)	25(3)	41(3)	22(3)	5(2)	12(2)	-1(2)
C(35)	22(3)	26(3)	26(3)	8(2)	2(2)	-6(2)
C(36)	20(3)	16(3)	36(3)	4(2)	1(2)	1(2)
C(37)	16(3)	21(3)	21(2)	-1(2)	3(2)	-4(2)
C(38)	18(3)	19(3)	20(2)	-2(2)	5(2)	3(2)
C(39)	25(3)	19(3)	32(3)	4(2)	15(2)	9(2)
C(40)	15(3)	24(3)	28(3)	4(2)	9(2)	6(2)
C(41)	20(3)	17(3)	18(2)	-1(2)	9(2)	2(2)
C(42)	13(2)	23(3)	23(2)	3(2)	4(2)	-3(2)
C(43)	48(4)	33(3)	27(3)	4(2)	16(3)	-4(3)
C(44)	58(4)	26(3)	20(3)	-2(2)	16(3)	-2(3)
C(45)	49(4)	24(3)	37(3)	3(3)	-7(3)	6(3)
C(48)	58(6)	83(7)	61(6)	-26(5)	22(5)	-44(6)
C(46A)	76(10)	54(10)	64(9)	-11(8)	28(8)	-13(8)

C(47A)	44(8)	41(8)	43(8)	-3(6)	24(6)	-10(6)
C(46B)	72(12)	57(13)	28(9)	6(9)	33(9)	-9(10)
C(47B)	38(9)	34(9)	40(8)	-13(7)	20(7)	2(8)
C(49)	25(3)	24(3)	49(3)	5(3)	12(3)	-5(2)
C(50)	27(3)	26(3)	31(3)	12(2)	14(2)	6(2)
C(51)	30(3)	30(3)	26(3)	12(2)	10(2)	10(3)
C(52)	17(3)	23(3)	22(2)	-1(2)	6(2)	1(2)
C(53)	17(3)	24(3)	17(2)	1(2)	3(2)	2(2)
C(54)	19(3)	27(3)	31(3)	5(2)	5(2)	1(2)
C(55)	19(3)	24(3)	37(3)	1(2)	12(2)	4(2)
C(56)	13(2)	18(3)	22(2)	-2(2)	0(2)	-3(2)
C(57)	28(3)	25(3)	28(3)	0(2)	18(2)	1(2)
C(58)	32(3)	29(3)	35(3)	-2(2)	11(3)	-5(3)
C(59)	41(4)	34(3)	39(3)	-3(3)	14(3)	-2(3)
C(60)	71(5)	49(4)	37(4)	-3(3)	10(4)	-5(4)

APPENDIX 9

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF

$C_{11}H_{15}N_4O_2I_2Rh$ (III-**9**)

Table 1. Crystal data and structure refinement for **$C_{11}H_{15}I_2N_4O_2Rh$**.

Identification code	**$C_{11}H_{15}I_2N_4O_2Rh$**	
Empirical formula	$C_{11}H_{15}I_2N_4O_2Rh$	
Formula weight	591.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	Cc	
Unit cell dimensions	a = 9.6927(5) Å	α= 90°.
	b = 13.3168(8) Å	β= 94.3140(10)°.
	c = 12.6872(7) Å	γ = 90°.
Volume	1632.97(16) $Å^3$	
Z	4	
Density (calculated)	2.408 Mg/m^3	
Absorption coefficient	4.833 mm^{-1}	
F(000)	1104	
Crystal size	0.45 x 0.10 x 0.01 mm^3	
Theta range for data collection	2.60 to 27.50°.	
Index ranges	$-12 \le h \le 12, -17 \le k \le 17, -16 \le l \le 16$	
Reflections collected	9857	
Independent reflections	3649 [R(int) = 0.0236]	
Completeness to theta = 27.50°	99.5 %	
Max. and min. transmission	0.9533 and 0.2197	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3649 / 2 / 241
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0184, wR2 = 0.0427
R indices (all data)	R1 = 0.0187, wR2 = 0.0428
Absolute structure parameter	0.225(14)
Largest diff. peak and hole	0.799 and -0.353 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **$C_{11}H_{15}I_2N_4O_2Rh$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	9000(1)	2310(1)	2446(1)	18(1)
I(2)	3935(1)	1145(1)	1103(1)	18(1)
Rh	6482(1)	1740(1)	1749(1)	11(1)
O(1)	6942(3)	2069(2)	122(2)	17(1)
O(2)	6068(3)	3231(2)	1102(2)	16(1)
N(1)	7938(3)	-216(2)	1515(2)	15(1)
N(2)	6642(3)	-264(2)	2808(2)	14(1)
N(3)	5695(3)	1008(2)	3841(2)	16(1)
N(4)	5903(3)	2612(2)	3839(2)	16(1)
C(1)	8694(4)	94(3)	606(3)	19(1)
C(2)	8087(4)	-1162(3)	1969(3)	18(1)
C(3)	7284(4)	-1195(3)	2769(3)	18(1)
C(4)	7032(4)	343(3)	2025(3)	14(1)
C(5)	5555(4)	-22(3)	3489(3)	17(1)
C(6)	5437(4)	1341(3)	4853(3)	17(1)
C(7)	5568(4)	2332(3)	4838(3)	19(1)
C(8)	5990(4)	1783(3)	3215(3)	15(1)
C(9)	6189(5)	3651(3)	3557(3)	20(1)

C(10)	6587(4)	2984(3)	244(3)	16(1)
C(11)	6783(5)	3759(3)	-582(3)	21(1)

Table 3. Bond lengths [Å] and angles [°] for **$C_{11}H_{15}I_2N_4O_2Rh$**.

I(1)-Rh	2.6442(4)
I(2)-Rh	2.6628(4)
Rh-C(8)	1.955(3)
Rh-C(4)	1.960(4)
Rh-O(2)	2.174(2)
Rh-O(1)	2.189(3)
O(1)-C(10)	1.279(5)
O(2)-C(10)	1.276(4)
N(1)-C(4)	1.352(5)
N(1)-C(2)	1.389(5)
N(1)-C(1)	1.471(5)
N(2)-C(4)	1.357(5)
N(2)-C(3)	1.390(5)
N(2)-C(5)	1.449(5)
N(3)-C(8)	1.346(5)
N(3)-C(6)	1.398(4)
N(3)-C(5)	1.446(5)
N(4)-C(8)	1.365(5)
N(4)-C(7)	1.383(5)
N(4)-C(9)	1.461(5)
C(2)-C(3)	1.325(6)
C(6)-C(7)	1.326(6)
C(10)-C(11)	1.492(5)
C(8)-Rh-C(4)	86.60(15)
C(8)-Rh-O(2)	106.34(13)
C(4)-Rh-O(2)	166.98(11)
C(8)-Rh-O(1)	166.61(12)
C(4)-Rh-O(1)	106.63(12)

O(2)-Rh-O(1)	60.38(9)
C(8)-Rh-I(1)	87.61(11)
C(4)-Rh-I(1)	88.89(11)
O(2)-Rh-I(1)	90.21(7)
O(1)-Rh-I(1)	90.56(7)
C(8)-Rh-I(2)	90.83(11)
C(4)-Rh-I(2)	90.34(11)
O(2)-Rh-I(2)	90.88(7)
O(1)-Rh-I(2)	91.11(7)
I(1)-Rh-I(2)	178.303(13)
C(10)-O(1)-Rh	90.1(2)
C(10)-O(2)-Rh	90.8(2)
C(4)-N(1)-C(2)	110.6(3)
C(4)-N(1)-C(1)	126.9(3)
C(2)-N(1)-C(1)	122.5(3)
C(4)-N(2)-C(3)	110.8(3)
C(4)-N(2)-C(5)	124.1(3)
C(3)-N(2)-C(5)	124.6(3)
C(8)-N(3)-C(6)	111.1(3)
C(8)-N(3)-C(5)	124.3(3)
C(6)-N(3)-C(5)	124.4(3)
C(8)-N(4)-C(7)	110.0(3)
C(8)-N(4)-C(9)	127.1(3)
C(7)-N(4)-C(9)	122.8(3)
C(3)-C(2)-N(1)	107.4(3)
C(2)-C(3)-N(2)	106.7(3)
N(1)-C(4)-N(2)	104.4(3)
N(1)-C(4)-Rh	128.0(3)
N(2)-C(4)-Rh	127.5(3)
N(3)-C(5)-N(2)	109.8(3)
C(7)-C(6)-N(3)	106.2(3)
C(6)-C(7)-N(4)	108.1(3)
N(3)-C(8)-N(4)	104.6(3)
N(3)-C(8)-Rh	128.1(3)

N(4)-C(8)-Rh	127.3(3)
O(2)-C(10)-O(1)	118.3(3)
O(2)-C(10)-C(11)	120.0(3)
O(1)-C(10)-C(11)	121.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **$C_{11}H_{15}I_2N_4O_2Rh$**. The anisotropic displacement factor exponent takes the form: $-2\square^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	16(1)	22(1)	17(1)	-1(1)	1(1)	-3(1)
I(2)	16(1)	16(1)	21(1)	-4(1)	-3(1)	2(1)
Rh	14(1)	10(1)	11(1)	-1(1)	1(1)	2(1)
O(1)	24(2)	12(1)	14(1)	-1(1)	3(1)	2(1)
O(2)	21(1)	12(1)	15(1)	0(1)	1(1)	4(1)
N(1)	18(2)	13(1)	15(1)	0(1)	1(1)	2(1)
N(2)	15(2)	12(2)	14(1)	0(1)	2(1)	0(1)
N(3)	14(2)	18(2)	15(1)	-1(1)	4(1)	0(1)
N(4)	15(2)	18(2)	14(1)	-3(1)	0(1)	0(1)
C(1)	20(2)	20(2)	18(2)	0(2)	10(2)	3(2)
C(2)	25(2)	11(2)	19(2)	-1(1)	3(2)	5(2)
C(3)	23(2)	10(2)	21(2)	2(1)	0(2)	1(1)
C(4)	14(2)	14(2)	14(2)	0(1)	0(1)	-1(1)
C(5)	21(2)	15(2)	17(2)	1(1)	8(1)	-1(1)
C(6)	15(2)	25(2)	12(2)	-1(1)	6(1)	-2(2)
C(7)	20(2)	23(2)	13(2)	-5(2)	3(1)	-1(2)
C(8)	14(2)	16(2)	15(2)	-1(1)	2(1)	1(1)
C(9)	27(2)	16(2)	19(2)	-8(2)	0(2)	2(2)

C(10)	19(2)	12(2)	16(2)	-1(1)	1(1)	0(2)
C(11)	25(2)	14(2)	22(2)	1(2)	0(2)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **$C_{11}H_{15}I_2N_4O_2Rh$**.

	x	y	z	U(eq)
H(1A)	8400(40)	800(30)	390(30)	9(9)
H(1B)	9550(50)	100(40)	750(30)	20(12)
H(1C)	8490(50)	-420(40)	70(40)	41(15)
H(2)	8560(50)	-1570(40)	1740(40)	27(13)
H(3)	7020(50)	-1730(30)	3270(40)	20(11)
H(5A)	5580(40)	-480(30)	3960(30)	7(9)
H(5B)	4660(40)	-110(30)	3080(30)	5(8)
H(6)	5120(60)	1050(40)	5320(50)	44(16)
H(7)	5460(40)	2730(30)	5360(40)	16(11)
H(9A)	5560(50)	4060(40)	3770(40)	23(12)
H(9B)	6270(50)	3630(40)	2890(40)	32(13)
H(9C)	7040(60)	3880(40)	3870(40)	40(15)
H(11A)	7390(50)	3610(40)	-1040(40)	22(11)
H(11B)	5860(60)	3990(40)	-880(40)	40(15)
H(11C)	7180(50)	4340(30)	-250(40)	23(12)

APPENDIX 10

SUPPLEMENTARY MATERIAL FOR THE X-RAY CRYSTAL STRUCTURE OF

$C_{30}H_{48}N_8Cl_3Rh$ (III-**12b**)

Table 1. Crystal data and structure refinement for $\mathbf{C_{30}H_{48}Cl_3N_8Rh}$.

Identification code	$\mathbf{C_{30}H_{48}Cl_3N_8Rh}$	
Empirical formula	C30 H48 Cl3 N8 Rh	
Formula weight	730.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.988(8) Å	α= 72.590(12)°.
	b = 12.579(9) Å	β= 64.693(11)°.
	c = 12.848(9) Å	γ = 87.021(13)°.
Volume	1665(2) Å^3	
Z	2	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	0.788 mm^{-1}	
F(000)	760	
Crystal size	0.11 x 0.09 x 0.02 mm^3	
Theta range for data collection	1.70 to 28.45°.	
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$	
Reflections collected	14893	
Independent reflections	7738 [R(int) = 0.0572]	
Completeness to theta = 28.45°	92.2 %	
Absorption correction	Semi-empirical from equivalents	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7738 / 0 / 386
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1205
R indices (all data)	R1 = 0.0927, wR2 = 0.1295
Largest diff. peak and hole	1.150 and -1.519 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{C_{30}H_{48}Cl_3N_8Rh}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

		x	y	z
Rh(1)	10000	5000	0	12(1)
Rh(2) 5000	0	5000	12(1)	
Cl(1)	7972(1)	4703(1)	207(1)	16(1)
Cl(2)	4943(1)	-1813(1)	4835(1)	17(1)
Cl(3)	8997(1)	252(1)	8080(1)	21(1)
N(1)	9802(4)	6648(3)	1470(3)	15(1)
N(2)	9075(4)	7243(3)	181(3)	16(1)
N(3)	8436(4)	3598(3)	2715(4)	17(1)
N(4)	10080(4)	2865(3)	1810(3)	14(1)
N(5)	3259(4)	27(3)	3718(4)	16(1)
N(6)	2425(4)	552(3)	5307(4)	16(1)
N(7)	2574(4)	-160(3)	7166(4)	16(1)
N(8)	6438(4)	1526(3)	2296(4)	19(1)
C(1)	10361(5)	6831(5)	4346(5)	31(1)
C(2)	11325(5)	6220(4)	3549(5)	25(1)
C(3)	11378(5)	6516(4)	2288(5)	23(1)
C(4)	10253(5)	5955(4)	2331(4)	19(1)
C(5)	9566(4)	6336(4)	666(4)	13(1)
C(6)	9449(5)	7712(4)	1499(4)	19(1)

C(7)	9001(4)	8095(4)	674(4)	19(1)
C(8)	8818(4)	7336(4)	-850(4)	14(1)
C(9)	6280(6)	5614(5)	5720(5)	38(2)
C(10)	6624(5)	5556(5)	4445(5)	25(1)
C(11)	7185(5)	4479(4)	4287(4)	20(1)
C(12)	7482(4)	4362(4)	3047(4)	17(1)
C(13)	9465(4)	3785(4)	1653(4)	12(1)
C(14)	8404(5)	2551(4)	3504(4)	18(1)
C(15)	9432(4)	2091(4)	2935(4)	16(1)
C(16)	5758(6)	-1834(8)	1297(8)	80(3)
C(17)	4425(5)	-1713(5)	1544(5)	35(2)
C(18)	3650(5)	-1436(4)	2697(5)	24(1)
C(19)	4109(4)	-335(4)	2688(4)	18(1)
C(20)	3504(4)	239(4)	4581(4)	13(1)
C(21)	2046(4)	226(4)	3915(5)	20(1)
C(22)	1517(5)	550(4)	4911(5)	21(1)
C(23)	2230(4)	784(4)	6414(4)	17(1)
C(24)	1790(5)	-765(4)	8346(4)	20(1)
C(25)	3084(6)	3128(5)	2225(6)	39(2)
C(26)	4374(6)	3553(5)	1233(5)	33(1)
C(27)	5315(5)	2685(4)	1178(5)	26(1)
C(28)	5553(5)	2352(4)	2300(5)	22(1)
C(29)	6329(4)	616(4)	3254(4)	13(1)
C(30)	7599(5)	1601(4)	1330(5)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **$C_{30}H_{48}Cl_3N_8Rh$**.

Rh(1)-C(5)	2.053(5)
Rh(1)-C(5)#1	2.053(5)
Rh(1)-C(13)	2.062(5)
Rh(1)-C(13)#1	2.062(5)
Rh(1)-Cl(1)#1	2.366(2)
Rh(1)-Cl(1)	2.366(2)

Rh(2)-C(29)#2	2.050(5)
Rh(2)-C(29)	2.050(5)
Rh(2)-C(20)#2	2.067(5)
Rh(2)-C(20)	2.067(5)
Rh(2)-Cl(2)#2	2.3593(19)
Rh(2)-Cl(2)	2.3593(19)
N(1)-C(5)	1.344(6)
N(1)-C(6)	1.389(6)
N(1)-C(4)	1.471(6)
N(2)-C(5)	1.362(6)
N(2)-C(7)	1.380(6)
N(2)-C(8)	1.454(6)
N(3)-C(13)	1.355(6)
N(3)-C(14)	1.391(6)
N(3)-C(12)	1.459(6)
N(4)-C(13)	1.351(6)
N(4)-C(15)	1.384(6)
N(4)-C(8)#1	1.446(6)
N(5)-C(20)	1.360(6)
N(5)-C(21)	1.388(6)
N(5)-C(19)	1.469(6)
N(6)-C(20)	1.354(6)
N(6)-C(22)	1.384(6)
N(6)-C(23)	1.457(6)
N(7)-C(29)#2	1.360(6)
N(7)-C(24)	1.388(6)
N(7)-C(23)	1.455(6)
N(8)-C(29)	1.369(6)
N(8)-C(30)	1.398(6)
N(8)-C(28)	1.445(6)
C(1)-C(2)	1.530(7)
C(2)-C(3)	1.524(7)
C(3)-C(4)	1.527(7)
C(6)-C(7)	1.342(7)

C(8)-N(4)#1	1.446(6)
C(9)-C(10)	1.534(7)
C(10)-C(11)	1.511(7)
C(11)-C(12)	1.529(6)
C(14)-C(15)	1.340(7)
C(16)-C(17)	1.499(9)
C(17)-C(18)	1.509(7)
C(18)-C(19)	1.512(7)
C(21)-C(22)	1.341(7)
C(24)-C(30)#2	1.316(7)
C(25)-C(26)	1.514(8)
C(26)-C(27)	1.523(8)
C(27)-C(28)	1.521(7)
C(29)-N(7)#2	1.360(6)
C(30)-C(24)#2	1.316(7)
C(5)-Rh(1)-C(5)#1	180.000(1)
C(5)-Rh(1)-C(13)	96.26(18)
C(5)#1-Rh(1)-C(13)	83.74(18)
C(5)-Rh(1)-C(13)#1	83.74(18)
C(5)#1-Rh(1)-C(13)#1	96.26(18)
C(13)-Rh(1)-C(13)#1	180.0(4)
C(5)-Rh(1)-Cl(1)#1	87.09(13)
C(5)#1-Rh(1)-Cl(1)#1	92.91(13)
C(13)-Rh(1)-Cl(1)#1	93.06(13)
C(13)#1-Rh(1)-Cl(1)#1	86.94(13)
C(5)-Rh(1)-Cl(1)	92.91(13)
C(5)#1-Rh(1)-Cl(1)	87.09(13)
C(13)-Rh(1)-Cl(1)	86.94(13)
C(13)#1-Rh(1)-Cl(1)	93.06(13)
Cl(1)#1-Rh(1)-Cl(1)	180.00(6)
C(29)#2-Rh(2)-C(29)	180.000(1)
C(29)#2-Rh(2)-C(20)#2	95.90(18)
C(29)-Rh(2)-C(20)#2	84.10(18)

C(29)#2-Rh(2)-C(20)	84.10(18)
C(29)-Rh(2)-C(20)	95.90(18)
C(20)#2-Rh(2)-C(20)	180.0
C(29)#2-Rh(2)-Cl(2)#2	92.24(13)
C(29)-Rh(2)-Cl(2)#2	87.76(13)
C(20)#2-Rh(2)-Cl(2)#2	86.60(12)
C(20)-Rh(2)-Cl(2)#2	93.40(12)
C(29)#2-Rh(2)-Cl(2)	87.76(13)
C(29)-Rh(2)-Cl(2)	92.24(13)
C(20)#2-Rh(2)-Cl(2)	93.40(12)
C(20)-Rh(2)-Cl(2)	86.60(12)
Cl(2)#2-Rh(2)-Cl(2)	180.000(6)
C(5)-N(1)-C(6)	111.8(4)
C(5)-N(1)-C(4)	126.8(4)
C(6)-N(1)-C(4)	121.1(4)
C(5)-N(2)-C(7)	112.7(4)
C(5)-N(2)-C(8)	122.3(4)
C(7)-N(2)-C(8)	124.6(4)
C(13)-N(3)-C(14)	110.5(4)
C(13)-N(3)-C(12)	127.0(4)
C(14)-N(3)-C(12)	122.5(4)
C(13)-N(4)-C(15)	111.4(4)
C(13)-N(4)-C(8)#1	123.1(4)
C(15)-N(4)-C(8)#1	124.9(4)
C(20)-N(5)-C(21)	110.1(4)
C(20)-N(5)-C(19)	127.7(4)
C(21)-N(5)-C(19)	122.2(4)
C(20)-N(6)-C(22)	111.8(4)
C(20)-N(6)-C(23)	123.5(4)
C(22)-N(6)-C(23)	124.5(4)
C(29)#2-N(7)-C(24)	112.1(4)
C(29)#2-N(7)-C(23)	123.2(4)
C(24)-N(7)-C(23)	124.5(4)
C(29)-N(8)-C(30)	109.5(4)

C(29)-N(8)-C(28)	126.1(4)
C(30)-N(8)-C(28)	124.2(4)
C(3)-C(2)-C(1)	112.6(4)
C(2)-C(3)-C(4)	110.6(4)
N(1)-C(4)-C(3)	113.2(4)
N(1)-C(5)-N(2)	103.0(4)
N(1)-C(5)-Rh(1)	133.7(4)
N(2)-C(5)-Rh(1)	122.7(3)
C(7)-C(6)-N(1)	107.1(4)
C(6)-C(7)-N(2)	105.4(4)
N(4)#1-C(8)-N(2)	108.9(4)
C(11)-C(10)-C(9)	111.2(4)
C(10)-C(11)-C(12)	112.8(4)
N(3)-C(12)-C(11)	112.0(4)
N(4)-C(13)-N(3)	104.5(4)
N(4)-C(13)-Rh(1)	122.4(3)
N(3)-C(13)-Rh(1)	132.5(3)
C(15)-C(14)-N(3)	107.1(4)
C(14)-C(15)-N(4)	106.4(4)
C(16)-C(17)-C(18)	114.4(5)
C(17)-C(18)-C(19)	112.2(4)
N(5)-C(19)-C(18)	112.7(4)
N(6)-C(20)-N(5)	104.4(4)
N(6)-C(20)-Rh(2)	122.0(3)
N(5)-C(20)-Rh(2)	133.2(3)
C(22)-C(21)-N(5)	107.9(4)
C(21)-C(22)-N(6)	105.8(4)
N(7)-C(23)-N(6)	108.8(4)
C(30)#2-C(24)-N(7)	105.9(4)
C(25)-C(26)-C(27)	114.1(5)
C(28)-C(27)-C(26)	111.8(4)
N(8)-C(28)-C(27)	114.1(4)
N(7)#2-C(29)-N(8)	103.7(4)
N(7)#2-C(29)-Rh(2)	122.5(3)

N(8)-C(29)-Rh(2)	133.7(3)
C(24)#2-C(30)-N(8)	108.8(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z #2 -x+1,-y,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$C_{30}H_{48}Cl_3N_8Rh$**. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	15(1)	13(1)	10(1)	-4(1)	-7(1)	0(1)
Rh(2)	13(1)	15(1)	10(1)	-5(1)	-6(1)	0(1)
Cl(1)	17(1)	18(1)	15(1)	-5(1)	-9(1)	-1(1)
Cl(2)	21(1)	15(1)	17(1)	-7(1)	-10(1)	1(1)
Cl(3)	25(1)	19(1)	25(1)	-8(1)	-16(1)	3(1)
N(1)	19(2)	19(2)	10(2)	-7(2)	-7(2)	2(2)
N(2)	19(2)	20(2)	14(2)	-9(2)	-9(2)	2(2)
N(3)	16(2)	21(2)	15(2)	-8(2)	-8(2)	3(2)
N(4)	16(2)	15(2)	13(2)	-4(2)	-9(2)	1(2)
N(5)	18(2)	17(2)	17(2)	-6(2)	-11(2)	3(2)
N(6)	11(2)	19(2)	16(2)	-6(2)	-5(2)	2(2)
N(7)	17(2)	17(2)	13(2)	-6(2)	-5(2)	-3(2)
N(8)	21(2)	19(2)	16(2)	-4(2)	-9(2)	-3(2)
C(1)	45(4)	31(3)	25(3)	-11(3)	-20(3)	1(3)
C(2)	28(3)	24(3)	30(3)	-5(2)	-20(3)	-1(2)
C(3)	26(3)	28(3)	19(3)	-7(2)	-13(2)	-2(2)
C(4)	26(3)	24(3)	10(2)	-4(2)	-9(2)	-4(2)
C(5)	11(2)	12(2)	11(2)	-2(2)	0(2)	-7(2)
C(6)	22(3)	22(3)	19(3)	-13(2)	-10(2)	2(2)
C(7)	22(3)	16(3)	23(3)	-11(2)	-9(2)	6(2)

C(8)	14(2)	15(2)	16(2)	-6(2)	-8(2)	1(2)
C(9)	44(4)	49(4)	37(4)	-33(3)	-23(3)	24(3)
C(10)	27(3)	33(3)	22(3)	-16(2)	-14(2)	14(2)
C(11)	23(3)	22(3)	15(3)	-5(2)	-8(2)	2(2)
C(12)	13(2)	22(3)	16(3)	-8(2)	-4(2)	2(2)
C(13)	18(2)	10(2)	11(2)	-3(2)	-8(2)	-4(2)
C(14)	26(3)	18(3)	10(2)	-3(2)	-7(2)	-1(2)
C(15)	23(3)	13(2)	11(2)	2(2)	-9(2)	-4(2)
C(16)	34(4)	126(8)	110(7)	-102(7)	-15(4)	16(5)
C(17)	32(3)	44(4)	31(3)	-28(3)	-4(3)	-2(3)
C(18)	26(3)	25(3)	24(3)	-11(2)	-10(2)	-1(2)
C(19)	16(2)	25(3)	16(3)	-7(2)	-8(2)	1(2)
C(20)	15(2)	9(2)	11(2)	-2(2)	-3(2)	-5(2)
C(21)	18(3)	24(3)	20(3)	-4(2)	-11(2)	-1(2)
C(22)	19(3)	22(3)	27(3)	-6(2)	-15(2)	3(2)
C(23)	14(2)	22(3)	18(3)	-14(2)	-4(2)	2(2)
C(24)	13(2)	32(3)	13(3)	-10(2)	1(2)	-6(2)
C(25)	51(4)	40(4)	44(4)	-13(3)	-37(3)	10(3)
C(26)	48(4)	24(3)	33(3)	1(3)	-30(3)	-4(3)
C(27)	36(3)	26(3)	19(3)	-1(2)	-16(3)	-5(2)
C(28)	30(3)	16(3)	20(3)	2(2)	-16(2)	-3(2)
C(29)	15(2)	15(2)	15(2)	-8(2)	-9(2)	1(2)
C(30)	23(3)	27(3)	15(3)	-4(2)	-6(2)	-5(2)