The [M(NHC)] (M=Pd, Pt) fragment in the synthesis of heteronuclear clusters

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2014

Liu, Y. (2014). The [M(NHC)] (M=Pd, Pt) fragment in the synthesis of heteronuclear clusters.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61775>

<https://doi.org/10.32657/10356/61775>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**The $[M(\text{NHC})]$ ($M = \text{Pd}, \text{Pt}$) FRAGMENT IN THE
SYNTHESIS OF HETERONUCLEAR CLUSTERS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2014

**The [M(NHC)] (M= Pd, Pt) FRAGMENT IN THE
SYNTHESIS OF HETERONUCLEAR CLUSTERS**

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2014

ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to my supervisor, A/P Leong Weng Kee for his invaluable guidance and constant support in all aspects of my work in the past four years. His cheerful and candid suggestions and comments, patience were constant inspiration for me to work harder and get better results. Without him, this work is impossible. I will forever be grateful for his guidance.

Thanks also go to my co-supervisor at NUS, A/P Han Vinh Huynh, for his guidance and help throughout my projects.

I would especially like to thank Dr Rakesh for his guidance and helping me solve all the crystal structures. I am grateful to thank my students Toh Zhen Siew Stephanie and Huang Chung Hao and Kwan Jian Ming for their assistance. Many thanks to all the members in our lab: Dr Garvin, Kumaran, Yu Qian, Jing Wei, Yong Jia, Shirley, Yingzhou, Bo Yang, Zhi Yong, Joey, Felicia, Chandan. Thank you guys for making my time in the lab so joyful and for all the help, support and fruitful discussions during group meeting.

I thank Nanyang Technological University for accepting me as a Ph.D student, providing me with financial support. I thank all the CBC staff, Eeling, Wenwei, Joan, Dr Li Yongxin for their kind assistance with instrument training and usage. Many thanks to my friends Li Dan, Meng Xiangjian, Jiang Yaojia, Ji Li, Zhao Kai *etc* for making my life in Singapore happy and colorful.

Finally, I would like to thank my dear parents, husband, and sister for their love, care and encouragement. Love you.

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Summary

While Os–Pd and Os–Pt mixed clusters containing PR_3 ligands are known, those containing N-heterocyclic carbene ligands (NHCs) are not. This thesis describes the results of work carried out on the synthesis of such heteronuclear clusters containing NHC ligands. An overview of NHCs and metal-NHC complexes is presented in Chapter 1. The experimental results are separated into four chapters.

In chapter 2, the syntheses of the first examples of Pd–Os mixed metal carbonyl clusters bearing NHC ligands, *viz.*, $[\text{Pd}_n\text{Os}_3(\text{CO})_{12}(\text{NHC})_n]$ ($n = 1\text{--}3$; **6–8**) and $[\text{PdOs}_3(\text{CO})_{12}(\text{NHC})_2]$ (**9**) are described. These clusters were obtained from the room temperature reaction of $[\text{Os}_3(\text{CO})_{12}]$ (**5**) with $[\text{Pd}(\text{NHC})_2]$, or with the $[\text{Pd}(\text{NHC})]$ fragment generated *in situ* from $[\text{PdCl}(\text{allyl})(\text{NHC})]$ and KO^tBu in IPA. Changing the reaction solvent in the latter from IPA to aprotic DCM afforded, in addition to these clusters, two new triosmium clusters $[\text{Os}_3(\text{CO})_{10}(\eta^3\text{-allyl})_2]$ (**10**) and $[\text{Os}_3(\text{CO})_9\{\mu, k^2C, O\text{-OOC}^t\text{Bu}\}(\text{allyl})]$ (**11**). The $[\text{Pd}(\text{NHC})]$ fragment, exemplified by $\text{NHC} = \text{IMes}$ and generated *in situ*, reacted readily with $[\text{Os}_3(\text{CO})_{11}(\text{ACN})]$, $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$, $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$ and $[\text{Os}_3(\text{CO})_{10}(\text{ACN})_2]$, but failed to react with the more electron-rich, disubstituted clusters $[\text{Os}_3(\text{CO})_{10}(\text{IMes})_2]$ and $[\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2]$. All the Os–Pd clusters obtained are structurally closely-related and can be viewed as adducts of **5** with one to three $[\text{Pd}(\text{NHC})]$ groups. With the exception of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{SIPr})_2]$ (**7d**), the metal cores comprise a triangular arrangement of three Os atoms, with Pd atoms bridging the Os–Os edges. Each of the Os–Pd bond is, in turn, bridged by a carbonyl ligand. In contrast, the structure of **7d** has one of the $[\text{Pd}(\text{NHC})]$ fragments adopting a spike position on the triosmium core. The solution-state structures of **7** were also studied via variable temperature NMR spectroscopy, as well as computationally.

Chapter 3 describes attempts at the use of the [Pt(NHC)] fragment with osmium carbonyl clusters to obtain analogous platinum-containing clusters. Several new clusters, *viz.*, [Pt_nOs₃(CO)₁₂(NHC)_n] (n = 1–3; **6'**–**8'**), as well as the electron-deficient cluster [Os₄(CO)₁₀(μ-H)₂(NHC)] (**16**), were obtained from the reaction of **5** with [PtCl(allyl)(NHC)] (**3'**). The overall structural features of **6'**–**8'** are similar to their corresponding Pd analogues. Variable temperature NMR studies on clusters **7'** showed that all the CO ligands undergo fast exchange above ~ -40 °C, and there was restricted rotation of the phenyl rings about the N–C_{ipso} bond at low temperatures. X-ray crystallographic studies on **16c** and **16d** indicated that they are four-electron deficient according to the EAN rule. The hydride resonances of **16** are unusually downfield for metal hydrides, occurring in the -6 to -10 ppm range. In solution, these clusters existed as an equilibrium mixture of three interconverting isomeric forms.

Chapter 4 describes investigations into the reactivity of the [M((NHC))] (M = Pd or Pt) fragments with [Ir₄(CO)₁₂] (**25**). The [M((NHC))] fragment, generated *in situ* from [MCl(allyl)(NHC)] (M = Pd, allyl = C₃H₅, **3**; M = Pt, allyl = C₄H₇, **3'**), readily reacted with **25** at room temperature to afford the clusters [PdIr₄(CO)₁₂(NHC)] and [M₂Ir₄(CO)₁₂(NHC)₂] (M = Pd, Pt). Several failed attempts at the generation of Cp*Ir(I) or Cp*Rh(I) complexes containing NHCs are also described.

In the final experimental chapter, the discovery and isolation of zwitterionic cluster intermediates from the reaction of free NHC with **5** are reported. These clusters, *viz.*, [Os₃(CO)₁₁{(C=O)*m*NHC}] (NHC = IMes, IPr, I^tBu), have been characterized by X-ray crystallographic studies. They were found to convert slowly in solution to the NHC–monosubstituted clusters [Os₃(CO)₁₁(*m*NHC)], and the mechanism for this transformation has been studied computationally through DFT calculations. This is the first definitive proof for the acyl reaction pathway in carbonyl substitution reactions.

Compound Numbering Scheme

The metallic frameworks of all molecular structures are drawn in outline. The short line extending from M (M=Os, Ru, Ir in the molecular structure diagrams) represents a coordinative bond from carbon monoxide to metal (M–CO). This is illustrated in the example below:

No	Molecular formula			
1				
	R = Mes	(a)	R = Mes	(b)
	2,6-di- ⁱ Pr-phenyl	(c)	2,6-di- ⁱ Pr-phenyl	(d)
	Me	(e)		
	^t Bu	(f)		
	Tol	(g)		
2				
	R = Mes	(a)		
	2,6-di- ⁱ Pr-phenyl	(c)		
	Me	(e)		
	^t Bu	(f)		
3				
	R= Mes	(a)	R= Mes	(b)
	2,6-di- ⁱ Pr-phenyl	(c)	2,6-di- ⁱ Pr-phenyl	(d)
3'				
	R= Mes	(a)	R= Mes	(b)
	2,6-di- ⁱ Pr-phenyl	(c)	2,6-di- ⁱ Pr-phenyl	(d)

4a
	Pd(IMes) ₂		
5
	M = Os Ru		
5(Ru)
6	M1=Os, M2 = Pd, L =IMes SIMes IPr SIPr	(a) 6' (b) (c) (d)	M1=Os, M2 = Pt, L = IMes SIMes IPr SIPr (a) (b) (c) (d)

7	M1=Os, M2 = Pd, L =IMes SIMes IPr SIPr	(a) 7' (b) (c) (d)	M1=Os, M2 = Pt, L = IMes SIMes IPr SIPr (a) (b) (c) (d)

8	M1=Os, M2 = Pd, L =IMes SIMes IPr SIPr	(a) 8' (b) (c) (d)	M1=Os, M2 = Pt, L = IMes SIMes IPr SIPr (a) (b) (c) (d)
8(Ru)	M1=Ru, M2 = Pd, L =IMes SIMes IPr SIPr	(a) (b) (c) (d)	
8'(Ru)	M1=Ru, M2 = Pt, L = IMes SIMes IPr SIPr	(a') (b') (c') (d')	

9		(a) (a')
10		$[\text{Os}_3(\text{CO})_{10}(\eta^3\text{-allyl})_2]$
12		L = IMes (a) <i>m</i> IMes (a') IPr (c) <i>m</i> IPr (c') I ^t Bu (f) <i>m</i> I ^t Bu (f') ACN (g) PPh ₃ (h) P(OMe) ₃ (i) P(OEt) ₃ (j)
14		$[\text{H}_2\text{Os}_3(\text{CO})_{10}]$
16		NHC = IMes (a) IPr (c) SIPr (d)
18a	{[(IMes)H] ⁺ [H ₃ Os ₄ (CO) ₁₂] ⁻ }	
18a(Ru)	{[(IMes)H] ⁺ [H ₃ Ru ₄ (CO) ₁₂] ⁻ }	
18c(Ru)	{[(IPr)H] ⁺ [H ₃ Ru ₄ (CO) ₁₂] ⁻ }	
11		$[\text{Os}_3(\text{CO})_9(\mu_2\text{-CO})(\text{allyl})(\text{O}^t\text{Bu})]$
13		L = IMes (a) ACN (g) PPh ₃ (h) P(OMe) ₃ (i)
15		$[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-Cl})]$
17		17 M = Os 17(Ru) Ru

19

20

21

22

23

24

25

26

(c)

(d)

27	M= Pd, NHC = IPr	(c)
	M= Pd, NHC = SIPr	(d)
27'	M= Pt, NHC = IPr	(c)
	M= Pt, NHC = SIPr	(d)

28	M = Ir	
28(Rh)	Rh

29	M = Ir	
29(Rh)	Rh

30	M = Ir	
30(Rh)	Rh	
31	{[Cp*Ir(Ime)(PPh ₃)Cl] ⁺ Cl ⁻ }	
31(Rh)	{[Cp*Rh(Ime)(PPh ₃)Cl] ⁺ Cl ⁻ }	
32
	[Cp*IrOs ₃ (μ-H) ₂ (CO) ₁₀]	
33
	R = Mes	(a')
	2,6-di- ⁱ Pr-phenyl	(c')
	^t Bu	(f')
34	[Os ₃ (μ-H)(CO) ₁₀ OP(OMe) ₂]	
37	[W(CO) ₆]	
38a	[W(CO) ₅ (IMes)]	

39a	$[\text{Ir}_4(\text{CO})_{11}(\text{IMes})]$
39a'	$[\text{Ir}_4(\text{CO})_{11}(m\text{IMes})]$
40	<p>The structure shows an iridium (Ir) center coordinated to two carbonyl (CO) groups and a 1-mesitylimidazole-2-ylidene (IMes) ligand. The IMes ligand consists of an imidazole ring with mesityl (2,4,6-trimethylphenyl) groups at the 1 and 3 positions. The iridium is also coordinated to a chlorine (Cl) atom. The CO ligands are shown with wedged and dashed bonds to indicate stereochemistry.</p> <p>$[\text{Ir}(\text{CO})_2(\text{IMes})\text{Cl}]$</p>
41	$\text{R} = \text{CH}_3$
41'	$\text{R} = \text{H}$

Abbreviations – Spectroscopy

NMR	nuclear magnetic resonance
Δ	NMR chemical shift
HMQC	heteronuclear multiple quantum coherence
HMBC	heteronuclear multiple bond correlation
^1H EXSY	proton exchange spectroscopy
S	singlet
D	doublet
T	triplet
Q	quartet
Sept	septet
M	multiplet
Br	broad
VT	variable temperature
IR	infrared
$\nu(\text{CO})$	stretching frequency in the carbonyl region
DFT	density functional theory
NBO	natural bond orbital
NAO	natural atomic orbital
ESI	electrospray ionization
m/z	mass to charge ratio

Abbreviations- Unit

Mg	milligram
G	gram
Mmol	millimole
Mol	mole
mL	millilitre
Min	minute
H	hour
cm^{-1}	wavenumber
$^{\circ}\text{C}$	degree
Å	Angstrom

Abbreviations- Chemical and Substituents

NHC	N-Heterocyclic carbene
<i>m</i> NHC	abnormally bound N-heterocyclic carbene
IMe	<i>N,N'</i> -bis(methyl)imidazolin-2-ylidene
IMes	<i>N,N'</i> -bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIMes	<i>N,N'</i> -bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene
IPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
SIPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene
<i>t</i> Bu	<i>N,N'</i> -bis(tert-butyl)imidazolin-2-ylidene
Hex	hexane
DCM	dichloromethane
ACN	acetonitrile
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl

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Publications

[1] Y. Liu, R. Ganguly, H. V. Huynh, W. K. Leong. Direct evidence for the attack of the a free N-heterocyclic carbene at a carbonyl ligand: A zwitterionic osmium carbonyl cluster. *Angewandte Chemie International Edition* **2013**, 52(46), 12110-12113.

[2] Y. Liu, R. Ganguly, H. V. Huynh, W. K. Leong. Palladium-Osmium Heterometallic Clusters Containing NHC ligands. *Organometallics* **2013**, 32(24), 7559-7563.

Chapter 1 Transition metal carbonyl clusters containing N-heterocyclic carbenes

1.1 Heteronuclear transition metal carbonyl clusters

An organometallic cluster compound has been defined as a polynuclear molecule held together by direct and substantial metal-metal bonding between the metal atoms.¹ Heterometallic clusters are clusters comprising different types of transition metals. Two examples are given below:²

Research into heterometallic clusters have gained considerable interest because of their potential as precursors for highly reactive heterogeneous catalysts that can be generated from them when they are deposited onto suitable supporting materials.³ This method of nanoparticle synthesis offers good control of the multimetallic composition, retaining its multimetallic ratio after ligand removal by calcination on a support. Many published work have shown that multi-metallic nanoparticles exhibit significantly different catalytic properties compared to their monometallic counterparts in the form of both higher activity and selectivity.⁴ The synergistic interaction between different component metal centres in the same cluster may also lead to novel reactivity, often with enhancement in the efficiency of catalytic reactions.

The preparation of catalysts via organometallic cluster precursors has been studied by various research groups over the years.⁵ For example, the mixed-metal cluster [Pd₆Ru₆(CO)₂₄]²⁻ was used as a single-source precursor for the synthesis of a

highly active hydrogenation catalyst. The resultant Pd–Ru bimetallic catalyst (the metal Pd readily takes up H₂, while Ru has a strong tendency to bind alkenes) showed a higher selectivity and reactivity than the monometallic analogues (Scheme 1.1).^{4b}

Scheme 1.1

In another example, Ru–Pt nanoparticles with a 5:1 ratio of the metals can be obtained from an organometallic cluster precursor, [PPh₄]₂[Ru₅PtC(CO)₁₅]. This has proven to be very active for ethanol steam reforming (ESR), a vital industrial hydrogen production process.⁶ The importance of developing rational syntheses of heteronuclear clusters thus should not be underestimated.

1.2 Synthetic strategies to heteronuclear carbonyl clusters

A number of synthetic methods to heteronuclear carbonyl clusters are known, they will be discussed briefly in this section.

1) Condensation reactions

Thermal condensation between small clusters either through pyrolysis (heating in the solid state) or thermolysis (heating in the presence of a solvent) can result in clusters of higher nuclearity,^{7,8} and hence is also a good route to heterometallic clusters. The formation of metal-metal bonds occurs due to the thermal elimination of CO. The loss of CO acts as a driving force for the reaction. For example, [Ru₄(μ-H)₂(CO)₁₃] reacts with [Ru₄Pt₂(CO)₁₈] to form the decanuclear cluster [Ru₈Pt₂(μ₃-H)₂(CO)₂₃] with the elimination of CO ligands (Scheme 1.2).⁹

2) Ionic coupling reactions

A rather more controlled method of preparing heterometallic clusters involves the coupling of a metal-containing cationic fragment with an anionic cluster. For example, reaction of the reactive cationic $\text{Pt}^{\text{II}}\text{L}_2$ fragment (generated via chloride abstraction by silica gel from PtL_2Cl_2) with an anionic carbido ruthenium cluster is a known synthetic method to produce Ru-Pt clusters in high yield (Scheme 1.3).¹⁰

Scheme 1.2

Scheme 1.3

3) Addition Reactions

Some clusters can undergo addition reactions in which small metal fragments are added to the cluster framework without the elimination of ligands to form clusters of higher nuclearity. For example, $[\text{Ir}_4(\text{CO})_{12}]$ reacts with excess $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ to give $[\text{Ir}_4(\text{CO})_{12}\{\text{Pt}(\text{P}^t\text{Bu}_3)\}_2]$ (Scheme 1.4).¹¹

Scheme 1.4

The development of new synthetic routes to heterometallic clusters remains of interest. On the other hand, the last decade has witnessed intense interests in the organometallic chemistry of N-heterocyclic carbenes (NHCs), in relation to their coordination chemistry and in homogeneous catalysis;¹² they have become useful ligands to synthesize various possible metal-NHCs complexes that are complementary to those of phosphines.

1.3 N-heterocyclic carbenes (NHCs)

NHCs are neutral ligands in which the carbon atom carrying the lone pair of electrons forms part of a heterocyclic ring with vicinal amino substituents.¹³ NHC was first reported as ligands in transition metal chemistry in 1968 by Öfele and Wanzlick.¹⁴ Later, in 1970, Wanzlick and coworkers synthesized the first imidazol-2-ylidene carbene intermediate via the deprotonation of an imidazolium salt.¹⁵ NHCs were found to be compatible with both high and low oxidation-state transition metals. The unequivocal synthesis and isolation of Arduengo's stable, crystalline, free NHC ligand (IAd) in 1991 (Scheme 1.5), catalyzed a significant increase in interest in NHCs as important and powerful ligands in organometallic chemistry and catalysis. IAd is stable at ambient temperature under an inert atmosphere, and melts at 240-241 °C without decomposition.¹⁶ Its stability is attributed to the very bulky substituents on N, as well as to the π -donation from the p orbitals of the adjacent nitrogen atoms to the

vacant p orbital of the carbene carbon.

Scheme 1.5

The potential of NHCs to serve as spectator ligands was recognized by Hermann *et al* in 1995.¹⁷ Soon thereafter, an intensive exploration of NHC as potential ligands in organometallic chemistry began owing to their easy preparation and unique properties. To date, a vast number of N-heterocyclic carbene frameworks have been reported, ranging from 4- to 7-membered rings.¹⁸ Some examples are shown in Figure 1.1.^{19,20,21}

This thesis deals with only the most common class of 5-membered NHCs; the electronically unsaturated imidazol-2-ylidene (A type) and saturated imidazolidin-2-ylidene (B type) (Figure 1.2).

1.3.1 Stereoelectronic properties of common types of NHCs

Phosphines have been systematically classified in the pioneering work by Tolman;²² and similar classifications for NHCs have been proposed to account for steric and electronic effects.²³ The most distinguishing feature of NHCs is their strong σ donating ability, enabling it to bond strongly to many metal centres. This property also leads to the stabilization of transition states or intermediates in reactions. NHCs have, as a result, been used to replace classical $2e^-$ donor ligands like amines, ethers, and phosphines in coordination chemistry. Electronic stabilization of the NHCs depends on the σ withdrawing properties of the N atoms and the electron-donating properties of the substituents. For example, the presence of alkyl and phenyl groups stabilizes NHCs due to their significant electron-donating ability. Modifying theazole ring can also affect its electronic properties significantly.^{12b, 24}

The electron-donor properties of NHC ligands have been quantified via a number of methods:

- a) pK_a values of the free ligands, obtained experimentally,²⁵ or computationally;²⁶
- b) metal-ligand bond dissociation energy of the NHC ligand;²⁷
- c) ν_{CO} stretching frequency of metal carbonyl complexes containing an NHC;²⁸
- d) $^{13}C\{^1H\}$ NMR chemical shift of the carbenoid carbon in trans-[PdBr₂(ⁱPr₂-bimyl)L]ⁿ⁻ complexes.

The last method is the most recent, and uses the chemical shift of the carbenoid carbon as a probe for the evaluation of the donor strength of the NHC ligands, as it was found that the ⁱPr₂-bimyl signal was sensitive to the donor strengths of the co-ligands.²⁹ Based on this last methodology, Huynh *et al* reported that the following carbenes can be arranged in order of decreasing donor strength: SIPr $\approx$ SIMes > IPr > IMes. Expanding the ring size from five to six and then to seven, leads to an increase in

electron richness.³⁰

NHCs have a steric environment that is best described as fence- or fan-like. The electronic and steric properties can be easily tuned via changing the substituent on the N atoms. Bulky substituents on the N atoms can provide steric hindrance that prevents dimerization of the NHCs. The steric property of NHCs can be measured via the ‘percentage buried volume’ method developed by Cavallo and coworkers.³¹ The buried volume (V_{bur}) denotes the volume of a sphere around the metal (with a certain radius r) buried by the overlap with atoms of the NHC ligand under investigation (Figure 1.3).³²

Figure 1.3. Definition of the buried volume % V_{bur} .

The same set of parameters has to be used for a given ligand class otherwise it is impossible to compare the results. A radius of 3.5 Å for the sphere and a distance of 2.0 Å between the metal and coordinating carbene atom are suggested to be a good choice to describe the steric demand.³² The bulkier a ligand is, the greater the % V_{bur} value. Ring-expanded carbenes have higher % V_{bur} values compared with their 5-membered analogues. For highly coordinated complexes, the buried volume decrease in the order: $t\text{Bu}/\text{IAd} > \text{SIPr}/\text{IPr} > \text{SIMes}/\text{IMes}$.³²

1.3.2 Comparison between NHCs and Phosphines

Herrmann was the first to point out the similarity of electronic properties between electron-rich tertiary phosphines and NHCs in metal coordination chemistry.³³ NHCs resemble phosphines in being monodentate 2e⁻ donor ligands that are sterically and electronically tunable, but are able to bind stronger to many transition metal atoms than do phosphines. For example, the bond strength of the NHC-Ru bond was calculated to be 20-40 kcal/mol stronger than that of the PR₃-Ru bond.³⁴ In contrast to phosphines, where the substituent R is directly attached to the phosphorus donor atom so that changing R leads to a change in both the steric and electronic environment of the ligand, the substituent in an NHC is not bonded to the carbene carbon so that changing the R group primarily affects the steric nature of the NHC. Transition metal NHC complexes are remarkably less sensitive to air and moisture than other ligands, facilitating catalysis in aqueous medium. This has made them appealing ligands in many catalytic reactions where a stable metal ligand bond and high electron density on the metal centre are often essential.³⁵ NHCs have been introduced as possible replacements for phosphines as ligands in organometallic catalysts, greatly extending the scope of application reached by phosphines.³⁶ The bonding of NHC to metal was believed to be purely σ in nature; but recent evidence indicates that a weak π back-donation may also be present.³⁷

The replacement of one labile phosphine group by a stabilizing NHC was reported independently by Nolan,³⁸ Grubbs,³⁹ Fürstner and Herrmann (Figure 1.4).⁴⁰

Figure 1.4. Examples for $[\text{Ru}(\text{PR}_3)(\text{NHC})]/[\text{Ru}(\text{NHC})_2]$.

These NHC/phosphine mixed systems gave rise to stable complexes like $[(\text{NHC})\text{Ru}(\text{PCy}_3)\text{Cl}_2(3\text{-pheyindenylid-1-ene})]$, which has proven to be superior to their bis-phosphine or bis-NHC analogs in overall olefin metathesis catalytic activity.^{41,42} The striking performance of these mixed catalysts may be due to the synergy of NHC and coordinatively labile PR_3 ligands. The sterically bulky NHC ligand can provide the metal center with considerable steric protection, and at the same time, the less labile NHC as a good electron donor, can stabilize the precatalyst as well as the coordinatively unsaturated, catalytically relevant intermediate.

1.4 Common methods to prepare metal-NHC complexes

Some free carbenes are commercially available, although they are relatively expensive. For example, 1 g of free IMes costs S\$280. Free carbenes can be easily prepared in high yields, or *in situ*, from the corresponding imidazolium salt. A large number of methods for the preparation of NHCs via the imidazolium salts have been reported. For example, the most commonly used IMes/IPr precursor azolium salts can be generated from glyoxal, a primary amine and formaldehyde in ~70% yield. Deprotonation with a strong base affords free IMe/IPr in ~80% yield.⁴³ Two other

methods are exemplified by the reduction of the diisobutyl-substituted thione with Na/K alloy in toluene,⁴⁴ and an endothermic decomposition with concomitant elimination of methanol or C₆F₅H (Scheme 1.6).⁴⁵ Generally, all the methods involve the elimination of a stable small molecule from a precursor.⁴⁶

Scheme 1.6

There are also a number of methods to synthesize metal NHC complexes from NHC precursors. Some of these include:

1) NHC transfer reagent

One of the most common and easy way of attaching a carbene is through transmetalation using NHC complexes of silver.⁴⁷ Simple treatment of an imidazolium salt with weakly basic silver oxide gives a disubstituted Ag(I) complex via *in situ* deprotonation.⁴⁸ The carbene ligand is easily transferred to other metals and no free carbene is generated throughout. This method is effective and desirable as an inert atmosphere is not needed, and the medium is only weakly basic and therefore unlikely

to interfere with sensitive organometallic compounds. For example, $[\text{Os}_3(\mu\text{-Cl})(\text{CO})_{10}(\mu\text{-Ag}(\text{IMes}))]$ was prepared using this method (Scheme 1.7).⁴⁹

Scheme 1.7

Other possible synthetic routes via W-, Mo-, Cr- or Si-carbene transfer have also been reported (Scheme 1.8).⁵⁰

Scheme 1.8

2) From the free carbene

Free carbenes can be used directly, or generated *in situ* via deprotonation by a strong base from the precursor imidazolium salt. These can substitute a carbonyl ligand.⁵¹ Cabeza *et al* reported the synthesis and characterization of the first trinuclear cluster containing NHC ligands via this method.⁵² Similarly, the treatment of $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ with free IPr gave an Ir(I) complex through dehydrogenation of one of the isopropyl substituents (Scheme 1.9).⁵³

Scheme 1.9

3) Cleavage of electron-rich enetetramines

As early as in 1977, Lappert and coworkers have reported the cleavage of enetetramine $(\text{R}_2\text{N})_2\text{C}=\text{C}(\text{NR}_2)_2$ upon heating in the presence of $[\text{Cr}(\text{CO})_6]$, to form $[\text{Cr}(\text{CO})_5(\text{NHC})]$.⁵⁴ Hahn also reported the room temperature reaction of the carbene dimer with palladium diiodide to give the dicarbene palladium complex (Scheme 1.10).⁵⁵

Scheme 1.10

4) *In-situ* deprotonation with a basic metal precursor

The oldest method for the generation of complexes containing NHC ligands is from the reaction of an imidazolium salt with a metal complex which contains basic ligands, such as, $[\text{HCr}(\text{CO})_5]$ ⁵⁶ or $[\text{Hg}(\text{OAc})_2]$.⁵⁷ Recently, Nolan reported a one-pot procedure for the synthesis of $[\text{Cu}(\text{NHC})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (Scheme 1.11).⁵⁸

Scheme 1.11

5) Oxidative addition to zerovalent metal complexes

Oxidation addition of various imidazolium cations to zerovalent metals can generate NHC carbene complexes (Scheme 1.12).⁵⁹

Scheme 1.12

1.5 Motivation and aim of the project

As mentioned above, heterometallic clusters are of interest as precursors for the preparation of highly reactive and stoichiometrically-precise heterogeneous catalysts. Such bi- and multi-metallic catalysts have exhibited advantages over their monometallic counterparts in the form of both higher activity and selectivity.^{60,61} For

this reason, the development of synthetic methodologies towards heterometallic clusters remain important. One group of heterometallic clusters that has attracted considerable attention is that of the ruthenium-platinum system. These are precursors for the preparation of very highly active metal catalysts for ethanol steam reforming, a reaction which is of importance for the production of hydrogen.⁶²

One interesting recent development in the synthesis of mixed metallic clusters is a series of reports by R. D. Adams that $[M(P^tBu_3)_2]$ (where $M = Pt$ or Pd) can lose one of its P^tBu_3 ligands readily in solution to give $[M(P^tBu_3)]$, which can then add to the metal-metal bonds of various metal-carbonyl complexes to afford a variety of new mixed metal-carbonyl complexes containing palladium or platinum. For example, $[Re_2(CO)_8(\mu-SnPh_2)_2\{Pd(P^tBu_3)\}_2]$, $[Ru_3(CO)_{12}\{Pd(P^tBu_3)\}_3]$ and $[Ru_6(CO)_{17}(\mu_6-C)\{Pd(P^tBu_3)\}_2]$ were obtained from the reaction of $[Re_2(CO)_8(\mu-SnPh_2)_2]/[Ru_3(CO)_{12}]/[Ru_6(CO)_{17}(\mu_6-C)]$ with $[Pd(P^tBu_3)_2]$ (Scheme 1.13).⁶³ $[Rh_4(CO)_{12}]$ reacts readily with $[Pd(P^tBu_3)_2]$ to afford the hexarhodium cluster complexes $[Rh_6(CO)_{12}\{Pd(P^tBu_3)\}_3]$ and $[Rh_6(CO)_{12}\{Pd(P^tBu_3)\}_4]$, which have three and four edge-bridging $[Pd(P^tBu_3)]$ groups, respectively.⁶⁴

Scheme 1.13

Palladium also can add across the very inert metal-metal bonds of $[\text{Os}_3(\text{CO})_{12}]$ to afford the bis- and tris- $\text{Pd}(\text{P}^t\text{Bu}_3)$ adducts, $[\text{Os}_3(\text{CO})_{12}\{\text{Pd}(\text{P}^t\text{Bu}_3)\}_2]$ and $[\text{Os}_3(\text{CO})_{12}\{\text{Pd}(\text{P}^t\text{Bu}_3)\}_3]$ (Figure 1.5).⁶⁵ It was reported that the $[\text{Pd}(\text{P}^t\text{Bu}_3)]$ groups are added and eliminated readily in this system at room temperature and all the three compounds existed in an equilibrium in solution.

Figure 1.5. Synthesis of $[\text{Os}_3(\text{CO})_{12}\{\text{Pd}(\text{P}^t\text{Bu}_3)\}_n]$ ($n=2,3$).

The $[\text{Pt}(\text{P}^t\text{Bu}_3)]$ group showed similar reactivity with its Pd analogue. For example, $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ reacted readily with $[\text{Os}_3(\text{CO})_{12}]$ to afford $[\text{Os}_3(\text{CO})_{12}\text{Pt}_n(\text{P}^t\text{Bu}_3)_n]$ ($n=1-3$).⁶⁶ The clusters $[\text{Ru}_3(\text{CO})_{12}\text{Pt}_3(\text{P}^t\text{Bu}_3)_3]$ and

$[\text{Ru}_3(\text{CO})_8\text{Pt}(\text{P}^t\text{Bu}_3)_2(\mu\text{-P}^t\text{Bu})(\mu\text{-H})_2]$ were obtained from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$.⁶⁷ A di-adduct, $[\text{Pt}_2\text{Ir}_4(\text{CO})_{12}(\text{P}^t\text{Bu}_3)_2]$ was formed when it was added to the metal-metal bonds of $[\text{Ir}_4(\text{CO})_{12}]$.⁶⁸ Other mixed-metal clusters also have been reported, e.g., $[\text{Re}_2(\mu\text{-SbPh}_2)_2(\text{CO})_8(\mu\text{-H})\{\text{Pt}(\text{P}^t\text{Bu}_3)_2\}]$,⁶⁹ and $[\text{Pt}_3\text{Re}_2(\text{CO})_6(\text{P}^t\text{Bu}_3)_2]$,⁷⁰ which obtained from the reaction of $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ with $[\text{Re}_2(\text{CO})_8(\mu\text{-SbPh}_2)_2]$ and $[\text{Pt}(\text{P}^t\text{Bu}_3)_2][\text{Re}_2(\text{CO})_{10}]$ respectively.

The propensity for the $[\text{M}(\text{P}^t\text{Bu}_3)]$ fragments (where $\text{M} = \text{Pd}$ or Pt) to add across metal-metal bonds suggests that an $[\text{M}(\text{NHC})]$ moiety should be able to react similarly. NHCs are strong neutral electron donors and they are better σ -donor ligands than even basic alkylphosphines.^{71,72} They are also less oxidation-sensitive than tertiary phosphines.^{24,73} It can therefore be expected that $[\text{Pd}(\text{PR}_3)(\text{NHC})]$ or $[\text{Pd}(\text{NHC})_2]$ will be even more basic than the $[\text{M}(\text{P}^t\text{Bu}_3)]$ fragment.

The aim of this research was therefore to investigate the reactivity of N-heterocyclic carbene complexes of Pd/Pt with osmium, ruthenium or iridium carbonyl clusters. Specifically, I wished to investigate:

1. The use of Pd(0) fragments containing an NHC ligand, generated either from a Pd(0) species such as $[\text{Pd}(\text{NHC})_2]$, or *in situ* from a Pd(II) species such as $[\text{PdCl}(\text{allyl})(\text{NHC})]$.
2. The reactions of the generated $[\text{Pt}(\text{NHC})]$ fragment with the groups 8 and 9 parent carbonyl clusters $[\text{Os}_3(\text{CO})_{12}]$, $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{Ir}_4(\text{CO})_{12}]$, and other carbonyl clusters.
3. The properties and reactivity of the heterometallic clusters obtained.

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CHAPTER 2 Nucleophilic attack of the [Pd(NHC)] fragment on osmium clusters

2.1 Introduction

Although the chemistry of osmium/ruthenium palladium mixed metal clusters have been reported, such mixed metal framework possessing an NHC ligand seems to be unexplored. This chapter describes the attempts made to develop synthetic strategies to heteronuclear OsPd and RuPd clusters containing NHC ligands. The following precursors are going to be used: NHC·HCl (**1a-d**), free carbene IMes (**2a**), [PdCl(allyl)(NHC)] (**3a-d**), and [Pd(IMes)₂] (**4a**) (Figure 2.1).

Figure 2.1. [Pd(NHC)] precursors used in this section.

2.2 Reactivity study of [Pd(NHC)] with [Os₃(CO)₁₂]

2.2.1 Reaction of [Pd(NHC)₂] with [Os₃(CO)₁₂]

The room temperature reaction of **4a** with [Os₃(CO)₁₂] (**5**) in hexane readily led to the formation of three new mixed-metal clusters [PdOs₃(CO)₁₂(IMes)] (**6a**), [Pd₂Os₃(CO)₁₂(IMes)₂] (**7a**), [PdOs₃(CO)₁₂(IMes)₂] (**9a**) (Scheme 2.1).

Cluster **6a** is stable in air in the solid state for a few days. Diffraction quality crystals of **6a** were obtained from hexane/DCM by slow evaporation. The molecular structure of compound **6a** is shown in Figure 2.2. Cluster **6a** consists of a triangular cluster of three osmium atoms with one bridging [Pd(IMes)] group across an Os–Os bond. It is an electron-precise cluster, with a valence electron count of 60, if each osmium atom has an 18-electron configuration and each palladium atom a 16-electron configuration. Cluster **6a** has the same number of CO ligands as the parent cluster **5** and thus can be regarded to have been formed by the addition of a [Pd(IMes)] group across an Os–Os bond. Each Os–Pd bond contains a bridging carbonyl ligand. The presence of bridging CO ligands enables additional electron density from the [Pd(NHC)] to be delocalized away from the metal core.¹ The DCM solution IR spectrum of **6a** has a broad, weak peak at 1814 cm⁻¹, showing the persistence of the bridging carbonyl in solution.

Figure 2.2. ORTEP diagram of compound **6a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

The identification of **7a** as $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{IMes})_2]$ was made on the basis of comparison of its IR pattern with that of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{SIMes})_2]$ (**7b**) for which the structure has been confirmed by a single crystal X-ray structural analysis to be discussed in the next section. Its ^1H NMR spectrum showed one set of IMes resonances, and the ESI-MS showed peaks at 1731.0, which were consistent with the proposed structure. As in the case of **6a**, the number of CO ligands in **7a** is the same as that for **5**, so that it may be regarded to have been formed by the addition of $[\text{Pd}(\text{IMes})]$ groups across two Os–Os bonds.

Red cluster **9a** is stable in air. Its IR spectrum in DCM exhibits a peak at 1810 cm^{-1} , showing the presence of bridging carbonyl. An ESI-MS spectrum shows a strong molecular ion cluster of peaks centered at $m/z=1595.1$, as well as a fragment cluster of peaks corresponding to loss of one carbonyl. Diffraction-quality crystals of **9a** were obtained by slow evaporation from a hexane/DCM solution. Two molecules of the

cluster were found in the asymmetric unit, as well as half a molecule of hexane solvate. The solid-state structure of **9a** shows that it is best regarded as derivative of **6a** in which one of the CO ligands on the unique osmium has been replaced by an IMes ligand (Figure 2.3).

Figure 2.3. ORTEP diagram of compound **9a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

The ease with which the reaction proceeded is particularly interesting since the metal-metal bonds in **5** are strong and do not generally participate in reactions at ambient temperatures.² As pointed out above, the structures of **6a** and **7a** suggest that **4** readily loses one of its NHC ligands in solution to form a [Pd(NHC)] fragment, which adds across an Os–Os bond under mild conditions. This may be attributed to the very electron rich metal center in the [Pd(NHC)] fragment.

2.2.2 Reactivity of [PdCl(allyl)(NHC)] with [Os₃(CO)₁₂]

One drawback in the use of the dicarbenes **4** is that they are very sensitive to oxygen and moisture. They are prepared by the reduction of [PdCl(allyl)(NHC)] (**3**) in

the presence of a base and IPA as the reducing reagent; the reaction was proposed to proceed via the generation of a $[\text{Pd}(\text{NHC})]$ species, which could be subsequently trapped by another NHC or 2-electron donor ligand (Scheme 2.2).⁵ It occurred to us that, in the absence of a trapping agent, the $[\text{Pd}(\text{NHC})]$ intermediate generated might react directly with a cluster. Such a route has the great advantage that the complex **3** can be easily prepared and are air-stable, and hence much easier to handle than **4**.

Scheme 2.2

The reaction of three molar equivalents of **3a** with **5** in IPA, in the presence of KO^tBu , afforded a purple precipitate **8a** as the major product, together with smaller amounts of **6a** and **7a**. Cluster **8a** is soluble in a range of solvents, including CH_2Cl_2 , toluene, tetrahydrofuran, dimethyl formamide, and ethyl acetate. Although it is stable in the solid state, it converted to **6a** and **7a** readily in dichloromethane solution. Attempts to grow a crystal suitable for X-ray crystal structural analysis failed as a consequence. A similar reaction, and observation, was made with the saturated SIMes analogue **3b**. In contrast, for the more bulky and electron-rich IPr and SIPr analogues **3c** and **3d**, the reaction did not result in any precipitate but a red-purple solution, from which the products **6c-d**, **7c-d**, **8c-d** were obtained (Scheme 2.3). Once isolated, all the products were relatively stable in the solid state over several days.

Scheme 2.3

All the products have been characterized spectroscopically and analytically, and in the case of **6a-d**, **7b-d** and **8c-d**, by single crystal structural analyses as well. ORTEP plots showing the structures of **6c**, **7c**, **7d** and **8c** are given in Figures 2.4-2.7, respectively. The solid state structures show that **6b-d** are isostructural to their corresponding IMes analogue **6a**. The IR spectral profiles for the carbonyl stretching vibrations for these four clusters are also similar.

While the structures of **7b** and **7c** show the same metal core, that for **7d** is different in that one of the [Pd(SIPr)] unit appears as a “spike”. There should therefore be two chemically distinct NHCs in **7d**, but its ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at

ambient temperature showed only one set of NHC signals, and its solution IR spectrum was also very similar in pattern to those for **7a-c**. These suggest that **7d** exists in solution as a mixture of rapidly interconverting isomers; the other isomer presumably has the structure found for **7a-c**. Unfortunately, we have not been able to isolate and structurally characterize the alternative isomer of either **7a-c** or **7d**. This point will be further explored in the VT-NMR study section. Monitoring by NMR spectroscopy showed that **7d** slowly converted to **6d**, and after a few days, a brown solution as well as an insoluble black solid was observed.

Figure 2.4. ORTEP diagram of $[\text{PdOs}_3(\text{CO})_{12}(\text{IPr})]$ (**6c**). Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 2.5. ORTEP diagram of molecule A of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{IPr})_2]$ (**7c**). Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Mean (maximum) deviation from Os_3Pd plane = 0.101 (0.191) Å.

Figure 2.6. ORTEP diagram of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{SIPr})_2]$ (**7d**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 2.7. ORTEP diagram of $[\text{Pd}_3\text{Os}_3(\text{CO})_{12}(\text{IPr})_3]$ (**8c**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

2.3 Crystallographic discussion

The clusters **6-8** are all structurally closely related. As suggested above, they all have the same number of CO ligands as the parent cluster **5** and hence can be viewed simply as adducts of **5** with $[\text{Pd}(\text{NHC})]_{1-3}$ groups. With the exception of **7d** the metal cores comprise a triangular arrangement of three Os atoms, with a Pd atom bridging one to three of the Os–Os edges.

No structural analogues of **6** (or **9**) have been reported. Phosphine analogues of **7b-c** and **8** are known (Figure 2.8 **B** and **C**),⁶ and the ‘terminal’ coordination mode of the Pd atom in **7d** is similar to that in $[\text{Os}_3(\text{CO})_{12}\{\text{Pd}(\text{bipy})\}_2]$ (**A**) (Figure 2.8).³

Selected bond parameters for **6a-d**, **7c** and **8c-d** are given in Figures 2.9 to 2.11, respectively. As may be expected, all the Pd-bridged Os–Os bonds are significantly longer than the unbridged Os–Os bonds; the former ranges from 2.9617(6) Å in **8d** to 2.9373(6) Å in **7d**, while the latter ranges from 2.8963(7) Å in **7c** to 2.8591(6) Å in **6c**. Interestingly, the Os–Pd bond in **7d** (2.6712(7) Å) is short compared to the others (2.79650(10) Å in **8d** to 2.7082(9) Å in **7c**), and is also shorter than the 2.727(1) Å in $[\text{Os}_3(\text{CO})_{12}\{\text{Pd}(\text{bipy})\}_2]$ **A**.⁸

The gross structural features of **7b-c** and **8** are similar to the reported P^tBu_3 analogues **B** and **C** (Figure 2.8). With each addition of a $[\text{Pd}(\text{PR}_3)]$ group, two Pd–Os bonds are formed, but only one of the two Pd–Os bonds contains a bridging CO ligand. In the NHC analogues **6-8**, all the Os–Pd bonds are each bridged by a carbonyl ligand and most probably reflects the greater electron donor ability of the NHCs.^{4,5} Although the bridging carbonyls are asymmetric, this does not appear to be related to stereoelectronic effects, or to the difference in the covalent radii of the metals. This is particularly clear in cluster **8**, where the Os–CO bond lengths for the bridging carbonyl ligand alternate around the Os_3Pd_3 perimeter (Figure 2.11). It is therefore likely that the asymmetry observed is due to crystal packing forces.

Another major difference is that in **B** and **C**, the Pd atoms lie significantly out of the Os_3 planes (Table 2-1), while the Os_3Pd_n planes are rather flat in the clusters **6-9**.⁶ This may be attributed to the fact that the bulky aromatic substituents on the NHC ligands tend to occupy the space above and below the metal core plane to reduce steric interactions; in the phosphine analogues there is less of such a constraint.

Figure 2.8. Structures of reported $[\text{Pd}_n\text{Os}_3(\text{CO})_{12}\text{L}_n]$ analogues.

Table 2-1. Mean and maximum deviation of metal atoms from the Os_3Pd_n plane in clusters **6c-d**, **7c-d**, **8c-d**, **B** and **C**.

Compound	Deviation from Os_3Pd_n plane	
	Mean (Å)	Maximum (Å)
6c	0.032	0.033
6d	0.026	0.027
7c (molecule A)	0.029	0.043
7c (molecule B)	0.103	0.213
7d	0.101	0.191
8c	0.098	0.173
8d	0.178	0.366
B	0.799	0.857
C	0.758	0.933

Figure 2.9. Selected metal-metal and metal-carbon bond lengths (Å). Top: for **6a** (above, normal font type) and **6b** (below, italics). Bottom: for **6c** (above, normal font type) and **6d** (below, italics).

Figure 2.10. Selected metal-metal and metal-carbon bond lengths (Å) for **7c**. Molecule A (above, normal font type) and molecule B (below, italics).

Figure 2.11. Selected metal-carbon bond lengths (Å) for **8d** (above, normal font type) and **8c** (below, italics).

2.4 Computational studies

As mentioned above, all the structures can be regarded as built up from the sequential addition of a [Pd(NHC)] fragment across an metal–metal bond. In fact, the increase in the reaction time led to an increase in the yield of **8** at the expense of **6** and **7**. We believe that the formation of Os₃Pd_n (n = 1-3) clusters results from the nucleophilic attack of [Pd(NHC)] fragment, which is afforded from the treatment of **3** with a strong base.⁷ Furthermore, we propose that the initial site of attack by a [Pd(NHC)] group is the carbon atom of a carbonyl ligand, which carries a δ⁺ charge,⁸ not the osmium atom. This may account for the presence of carbonyls bridging all the Pd–Os edges; it is the interaction of the [Pd(NHC)] fragment with the CO which draws the fragment in towards the Os–Os bond. In the case of **7d**, the [Pd(SIPr)] unit appear to have been drawn towards the two *cis* carbonyls on the unique Os vertex of **6d**. The reason is not clear but does not appear to be steric effect as IPr and SIPr are very similar in steric bulk, and approach towards an Os–Os edge is clearly less sterically hindered than towards an Os vertex. It is possible that the more electron-rich SIPr (compared to IPr) favours attack of the [Pd(SIPr)] fragment at two *cis* carbonyls simultaneously, rather than a (presumably) sequential attack of carbonyls on adjacent Os vertices.⁹

In order to better understand the structures of **7** as well as to shed light on the formation of these two isomers, a natural bond orbital (NBO) analysis of **6c** and **6d** was carried out with density functional theory (DFT) at the MPW1PW1/LANL2DZ level of theory. The analysis suggests that the osmium core carries a negative charge, while the carbonyl carbons are positively charged (Figure 2.12). This supports the proposal that the initial site of attack by the [Pd(NHC)] group is the carbon atom of a carbonyl ligand and not an osmium atom. The charge distribution is, however, almost

the same for both compounds and cannot account for the different structures of the products, viz., **7c** and **7d**, obtained.

Figure 2.12. NBO calculation-natural charge for **6d** (left) and **6c** (right).

We have also calculated the Gibbs' free energies of **7c**, **7d** and their corresponding isomers (Figure 2.13). The calculated relative energies indicate that for both the IPr and SIPr ligands, the “spike” structure is at lower energy and hence should be thermodynamically more stable. This is not compatible with the experimental observation, although for both cases, the energy difference is small (0.43 and 24.9 KJ/mol for **7d** and **7c**), indicating that both structures may exist.

Figure 2.13. Relative energy profiles involved in **7d**, **7c** and their isomers.

2.5 Solution structures

The variable temperature ^1H NMR spectra of **6c** and **6d** showed only one set of NHC signals over the temperature range $-80\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$, with the resonances remaining sharp at $-40\text{ }^{\circ}\text{C}$ and above but these broadened at lower temperatures. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6d** at $-40\text{ }^{\circ}\text{C}$ showed two resonances for the CO ligands at δ 185.2 and 176.7 ppm with almost the same relative intensities, while that for **6c** at $-80\text{ }^{\circ}\text{C}$ showed only a weak and broad peak in the CO region. Similarly, the VT ^1H NMR spectra of **7c** and **7d** also showed only one set of NHC resonances over the temperature range $-80\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7d** at $-40\text{ }^{\circ}\text{C}$ showed two broad resonances with almost the same relative intensities at δ 187.4 and 183.0 ppm; these coalesced into a single broad peak at $-80\text{ }^{\circ}\text{C}$ (Figure 2.14). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a ^{13}C -labeled sample of **7d** showed a very broad hump at $-80\text{ }^{\circ}\text{C}$ for the CO resonances which decoalesced into four sharp resonances between -40 and $-20\text{ }^{\circ}\text{C}$. As the temperature was increased further, these peaks again broadened. All these are indicative of rapid fluxionality of the carbonyl ligands in these clusters, even down to $-80\text{ }^{\circ}\text{C}$.

In contrast, the solution spectra for **8** suggest that these clusters are not fluxional, as may be expected. Thus the ^1H NMR spectra of **8c** and **8d** showed only one set of NHC signals over the temperature range from $-80\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8d** under different condition (room temperature with pulse delay of 2 s and 10 s; $-80\text{ }^{\circ}\text{C}$ with pulse delay of 2 s; inverse-gated H-decoupling at room temperature with pulse delay of 10 s) were found to be almost the same. The latter showed two CO resonances of the same intensity at around δ 189.5 and 189.8 ppm, both with T_1 of about 0.8 s, which may be assigned to the terminal and bridging carbonyls respectively. The carbene carbon signal of NHC showed up at 234.2 ppm,

with a T_1 of about 0.7 s.

Figure 2.14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7d** (CO and carbene carbon region) at -80°C (bottom), -40°C (middle) and at room temperature (top).

2.6 Reactions under different conditions

Others have observed that the nature of the solvent can dramatically affect the outcome of the reduction of Pd^{II} to Pd^0 ; the activation mechanism of $[\text{PdCl}(\text{allyl})(\text{NHC})]$ in aprotic solvents and in isopropanol are different. It has been hypothesized that with isopropanol as solvent, the isopropoxide anion generated from deprotonation substitutes the chloride in **3**. This is followed by a β -hydride elimination and reductive elimination leading to the Pd^0 (Scheme 2.2).¹⁰ In aprotic solvents, on the other hand, either a direct nucleophilic attack of *tert*-butoxide anion on the coordinated allyl moiety or a chloride/*tert*-butoxide metathesis on the Pd center followed by reductive elimination (allyl *tert*-butyl ether is formed in both case) leads to the Pd^0 (Scheme 2.4).¹⁰

Scheme 2.4

It therefore seemed reasonable to expect that the use of aprotic solvents like DCM in place of IPA should afford similar products. Indeed, the reaction of three molar equivalents of **3a** with **5** in DCM with KO^tBu as the base also caused a color change to reddish-purple. In addition to **6a** and **7a**, however, TLC separation gave the clusters [Os₃(CO)₁₀(η³-allyl)₂] (**10**) and [Os₃(CO)₉{μ,κ²C,*O*-OOC^tBu}(allyl)] (**11**) as well (Scheme 2.5). The reaction could also proceed with KOH as the base, to afford **6a** as the major product. The solid state structures of **10** and **11** have been established by single crystal X-ray crystallographic studies; their ORTEP plots are displayed in Figures 2.15 and 2.16, respectively.

Scheme 2.5

The molecular structure of **10** shows that the three osmium atoms are linear, with $\angle\text{Os-Os-Os} = 180.000(11)^\circ$. A η³-allyl group is coordinated at each of the terminal Os atoms, and the carbonyl ligands on adjacent Os centers are in staggered conformations (Figure 2.15). The closest known analogue is [(η³-allyl)Os(CO)₃-Os(CO)₄-Os(CO)₂Br(ACN)], which was reported to form from the reaction of [Os₃(CO)₁₁(ACN)] (**12g**) with allyl bromide. The structure of **11** is unusual in that it is the first example of an osmium cluster containing a [μ,κ²C,*O*-OOC^tBu] ligand (Figure

2.16); a similar bonding mode was reported in bis- $[\mu, \kappa^2 C, O\text{-OOC}^t\text{Bu}] \text{Fe}_2(\text{CO})_6$.¹¹ It is likely that **11** was formed via nucleophilic attack of an O^tBu^- group at a carbonyl carbon to form an alkoxycarbonyl, the O atom of which subsequently displaced a carbonyl ligand on an adjacent osmium.

Figure 2.15. ORTEP diagram of **10**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 2.16. ORTEP diagram of **11**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

2.7 Electronic effects

As NHCs are strong electron donating ligands, the electron-rich metal center in the [Pd(NHC)] fragment should be reactive with electron-poor but not electron-rich clusters. We attempted to examine this idea with a number of clusters with different electronic properties. The reaction of the [Pd(IMes)] fragment, generated from **3a**, with [Os₃(CO)₁₁(ACN)] (**12g**) gave clusters **9a** and [Os₃(CO)₁₁(IMes)] (**12a**) as the major products. The molecular structure of **12a** was determined by an X-ray crystallographic analysis and the ORTEP plot is shown in Figure 2.17. Although there have been reports of [Os₃(CO)₁₁(NHC)] clusters, the structural determination of **12a** here is the first to be reported for the IMes ligand.

Figure 2.17. ORTEP diagram of **12a**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

The [Pd(NHC)] fragment can also react with triosmium clusters containing one two-electron donor ligand. The mixed-metal clusters [PdOs₃(CO)₁₂(IMes)₂] (**9a**) and [PdOs₃(CO)₁₂(IMes)(*m*IMes)] (**9a'**) were formed as the only products from the reaction of [Pd(IMes)₂] with [Os₃(CO)₁₁(IMes)] (**12a**) and [Os₃(CO)₁₁(*m*IMes)] (**12a'**) respectively, by the loss of one IMes group (Scheme 2.6). Similarly, the reaction of complex **3a** with [Os₃(CO)₁₁P(OMe)₃] (**12i**) in the presence of a strong base yielded one red product, the infrared spectrum of this complex displayed a similar carbonyl absorption pattern to those of **9a**, indicating that the complex can be tentatively formulated as [PdOs₃(CO)₁₁P(OMe)₃(IMes)]. Unfortunately, repeated attempts to obtain crystals suitable for single crystal X-ray diffraction studies proved unsuccessful.

Scheme 2.6

The reaction of $[\text{Pd(NHC)}]$ with $[\text{Os}_3(\text{CO})_{10}(\text{ACN})_2]$ (**13g**), which contains two labile acetonitrile ligands, was complicated; spot TLC showed many products. However, **4a** failed to react with the more electron-rich disubstituted clusters $[\text{Os}_3(\text{CO})_{10}(\text{IMes})_2]$ (**13a**) and $[\text{Os}_3(\text{CO})_{10}\{\text{P(OMe)}_3\}_2]$ (**13i**) at RT or 40 °C, even after 3 days (based on IR and spot TLC). All these results seem to indicate that the electron-rich $[\text{Pd(NHC)}]$ group does not react well with electron-rich clusters.

On the other hand, the cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ (**14**), an electronically unsaturated, 46 valence electron cluster, reacted with **3a** in hexane to afford a large number of products: the hydrido compounds $[\text{Os}_4(\mu\text{-H})_2(\mu\text{-CO})(\text{CO})_{12}]$ (**20**), $[\text{PdOs}_5(\mu\text{-H})_5(\mu\text{-Cl})(\text{CO})_{16}]$ (**21**) and $[\text{PdOs}_5(\mu\text{-H})_6(\text{CO})_{15}(\text{IMes})]$ (**22**), and two known osmium clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-Cl})]$ (**15**),¹² and $[\text{PdOs}_5(\mu\text{-H})_6(\text{CO})_{16}]$ (**23**),¹³ were isolated from the supernatant, and the yellowish-brown precipitate was identified as $[\{(\text{allyl})_2\text{Pd}_2(\text{IMes})_2(\mu\text{-Cl})\}^+\{\text{H}_3\text{Os}_4(\text{CO})_{12}\}^-]$ (**24**) (Scheme 2.7). Clusters **20-23** have been characterized spectroscopically and analytically, as well as by single crystal X-ray crystallography studies.

Scheme 2.7

Cluster **15** is probably formed via reaction with chloride ions from the starting material **3a**. The ORTEP plot for the tetraosmium cluster **20** is shown in Figure 2.18 (top); it is an isomer of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{13}]$ (**19**), which was reported by Shore and coworkers (Figure 2.18, bottom).¹⁴ The main structural difference between them is that while **20** contains one bridging CO ligand, the CO ligands in **19** are all terminal. The reported NMR spectrum in CDCl_3 for **19** showed one hydride peak at -21.4 ppm, and the IR spectrum (in THF) showed a broad peak at 1875 cm^{-1} . On the other hand, the ^1H NMR spectrum (in C_6D_6) of **20** showed two nonequivalent hydrides (singlets at -20.5, -21.4 ppm). A VT ^1H NMR study in d_8 -toluene from $-80\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$ showed that it was stable within this temperature range and did not convert to **19**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed no distinct CO resonances; this is indicative of rapid fluxionality of

Figure 2.18. ORTEP diagram of **20** (top) and the reported isomer **19** (bottom). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

the carbonyls in solution. The solution IR spectrum (in dcm) only show resonance for terminal carbonyl ligands.

ORTEP diagrams of complexes **21** and **22** are depicted in Figure 2.19. The structures of **21-23** are similar; both **21** and **22** can be considered as derivatives of **23**. Cluster **22** is also the first mixed metal Pd-Os₅ cluster known that contains an NHC ligand. A common atomic numbering scheme and selected bond parameters for **21-23** are given in Table 2-2. Their metal skeletons comprise an Os₂Pd triangle fused to an Os₃Pd tetrahedron at the palladium apex, with all three Os-Os bonds in the tetrahedron bridged by hydride ligands. Each osmium atom has three carbonyl ligands except for Os4, which contains four. All the carbonyl ligands are terminal. Three kinds of Os-Pd bonds are observed in these three clusters: unsupported [Pd1-Os1, Pd1-Os2, Pd1-Os3], singly hydride-bridged [Pd1-Os4] and doubly bridged [Pd1-Os5]. The unsupported Pd-Os bonds are the shortest for all the three complexes; Pd1-Os4 is the longest. Both **22** and **23** have 88 valence electrons, which make them two electron-deficient according to the EAN rule, while cluster **21** has 90 valence electrons which is electron-precise as it contains one 3-electron donor (bridging Cl) in place of the 1-electron bridging H ligand; if both osmium atom and palladium atom have a 18-electron configuration. The electron deficiency in clusters **22** and **23** may account for the short Pd1-Os5 bond (2.7642(8) and 2.743(3) Å, respectively). A similar effect was observed in the well-known and -studied 46-electron triangular cluster complex [Os₃(μ-H)₂(CO)₁₀].¹⁵ In comparison, the Pd1-Os5 in cluster **21**, at 2.8672(9) Å, is significantly longer.

Table 2-2. Common atomic numbering scheme and selected bond parameters
for **21-23**.

	Bond Lengths (Å)		
	21	22	23
Pd1-Os1	2.6767(10)	2.7213(5)	2.682(3)
Pd1-Os2	2.6782(10)	2.6788(8)	2.684(3)
Pd1-Os3	2.6783(9)	2.6919(8)	2.697(3)
Pd1-Os4	3.0912(10)	2.9750(8)	2.997(3)
Pd1-Os5	2.8672(9)	2.7642(8)	2.743(3)
Os1-Os2	2.8874(6)	2.8863(5)	2.882(2)
Os2-Os3	2.8482(6)	2.8723(5)	2.873(2)
Os1-Os3	2.8692(6)	2.8186(5)	2.828(2)
Os4-Os5	2.9005(6)	2.8939(5)	2.909(2)

Figure 2.19. ORTEP diagram of compounds **21** and **22**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity except for metal hydrides.

Complex **24** is a salt, containing a chloride-bridge dipalladium cation and the $[\text{H}_3\text{Os}_4(\text{CO})_{12}]$ monoanion. Similar cations have already been reported.¹⁶

Figure 2.20. ORTEP diagram of **24**. Ellipsoids are drawn at 50% probability level. Organic hydrogen atoms have been omitted for clarity.

We have also attempted to extend the reactions above with ruthenium carbonyl clusters. Thus the reaction of **3a** with $[\text{Ru}_3(\text{CO})_{12}]$ **5(Ru)** in IPA afforded a blue colored precipitate in a reddish brown supernatant. The reddish brown solution was very unstable on silica gel. The IR spectrum of the precipitate exhibited a similar pattern in the carbonyl region to those for clusters **8**, and thus the product has been tentatively identified as $[\text{Pd}_3\text{Ru}_3(\text{CO})_{12}(\text{IMes})_3]$ **8a(Ru)**. Due to the instability of this compound, X-ray diffraction quality crystals have not been obtained.

2.8 Reactivity and stability studies of $[\text{Pd}_n\text{Os}_3(\text{CO})_{12}(\text{NHC})_n]$

The stability and some preliminary exploration of the reactivity of the clusters obtained above have also been carried out. It was found that **6a** was unstable and decomposed into **12a** and some black solid upon heating overnight at 100 °C, or even at 60 °C. The ^1H NMR spectrum of the solid was complicated and the IR spectrum

showed only terminal COs, suggesting the formation of one or more organometallic cluster species.

When a hexane solution of **6a** was treated with three molar equivalents of PPh₃ at room temperature, an orange precipitate in a yellow solution was obtained. The precipitate remains unidentified but its IR spectrum showed broad CO absorptions (2008vs, 1933m and 1821w cm⁻¹), and its ¹H NMR spectrum showed that it contained PPh₃ and NHC ligands; the ³¹P{¹H} NMR spectrum showed one peak at 30 ppm. Attempts to grow a crystal suitable for X-ray analysis were unsuccessful. The clusters [Os₃(CO)₁₁(PPh₃)] (**12h**),¹⁷ [Os₃(CO)₁₀(PPh₃)₂] (**13h**),²⁵ and **12a**, were separated out from the supernatant, and their formation suggested that the [Pd(IMes)] groups are labile.

There are many reported examples of high nuclearity complexes containing a large number of hydride ligands, for example, [Rh₆(PR₃)₆H₁₂][BAr^F₄]₂ (BAr^F₄ = B{C₆H₃(CF₃)₂})₄) is capable of reversibly adding two equivalents of hydrogen under mild conditions.¹⁸ Adams has also shown that introducing [Pt(P^{*i*}Bu₃)] groups into Pt-Os mixed metal carbonyl clusters can provide highly unsaturated polynuclear metal cluster complexes that can activate hydrogen reversibly under mild conditions (Scheme 2.8).¹⁹

Scheme 2.8

We have found that **8d** did not react with hydrogen under ambient conditions, but in refluxing octane, a large quantity of brown precipitate was observed. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the precipitate were quite clean; they showed one set of NHC resonances and one hydride resonance, and the integration ratio indicated the presence of NHC and hydride in a 1:2 ratio. This indicates that three moles of H_2 have reacted with each mole of **8d**.

2.9 Conclusion

It was found that the heterometallic clusters $[\text{PdOs}_3(\text{CO})_{12}(\text{NHC})]$ (**6**), $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{NHC})_2]$ (**7**), $[\text{Pd}_3\text{Os}_3(\text{CO})_{12}(\text{NHC})_3]$ (**8**) and $[\text{PdOs}_3(\text{CO})_{12}(\text{IMes})_2]$ (**9**) (NHC = SIPr, IPr, IMes, SIMes) could be obtained from the reaction of the $[\text{Pd}(\text{NHC})]$ fragment with $[\text{Os}_3(\text{CO})_{12}]$ (**5**). The $[\text{Pd}(\text{NHC})]$ fragment could be generated *in situ* either from $[\text{Pd}(\text{NHC})_2]$, or more conveniently, from $[\text{PdCl}(\text{allyl})(\text{NHC})]$ (**3**) and a base in IPA. In the aprotic solvent DCM, the latter reaction afforded **6** and **7**, as well as the triosmium clusters $[\text{Os}_3(\text{CO})_{10}(\eta^3\text{-allyl})_2]$ and $[\text{Os}_3(\text{CO})_9\{\mu, \kappa^2\text{C}, O\text{-OOC}^t\text{Bu}\}(\text{allyl})]$. The electron-rich $[\text{Pd}(\text{NHC})]$ fragment was also found to react readily with the substituted clusters $[\text{Os}_3(\text{CO})_{11}\text{L}]$ and $[\text{Os}_3(\text{CO})_{10}(\text{ACN})_2]$, but not with the more electron-rich, disubstituted clusters $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$ ($\text{L} = \text{P}(\text{OMe})_3$ or IMes). Its reaction with the electronically unsaturated cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ afforded a complex mixture of products. NBO analyses of **6c** and **6d** suggested that initial attack of the $[\text{Pd}(\text{NHC})]$ could have occurred at the carbon atom of a carbonyl ligand.

The metal core of the heterometallic clusters **6-9** consisted of a triangular arrangement of three osmium atoms with $[\text{Pd}(\text{NHC})]$ groups bridging across one to three Os-Os bonds, respectively. All the metal atoms were essentially coplanar, in contrast to their known phosphine analogues. Each of the Os-Pd bonds was in turn

bridged by a carbonyl ligand. The structure of **7d** was an exception, in that one of the Pd(NHC) fragment adopted a spike position.

Computational studies, using DFT, on **7c**, **7d** and their isomers indicated that the energy difference between both structures was small. Their VT ^1H NMR spectra, however, showed only one set of NHC resonances throughout the temperature range observed, thus suggesting the presence of only the non-spiked structure in solution. VT NMR studies of **6-8** showed that there was fluxionality of the carbonyl ligands in **6** and **7**, but not in **8**.

The cluster **6a** was found to be unstable and decomposed readily upon heating. At room temperature, it reacted rapidly with PPh_3 to afford the substituted triosmium clusters $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)]$, $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ and $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$, as well as some other unknown products. These observations suggested that the $[\text{Pd}(\text{NHC})]$ unit could rapidly detach and re-attach itself to the precursor cluster. Cluster **8d** was found to react with three equivalents of H_2 in refluxing octane; it may therefore have potential in hydrogen storage.

2.10 Experimental

2.10.1 General Procedures

All manipulations involving organometallic compounds were carried out under argon using standard Schlenk techniques. Solvents used in reactions were of AR grade, and were dried under the appropriate drying agent and distilled under argon; and stored in flasks fitted with Teflon valves prior to use. Hexane was dried over sodium/benzophenone, IPA over manganese/ I_2 , DCM over calcium hydride. The products were generally separated by column chromatography on silica gel 60 (230-430 mesh ASTM) or by thin-layer chromatography (TLC), using Merck silica gel 60 Å F_{254} 20×20 cm^2 plates. ^1H NMR spectra were collected using a JEOL ECA 400, ECA

400-SL, BBFO1, or AV 300 NMR spectrometer, while variable temperature and 2D NMR spectra were obtained on a Bruker BBFO2 NMR spectrometer, with chemical shifts referenced to residual solvent peaks. $^{31}\text{P}\{^1\text{H}\}$ chemical shifts reported are relative to the signal for 85% aqueous H_3PO_4 (external standard). Infrared spectra were recorded with a Bruker Alpha FTIR spectrometer at a resolution of 2 cm^{-1} using solution cells with NaCl windows and a pathlength of 0.1 mm. All mass spectrometry was using electrospray ionization (ESI) mode and performed by a waters Q-ToF Premier Micromass instrument. Elemental analyses were performed by the microanalytical laboratory at NTU. $[\text{Os}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{12}]$ were purchased from Oxkem. $[\text{Os}_3(\text{CO})_{12}]$ was isotopically and uniformly enriched to approximately 35% following the reported method.²⁰ $\text{IMes}\cdot\text{HCl}$,²¹ $\text{IPr}\cdot\text{HCl}$,²² $[\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)]$,²³ $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$,²⁴ $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OEt})_3]$,²⁵ $[\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2]$,²⁶ $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$,²⁷ $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$,²⁸ $[\text{Pd}(\text{IMes})_2]$,²⁹ $[\text{PdCl}(\text{allyl})(\text{IMes})]$,³⁰ $[\text{PdCl}(\text{allyl})(\text{SIMes})]$,³⁰ $[\text{PdCl}(\text{allyl})(\text{SIPr})]$ ³⁰ and $[\text{PdCl}(\text{allyl})(\text{IPr})]$ ³⁰ were prepared according to the published methods. All other reagents were used as received from commercial suppliers. The crystal structure determinations were carried out by Dr Rakesh Ganguly.

2.10.2 X-ray Crystallographic Studies

The crystals were mounted on quartz fibers. X-ray diffraction data were collected on a Bruker X8 APEX Single-Crystal X-ray Diffractometer at 103(2) K, using Mo $\text{K}\alpha$ radiation, with the SMART programs.³¹ Reflections data was processed and corrected for Lorentz and polarization effects with SAINT,³² and for absorption effects with SADABS.³³ Heavy atoms were located by direct methods, and subsequent difference maps were used for locating the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. In the final

model all non-hydrogen atoms were given anisotropic displacement parameters. Structural solution and refinement were carried out using the SHELXTL suite of programs.³⁴

Hexane solvates were found in the crystals of **6d**, **6c** and **8c**; a full occupancy molecule in the first, a half occupancy molecule in the second and a quarter occupancy molecule sitting on a two-fold axis in the last. There were also disorder of an isopropyl group in **7c** and **8c**; these were modeled with two alternative sites of equal occupancy in each, with appropriate restraints.

Structure of **9a** was solved by Patterson method followed by difference maps to locate all the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic thermal displacement parameters. There are two molecules of the compound in the asymmetric unit, as well as half a molecule of hexane solvate. To keep the thermal parameters reasonable, isotropic restraints were placed on the carbon atoms, as well as a rigid-bond restraint on all atoms. The largest residuals and hole in the final model were near to the osmium atoms.

2.10.3 Computational Studies

All optimized structures were calculated by density functional theory (DFT) using the MPW1PW91 density-functional, which have been shown to be a reliable method for the prediction of structures and vibrational frequencies of third row transition metal carbonyl compounds.^{35,36} The LANL2DZ (Los Alamos Effective Core Potential Double- ξ) basis set was employed for all atoms, together with polarization functions are employed for Os and Pd atom. Natural Bond Orbital (NBO) analysis was carried out with the NBO program implemented within Gaussian.^{37,38} All calculations were performed using the Gaussian 09 suite of program.³⁹

2.10.4 Reaction of [Pd(IMes)₂] and [Os₃(CO)₁₂]

Compound **4a** (20 mg, 0.028 mmol) and **5** (25 mg, 0.028 mmol) were added into a round-bottom flask, followed by hexane (10 ml). The mixture was stirred at room temperature overnight, the color changing to red. The solvent was removed in vacuo and the residue was redissolved in the minimum volume of DCM for TLC separation using hexane-DCM (3:1, v/v) as eluant. Three bands were obtained.

Band 1. [PdOs₃(CO)₁₂(IMes)] (**6a**). Red-orange. R_f = 0.38. Yield = 10 mg (28%).

Band 2. [Pd₂Os₃(CO)₁₂(IMes)₂] (**7a**). Purple-red. R_f = 0.22. Yield = 3 mg (6%).

Band 3. [PdOs₃(CO)₁₁(IMes)₂] (**9a**). Red. R_f = 0.18. Yield = 5 mg (11%).

IR (hexane): ν_{CO} 2105 vw, 2086 vw, 2049 w, 2032 m, 2014 m, 2008 s, 1987 w, 1966 w, 1952 w, 1942 w, 1818 w cm⁻¹.

¹H NMR (C₆D₆): δ 6.79 (s, 4H), 6.76 (s, 4H), 6.31 (s, 2H), 5.78 (s, 2H), 2.18 (s, 12H), 2.07 (s, 6H), 2.02 (s, 6H), 2.00 (s, 12H) ppm.

HRMS-ESI: m/z 1595.1252 ([M+H]⁺). Calculated for C₅₃H₄₉N₄O₁₁¹⁰⁴Pd¹⁹⁰Os¹⁹²Os₂ 1595.1252

2.10.5 Reaction of [PdCl(allyl)(NHC)] and [Os₃(CO)₁₂] in IPA

In a 100 ml Schlenk round-bottomed flask, **3a** (81 mg, 0.170 mmol), KO^tBu (19 mg, 0.017 mmol) and [Os₃(CO)₁₂] (50 mg, 0.055 mmol) were added, followed by IPA (10 ml). After stirring overnight, the purple precipitate **8a** was filtered, washed with IPA (10 ml) and hexane (10 ml), and then extracted from the sinter with cold DCM. TLC separation (hex/DCM = 3:1, v/v) of the red filtrate yielded **6a** and **7a** as minor products.

Similar reactions using the same molar quantities of **3b-d** with **5** were carried out. For **3c** and **3d**, no precipitation was observed, and the reaction mixture was separated by column chromatography at -15 °C.

The yields and separation data are given in table 2–3, and analytical and spectroscopic data for the products are tabulated in table 2–4.

Table 2-3. Reaction of **3** with **5**.

<i>Pd precursor</i>	<i>Separation data</i>	<i>Product</i>	<i>Color</i>	<i>Yield</i>
3a	Precipitate	8a	purple ppt	70 mg, 59%
	R _f = 0.44	6a	orange-red	7 mg, 9%
	R _f = 0.28	7a	reddish-purple	Trace
3b	Precipitate	8b	purple ppt	60 mg, 51%
	R _f = 0.40	6b	orange-red	2 mg, 2%
	R _f = 0.21	7b	reddish-purple	4 mg, 3%
3c	Hex/DCM=4:1	6c	orange-red	10 mg, 13%
	Hex/DCM=3:1	7c	reddish-purple	21 mg, 20 %
	Hex/DCM=2:1	8c	purple	22 mg, 17%
3d	Hex/DCM=4:1	6d	orange-red	16 mg, 21%
	Hex/DCM=3:1	7d	reddish-purple	17 mg, 16%
	Hex/DCM=2:1	8d	purple	31 mg, 24%

Table 2-4. Characterization of complexes **6–8a–d**.

	IR[ν_{co} (cm^{-1})]	^1H NMR [δ /(ppm)]	HRMS-ESI: m/z
6a	(DCM): 2111w, 2068m, 2056m, 2047m, 2026s, 2003w, 1961w, 1814w	(C_6D_6) 6.81 (s, 4H, Ar-H), 6.25 (s, 2H, Im-H), 2.13 (s, 6H, CH_3), 2.10 (s, 12H, CH_3)	1319.9238 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{33}\text{H}_{25}\text{N}_2\text{O}_{12}^{108}\text{Pd}^{187}\text{Os}^{192}\text{Os}_2$ 1319.9234
7a	(hex): 2110w, 2036m, 2027w, 2017s, 2004m, 1978 w, 1970w, 1921w, 1817w	(CDCl_3) 7.11 (s, 2H), 6.97 (s, 4H), 2.31 (s, 6H), 2.11 (s, 12H)	1731.0107 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{54}\text{H}_{49}\text{N}_4\text{O}_{12}^{110}\text{Pd}_2^{188}\text{Os}_2^{190}\text{Os}$ 1731.0152
8a	(DCM): 2023w, 2001s, 1894m, 1800w	(CDCl_3) 7.05 (s, 2H), 6.88 (s, 4H), 2.28 (s, 6H), 2.05 (s, 12H)	2135.1204 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{75}\text{H}_{73}\text{N}_6\text{O}_{12}^{102}\text{Pd}^{104}\text{Pd}^{110}\text{Pd}^{186}\text{Os}^{192}\text{Os}_2$ 2135.1203
6b	(DCM): 2111w, 2068m, 2056sh, 2048m, 2026s, 2004w, 1962w, 1815w	(C_6D_6): δ 6.82 (s, 4H, Ar-H), 3.13 (s, 4H, Im-H), 2.26 (s, 12H, CH_3), 2.14 (s, 6H, CH_3)	1318.9351 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{33}\text{H}_{27}\text{N}_2\text{O}_{12}^{108}\text{Pd}^{189}\text{Os}^{190}\text{Os}_2$ 1318.9351
7b	(hex): 2094w, 2036m, 2027w, 2017s, 2004m, 1978w, 1970w, 1921w, 1817w	(C_6D_6): δ 6.78 (s, 4H, Ar-H), 3.10 (s, 4H, Im-H), 2.25 (s, 12H, CH_3), 2.14 (s, 6H, CH_3)	1733.0428 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{54}\text{H}_{53}\text{N}_4\text{O}_{12}^{110}\text{Pd}_2^{188}\text{Os}_3$ 1733.0439
8b	(DCM): 2026w, 2004s, 1888m, 1798w, 1793w.	NA	2146.1594 ($[\text{M}+\text{H}]^+$). Calculated for $\text{C}_{75}\text{H}_{79}\text{N}_6\text{O}_{12}^{106}\text{Pd}^{110}\text{Pd}_2^{187}\text{Os}^{188}\text{Os}^{190}\text{Os}$ 2146.1595

	IR[ν_{co} (cm ⁻¹)] (DCM)	¹ H NMR [δ /(ppm)] (CD ₂ Cl ₂ -40 °C)	¹³ C{ ¹ H} NMR [δ /(ppm)] (CD ₂ Cl ₂ -40 °C)	Elemental Analysis	ESI-MS ⁺ m/z:
6c	2110w, 2068w, 2055m, 2047 m, 2025s, 2003m, 1966w, 1824w.	7.42 (t, ³ J _{H,H} = 7.6 Hz, 2H, Ar-H); 7.26 (d, 4H, Ar-H), 7.20 (s, 2H, Im- H), 2.76 (m, 4H, CH); 1.23 (d, 12H, CH ₃); 1.07 (d, 12H, CH ₃).	(-80°C) 213.4 (NCN), 145.3 (o-Ph-C), 135.4 (ipso-Ph-C), 129.0 (p-Ph-C), 123.3 (m-Ph-C), 123.0 (NCCN), 27.7 (CH), 25.6 (CH ₃), 22.6 (CH ₃).	Anal. Calcd for 3b .C ₆ H ₁₄ : C, 36.32; H, 3.39; N, 1.88. Found: C, 36.57; H, 3.84; N, 1.91	1403.2 [M+H] ⁺
7c	(hex) 2110vw, 2094w, 2050w, 2036m, 2027w, 2017s, 2004m, 1978w, 1972w, 1920w, br, 1813w, br	7.41 (t, ³ J _{H,H} = 7.6 Hz, 2H, Ar-H); 7.24 (d, 4H, Ar-H), 7.16 (s, 4H, Im- H), 2.72 (m, 4H, CH); 1.16 (d, 12H, CH ₃); 1.05 (d, 12H, CH ₃)	(-80°C) 211.7 (NCN), 187.5 (CO, br), 145.3 (o-Ph-C), 135.2 (ipso-Ph-C), 129.0 (p-Ph-C), 123.3 (m-Ph-C), 123.1 (NCCN), 27.6 (CH), 25.6 (CH ₃), 22.6 (CH ₃).	Anal. Calcd for 4b .0.2C ₆ H ₁₄ : C, 42.17; H, 3.94; N, 2.93. Found: C, 42.15; H, 4.22; N, 2.75	1898.3 [M+H] ⁺
8c	2025m, 2006s, 1903m, 1815w, 1806w	7.38 (t, ³ J _{H,H} = 8.0 Hz, 2H, Ar-H); 7.20 (d, 4H, Ar-H), 7.11 (s, Im-H, 4H), 2.81 (septet, ³ J _{H,H} = 6.8 Hz, 4H, CH); 1.14 (d, 12H, CH ₃); 1.06 (d, 12H, CH ₃).	(-80°C) 210.8 (NCN), 191.0 (CO), 189.5 (CO), 145.2 (o-Ph-C), 135.1 (ipso-Ph-C), 128.9 (p-Ph-C), 123.2 (m-Ph-C), 122.9 (NCCN), 27.6 (CH), 25.6 (CH ₃), 22.0 (CH ₃)	Anal. Calcd: C, 46.70; H, 4.55; N, 3.51. Found: C, 46.69; H, 5.06; N, 3.34	2390.2 [M] ⁺

	IR[ν_{co} (cm^{-1})] (DCM)	^1H NMR [δ /(ppm)] (CD_2Cl_2 -40 °C)	$^{13}\text{C}\{^1\text{H}\}$ NMR [δ /(ppm)] (CD_2Cl_2 -40 °C)	Elemental Analysis	ESI-MS ⁺ m/z:
6d	2111w, 2068w, 2055m, 2048m, 2025s, 2004m, 1965w, 1819w, br	7.33 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 2H, Ar-H); 7.21 (d, $^3J_{\text{H,H}} = 7.6$ Hz, 4H, Ar-H), 3.91 (s, 4H, Im-H), 3.25 (m, 4H, CH); 1.27 (d, $^3J_{\text{H,H}} = 6.4$ Hz, 12H, CH ₃); 1.21 (d, 12H, CH ₃)	235.0 (NCN), 185.2 (CO), 176.7 (CO), 146.9 (o-Ph-C), 136.1 (ipso-Ph-C), 128.7 (p-Ph-C), 124.2 (m-Ph-C), 28.1 (CH), 26.1 (CH ₃), 23.8 (CH ₃).	Anal. Calcd: C, 33.37; H, 2.73; N, 2.00. Found: C, 33.82; H, 2.70; N, 1.91.	1403.8 [M] ⁺
7d	(hex) 2095w, 2037 m, 2027w, 2018s, 2003m, 1978w, 1971w, 1920w, br, 1828w, 1809w	7.32 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 2H, Ar-H); 7.17 (d, 4H, Ar-H), 3.86 (s, 4H, Im-H), 3.19 (m, 4H, CH); 1.18 (d, 24H, $^3J_{\text{H,H}} = 5.7$ Hz, CH ₃).	233.8 (NCN), 187.4 (CO), 183.0 (CO), 146.8 (o-Ph-C), 136.0 (ipso-Ph-C), 128.6 (p-Ph-C), 124.1 (m-Ph-C), 28.0 (CH), 26.1 (CH ₃), 23.6 (CH ₃).	Anal. Calcd for 4a . $\frac{1}{2}\text{C}_6\text{H}_{14}$: C, 42.63; H, 4.30; N, 2.88. Found: C, 42.34; H, 4.19; N, 2.74.	1902.3 [M+H] ⁺
8d	2026m, 2007vs, 1904m, 1821w, 1803w	rt.): δ 7.30 (t, $^3J_{\text{H,H}} = 8$ Hz, 2H, Ar-H); 7.14 (d, 4H, Ar-H), 3.86 (s, 4H, Im-H), 3.25 (septet, $^3J_{\text{H,H}} = 6.7$ Hz, 4H, CH); 1.18 (m, 24H, CH ₃).	(-80 °C): δ 232.3 (NCN), 189.8 (CO), 189.4 (CO), 146.4 (o-Ph-C), 135.5 (ipso-Ph-C), 128.1 (p-Ph-C), 123.6 (m-Ph-C), 27.6 (CH), 26.0 (CH ₃), 23.0 (CH ₃).	Anal. Calcd: C, 46.58; H, 4.79; N, 3.50. Found: C, 46.76; H, 5.12; N, 3.45.	2396.2 [M] ⁺

2.10.6 Reaction of [PdCl(allyl)(IMes)] and [Os₃(CO)₁₂] in DCM

Compound **3a** (41 mg, 0.084 mmol), KO^tBu (9 mg, 0.084 mmol) and **5** (25 mg, 0.028 mmol) were added in a 100 ml Schlenk round-bottomed flask, followed by DCM (10 ml). After stirring under room temperature overnight, the solvent was removed under vacuo, the residue redissolved in the minimum volume of DCM and subjected to TLC using hexane-dichloromethane (3:1, v/v) as eluant afforded:

First band contained trace amount of pale yellow product **10**.

IR (DCM): ν_{co} 2101 vw, 2081 w, 2071 m, 2058 m, 2049 m, 2014 m, 1994 s, 1972 w, 1945 w cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 4.49 (m, 1H), 3.65 (m, 1H), 2.89 (m, 1H), 2.57 (m, 1H), 1.64 (m, 1H) ppm.

HRMS-ESI: m/z 934.9138 ([M+H]⁺). Calculated for C₁₆H₁₁O₁₀¹⁹⁰Os₂¹⁹²Os 934.9136.

Second band contained yellow product **11**. Yield =4 mg, (7%).

¹H NMR (400 MHz, C₆D₆): δ 4.86 (m, 1H), 4.36 (m, 1H), 4.08 (dd, J = 3Hz, J = 10 Hz, 1H), 1.85 (d, J = 12 Hz, 1H), 1.08 (d, J = 12 Hz, 1H), 0.94 (s, 18H) ppm.

IR (DCM): ν_{co} 2097 m, 2051 s, 2017 s, 1996 s, 1973 m, 1909 w, br cm^{-1} .

ESI: m/z 962.93 [M+H]⁺, 891.24 [M–O^tBu+H]⁺.

HRMS-ESI: m/z 962.9280 [M+H]⁺. Calculated for C₁₇H₁₅O₁₁¹⁸⁸Os¹⁹⁰Os₂.

Third band was identified as **6a**. Yield=4 mg, (10%).

Fourth band was identified as **7a**. Yield=1 mg, (2%).

Crystals of **10** and **11** were obtained by slow diffusion of DCM/hexane solutions at room temperature.

2.10.7 Reaction of [PdCl(allyl)(IMes)] and [Ru₃(CO)₁₂]

In a 100 ml Schlenk round-bottomed flask, **3a** (91 mg, 0.188 mmol), KO^tBu (21 mg, 0.188 mmol) and **5(Ru)** (40 mg, 0.063 mmol) were added in IPA (10 ml). After stirring overnight, the mixture was filtered and the residue was washed with IPA (10 ml) followed by ether (10 ml). It was then extracted with cold DCM to afford **8a(Ru)** as a blue color compound. Yield: 5 mg, 4%.

IR (DCM): ν_{CO} 2014 m, 2000 s, 1891 m, 1802 w cm^{-1} .

2.10.8 Reaction of [PdCl(allyl)(IMes)] with [(μ -H)₂Os₃(CO)₁₀]

[Os₃(μ -H)₂(CO)₁₀] (90 mg, 0.10 mmol) and **3a** (56 mg, 0.11 mmol) were added into round-bottom flask, followed by hexane (20 ml), and the reaction mixture was stirred at room temperature overnight. A yellow-brown precipitate was separated by filtration from the orange-red supernatant. Solvent and volatiles were removed from the latter and the residue separated by TLC with DCM-hexane (1:2, v/v) as eluant. Six bands were obtained.

Band 1. [Os₃(CO)₁₀(μ -H)(μ -Cl)]. Yield: 16 mg, 17%.

Band 2. Compound **20**. Orange. R_f = 0.57. Yield: 3 mg, 2%.

IR (hex): ν_{CO} 2088 w, 2081 m, 2068 m, 2056 m, 2036 m, 2023 m, 2016 w, 2004 w, 1991 m cm^{-1} .

¹H NMR (300 MHz, C₆D₆): δ -20.7, -21.6 ppm.

ESI-MS: m/z 1102.81 [M-CO]⁺, 1072.81 [M-2CO]⁺, 1042.81 [M-3CO]⁺, 1014.80 [M-4CO]⁺.

Band 3. Compound **23**. Dark Orange. R_f = 0.49. Yield: 1 mg, 1%.

Band 4. Compound **21**. Orange. R_f = 0.43. Yield: 2 mg, 2%.

¹H NMR (400 MHz, C₆D₆): δ -10.2 (s, hydride), -13.4 (s, 1hydride), -16.8 (s, hydride), -20.0 (s, hydride), -20.7 (s, hydride) ppm.

IR (hex): ν_{co} 2122 vw, 2104 w, 2087 s, 2069 m, 2055 w, 2046 m, 2036 m, 2023 m, 2015 m, 2007 w, 2001 w, 1983 w, 1977 vw cm^{-1} .

ESI-MS: m/z 1510.77 $[\text{M}-\text{Cl}]^+$, 1482.95 $[\text{M}-\text{Cl}-\text{CO}]^+$.

Band 5. Compound **22**. Orange-Red. $R_f = 0.33$. Yield: 4 mg, 4%.

^1H NMR (400 MHz, C_6D_6): δ 6.77 (s, 4H, Ar-H), 5.84 (s, 2H, Im-H), 2.12 (s, 6H, CH_3), 1.80 (s, 12H, CH_3), -14.07 (d, hydride), -16.6 (s, hydride), -20.7 (s, hydride) ppm.

IR (hex): ν_{co} 2106 w, 2086 m, 2074 s, 2069 m, 2055 w, 2047 m, 2037 s, 2028 m, 2021 m, 2012 m, 1995 s, 1981 w, 1966 m cm^{-1} .

ESI-MS: m/z 1790.95 $[\text{M}+\text{H}]^+$, 1795.94 $[\text{M}-\text{CO}]^+$.

Compound **24**. Yellow precipitate. Yield: 56 mg, 37%.

^1H NMR (400 MHz, CDCl_3): δ -20.50 (s, hydride).

IR (DCM): ν_{co} 2113 w, 2085 w, 2068 s, 2046 s, 2037 s, 2021 vs, 1999 s, 1979 m, 1964 m, 1946 w, 1917 w cm^{-1} .

ESI-MS: m/z 451.13 $[(\text{allyl})\text{Pd}(\text{IMes})]^+$, 1102.80 $[\text{H}_3\text{Os}_4(\text{CO})_{12}+2\text{H}]^-$, 1072.80 $[\text{H}_3\text{Os}_4(\text{CO})_{11}]^-$, 1042.80 $[\text{H}_3\text{Os}_4(\text{CO})_{10}]^-$, 1014.80 $[\text{H}_3\text{Os}_4(\text{CO})_9]^-$.

2.10.9 The reaction of $[\text{Pd}(\text{IMes})]$ with $[\text{Os}_3(\text{CO})_{11}\text{L}]/[\text{Os}_3(\text{CO})_{10}\text{L}_2]$

In a 100 ml round-bottom flask, **4a** (or KO^tBu and **3a** which are in 1:1 ratio) was added into DCM, followed by one equivalent of **12** or **13**. At the end of the reaction, the solvent was removed under reduced pressure and the residue obtained was redissolved in the minimum volume of dichloromethane and chromatographed on silica-gel TLC plates using DCM-hexane (1:2, v/v) as eluant. The reaction conditions and yields are summarized in Table 2-5. The analytical and spectroscopic data are tabulated in table 2-6.

Table 2-5. Reaction of [Pd(IMes)] with [Os₃(CO)₁₁L]/[Os₃(CO)₁₀L₂]

<i>Amount of</i>	<i>Amount of</i>	<i>Amount of KOtBu</i>	<i>Conditions</i>	<i>Separation data</i>	<i>Product (Color)</i>	<i>Yield</i>
12g 10 mg, 0.011 mmol	3a , 5 mg, 0.011 mmol	2 mg, 0.017 mmol	DCM 20 ml, RT, 30 min	R _f =0.45	12a	trace
				R _f =0.30	red 9a	trace
12i 30 mg, 0.030 mmol	3a , 15 mg, 0.030 mmol	4 mg, 0.030 mmol	DCM 20 ml, RT overnight	R _f =0.51	unreacted 12i	15 mg
				R _f =0.33	red 9i	6 mg
12a 13 mg, 0.011 mmol	4a , 9 mg, 0.012 mmol	NA	Hex 10 ml, RT, overnight	R _f =0.44	unreacted 12a	3 mg
				R _f =0.28	red 9a	10 mg, 57%
12a' 21 mg, 0.018 mmol	4a , 13 mg, 0.018 mmol	NA	Hex 10 ml, RT, 3days	R _f =0.38	unreacted 12a'	17 mg
				R _f =0.20	9a'	5 mg, 17%
13a 7 mg, 0.005 mmol	4a , 4 mg, 0.005 mmol	NA	Hex 10 ml, RT, 3days	NA	unreacted 13a	recovered
13h 120 mg, 0.110 mmol	3a , 53 mg, 0.110 mmol	12 mg, 0.110 mmol	DCM 20ml, RT overnight	NA	unreacted 13h	recovered

Table 2-6. Characterization of complexes **9a'**, **9i** and **9j**.

	IR [ν_{co} (cm^{-1})]	^1H NMR [δ /(ppm)]	$^{31}\text{P}\{^1\text{H}\}$ NMR/ ESI-MS $^+$ m/z:
9i	(DCM): 2110 w, 2092 w, 2056 m, 2037 m, 2018 sh, 2010 s, 1987 m, 1972 m, 1923 w, br	(C_6D_6) 6.85 (s, 4H, CH_{ph}), 6.31 (s, 2H, CH_{imid}), 3.01 (m, 6H, CH_2), 2.20 (s, 12H, CH_3), 2.14 (s, 6H, CH_3), 1.55 (m, 9H, CH_3)	101.3 (s)
9a	(hex): 2104 vw, 2086 vw, 2049 w, 2032 m, 2014 m, 2008 s, 1987 w, 1966 w, 1952 w, 1942 w, 1818 w (DCM): 2103 w, 2085 w, 2047 w, 2030 m, 2007 sh, 2004 s, 1972 m, 1954 m, 1804 w.	(C_6D_6) 6.79 (s, 4H), 6.76 (s, 4H), 6.31 (s, 2H), 5.78 (s, 2H), 2.18 (s, 12H), 2.07 (s, 6H), 2.02 (s, 6H), 2.00 (s, 12H)	1594.13 $[\text{M}]^+$
9a'	(DCM): 2097 w, 2081 w, 2039 m, 2023 m, 2007 sh, 1997 s, 1972 m, 1953 m, 1805 w. (Hex): 2098 w, 2082 w, 2041 m, 2025 m, 2009 s, 2001 s, 1984 m, 1978 m, 1959 m, 1943 m, 1937 sh, 1816 w	(C_6D_6) 6.83 (s, 4H, Ar-H), 6.75 (s, 2H, Ar-H), 6.53 (d, 1H, Im-H), 6.44 (s, 2H, Ar-H), 6.34 (s, 2H, Im-H), 5.32 (d, 1H, Im-H), 2.23 (s, 12H, CH_3), 2.13 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.90 (s, 6H, CH_3), 1.66 (s, 3H, CH_3), 1.58 (s, 6H, CH_3)	1593.13 $[\text{M}]^+$

2.10.10 The reaction of [PdOs₃(CO)₁₂(IMes)] with PPh₃

Compound **6a** (11 mg, 0.008 mmol) was dissolved in hexane (10 ml) and 3 molar equivalents of PPh₃ (10 mg, 0.038 mmol) was added. The mixture was stirred at room temperature for 30 min, some orange precipitate dropped out while the color of the solution turned from red to yellow. The orange color precipitate was filtered off. TLC separation of the filtrate using DCM-hexane (1:3, v/v) as eluant gave three bands.

Band 1. [Os₃(CO)₁₁(PPh₃)]. Yellow. R_f = 0.58.

Band 2. [Os₃(CO)₁₁(IMes)]. Orange. R_f = 0.51.

Band 3. [Os₃(CO)₁₀(PPh₃)₂]. Orange. R_f = 0.40.

The orange precipitate can be dissolved in DCM. IR (DCM): ν_{co} 2008 s, 1993 m, 1821 w cm⁻¹. ¹H NMR in CDCl₃ was complicated.

2.10.11 Thermal decomposition of [PdOs₃(CO)₁₂(IMes)]

Compound **6a** (17 mg, 0.013 mmol) was dissolved in octane (10 ml) and heated at 100 °C overnight. The color of the solution turned from red to yellow, and some black solid was observed. The black precipitate was filtered off and washed with hexane (10 ml). TLC separation of the filtrate using DCM-hexane (1:3, v/v) as eluant gave [Os₃(CO)₁₁(IMes)] (4 mg, 29%).

The black solid could be dissolved in DCM. IR (DCM): ν_{co} 2068 s, 2034 s, 2024 s, 2015 s, 1969 w cm⁻¹. ¹H NMR spectrum was complicated.

2.10.12 Reaction of [Pd₃Os₃(CO)₁₂(SIPr)₃] with H₂

A solution of **8d** (30 mg, mmol) in octane (20 ml) was heated to reflux for 20 min under a slow stream of hydrogen. A large quantity of brown precipitate was observed. The solvent was removed in vacuo, and the product washed with hexane to afford a brown solid.

IR (DCM): ν_{co} 2068 s, 2021 s, 2001 vs, 1951 m, 1911 m cm^{-1} .

^1H NMR (400 MHz, CD_2Cl_2): δ 7.42(m, 2H, aromatic-H); 7.26(d, $^3J_{\text{H,H}} = 8$ Hz, 4H, aromatic-H); 3.91 (s, Im-H, 4H); 3.06 (m, 4H, CH); 1.38 (d, $^3J_{\text{H,H}} = 8$ Hz, 12H, CH_3); 1.27(d, $J = 8$ Hz, 12H, CH_3); -7.92 (s, 2H, hydride).

$^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 195.6, 181.0, 178.7, 147.2, 129.7, 125.1, 29.0, 25.9, 23.7.

Table 2-7. Crystal and structure refinement data for **6-8, 9, 10, 11, 12a, 20, 21** and **22**.

Compound	6a	6c	6d
Formula	C ₃₃ H ₂₄ N ₂ O ₁₂ Os ₃ Pd	C ₃₉ H ₃₆ N ₂ O ₁₂ Os ₃ Pd	C ₃₉ H ₃₈ N ₂ O ₁₂ Os ₃ Pd
Fw	1317.66	1401.82	1403.84
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /n	P $\bar{1}$	P $\bar{1}$
a (Å)	12.6375(5)	12.1539(11)	12.1588(10)
b (Å)	19.2149(7)	12.5963(8)	12.6035(10)
c (Å)	16.3106(6)	18.4294(14)	18.1256(13)
α (°)	90	96.941(3)	96.546(2)
β (°)	102.736(2)	108.704(2)	107.720(2)
γ (°)	90	109.399(2)	109.278(2)
Volume (Å ³)	3863.2(3)	2437.7(3)	2425.4(3)
Z	4	2	4
Density (mg•m ⁻³)	2.411	1.968	2.040
Absorption coefficient, mm ⁻¹	10.494	8.213	8.258
F(000)	2592	1358	1412
Crystal size (mm ³)	0.20×0.20×0.10	0.26 × 0.22 ×0.14	0.34×0.28×0.24
Reflections collected	91419	13469	9847
Independent reflections (R _{int})	16595	9903	9847
	[R(int) = 0.00399]	[R(int) = 0.0499]	[R(int) = 0.0000]
Max. and min. transmission	0.4201 and 0.2280	0.3927 and 0.2240	0.2419 and 0.1656
Data/restraints/parameters	16595/0/493	9903/244/546	9847/2/578
Goodness-of-fit on F ²	1.190	1.134	1.071
Final R indices [I>2 σ (I)]	R1 = 0.0243	R1 = 0.0436	R1 = 0.0270
	wR2 = 0.0614	wR2 = 0.1292	wR2 = 0.0649
R indices (all data)	R1 = 0.0357	R1 = 0.0628	R1 = 0.0341
	wR2 = 0.0770	wR2 = 0.1515	wR2 = 0.0688
Largest diff. peak and hole (e Å ⁻³)	1.408 and -2.234	3.185 and -2.002	2.012 and -2.757

Compound	7c	7d	10
Formula	C ₆₆ H ₇₄ N ₄ O ₁₂ Os ₃ Pd ₂	C ₆₆ H ₇₆ N ₄ O ₁₂ Os ₃ Pd ₂	C ₁₆ H ₁₀ O ₁₀ Os ₃
Fw	1898.84	1900.71	932.84
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2(1)/c	P2 ₁ /n
a (Å)	19.8497(9)	19.1710(7)	7.6845(7)
b (Å)	20.6112(9)	19.3304(5)	9.8957(9)
c (Å)	33.6302(16)	19.6561(7)	13.6565(12)
α(°)	90	90	90
β(°)	90	112.4930(10)	105.989(3)
γ(°)	90	90	90
Volume (Å ³)	13759.0(11)	6730.1(4)	998.31(16)
Z	12	4	2
Density (mg•m ⁻³)	1.831	1.876	3.103
Absorption coefficient, mm ⁻¹	6.093	6.228	19.095
F(000)	7296	3664	828
Crystal size (mm ³)	0.28×0.24×0.16	0.10 × 0.08 ×0.08	0.30×0.24×0.18
Reflections collected	229545	53044	16116
Independent reflections (R _{int})	28087	13744	3200
	[R(int) = 0.1258]	[R(int) = 0.0000]	[R(int) = 0.0559]
Max. and min. transmission	0.4423 and 0.2803	0.6356 and 0.5747	0.1304 and 0.0693
Data/restraints/parameters	28087/979/1573	13744/0/800	3200/9/140
Goodness-of-fit on F ²	1.101	1.052	1.215
Final R indices [I>2σ(I)]	R1 = 0.0456	R1 = 0.0425	R1 = 0.0326
	wR2 = 0.1057	wR2 = 0.0975	wR2 = 0.0834
R indices (all data)	R1 = 0.0701	R1 = 0.0713	R1 = 0.0372
	wR2 = 0.1280	wR2 = 0.1234	wR2 = 0.0852
Largest diff. peak and hole (e Å ⁻³)	1.915 and -1.686	3.840 and -1.641	2.530 and -3.714

Compound	9a	8c	8d
Formula	C ₅₃ H ₄₈ N ₄ O ₁₁ Os ₃ Pd	C ₉₃ H ₁₀₈ N ₆ O ₁₂ Os ₃ Pd ₃	C ₉₃ H ₁₁₄ N ₆ O ₁₂ Os ₃ Pd ₃
Fw	1594.08	2391.84	2397.70
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	P2 ₁ /c	I 4	P2 ₁ /c
a (Å)	17.2365(6)	25.8167(15)	16.5278(19)
b (Å)	41.1788(14)	25.8167(15)	12.1286(15)
c (Å)	16.9107(5)	28.941(2)	46.099(5)
α(°)	90	90	90
β(°)	90.328(2)	90	92.759(2)
γ(°)	90	90	90
Volume (Å ³)	12002.7(7)	19289(2)	9230.3(19)
Z	8	24	4
Density (mg•m ⁻³)	1.788	1.662	1.725
Absorption coefficient, mm ⁻¹	6.682	4.543	4.746
F(000)	6148	9460	4704
Crystal size (mm ³)	0.30×0.10×0.08	0.18 × 0.16 × 0.14	0.34×0.28×0.24
Reflections collected	171518	72940	130387
Independent reflections (R _{int})	43631	28296	18831
	[R(int) = 0.1081]	[R(int) = 0.0683]	[R(int) = 0.0669]
Max. and min. transmission	0.6170 and 0.2391	0.5688 and 0.4952	0.3954 and 0.2952
Data/restraints/parameters	43631/1163/1377	28296/690/1109	18831/666/1078
Goodness-of-fit on F ²	1.097	1.066	1.264
Final R indices [I>2σ(I)]	R1 = 0.0980	R1 = 0.0447	R1 = 0.0676
	wR2 = 0.1834	wR2 = 0.0983	wR2 = 0.1374
R indices (all data)	R1 = 0.1852	R1 = 0.0832	R1 = 0.0911
	wR2 = 0.2104	wR2 = 0.1278	wR2 = 0.1507
Largest diff. peak and hole (e Å ⁻³)	5.371 and -8.729	1.419 and -1.577	2.705 and -4.097

Compound	11	6b	7b
Formula	C ₁₇ H ₁₄ O ₁₁ Os ₃	C ₃₃ H ₂₆ N ₂ O ₁₂ Os ₃ Pd	C ₅₄ H ₅₂ N ₄ O ₁₂ Os ₃ Pd ₂
Fw	964.88	1319.56	1732.56
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P 1	P 1	P2 ₁ /c
a (Å)	11.0223(8)	10.7616(5)	12.9778(3)
b (Å)	14.4146(10)	12.3104(5)	21.5529(6)
c (Å)	15.0393(11)	16.8682(7)	22.5894(7)
α(°)	102.825(2)	85.2520(10)	90
β(°)	104.078(2)	77.6170(10)	98.3090 (10)
γ(°)	94.973(2)	75.6580(10)	90
Volume (Å ³)	2234.7(3)	2113.64(16)	6252.1(3)
Z	4	4	4
Density (mg•m ⁻³)	2.868	2.209	1.991
Absorption coefficient, mm ⁻¹	17.069	9.468	6.841
F(000)	1728	1316	3560
Crystal size (mm ³)	0.28×0.24×0.16	0.40 × 0.36 ×0.12	0.20×0.14×0.04
Reflections collected	9343	11742	14869
Independent reflections (R _{int})	9343	8632	14869
	[R(int) = 0.0000]	[R(int) = 0.0000]	[R(int) = 0.0000]
Max. and min. transmission	0.2801 and 0.0735	0.3962 and 0.1159	0.7707 and 0.3403
Data/restraints/parameters	9343/132/390	8632/36/539	14869/30/770
Goodness-of-fit on F ²	1.069	1.176	1.088
Final R indices [I>2σ(I)]	R1 = 0.0744	R1 = 0.0259	R1 = 0.0577
	wR2 = 0.2108	wR2 = 0.0775	wR2 = 0.1383
R indices (all data)	R1 = 0.0872	R1 = 0.0336	R1 = 0.1090
	wR2 = 0.2255	wR2 = 0.0931	wR2 = 0.1769
Largest diff. peak and hole (e Å ⁻³)	3.308 and -5.722	1.681 and -2.049	3.595 and -3.068

Compound	12a	20	21
Formula	C ₃₂ H ₂₄ N ₄ O ₁₁ Os ₃	C ₁₃ H ₂ N ₂ O ₁₃ Os ₄	C ₁₆ H ₅ ClO ₁₆ Os ₅ Pd
Fw	1183.24	1126.95	1546.05
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Pbca	P 1	P2 ₁ /n
a (Å)	11.2269(8)	8.9284(2)	9.5709(7)
b (Å)	22.8062(17)	9.0410(2)	15.2468(10)
c (Å)	31.209(2)	26.2306(5)	19.2133(15)
α(°)	90	81.7690(10)	90
β(°)	90	87.8780(10)	98.549(2)
γ(°)	90	67.6390(10)	90
Volume (Å ³)	7990.9(10)	1937.64(7)	2772.6(3)
Z	8	4	4
Density (mg•m ⁻³)	2.038	3.856	3.704
Absorption coefficient, mm ⁻¹	9.573	26.212	23.624
F(000)	4568	1944	2688
Crystal size (mm ³)	0.34×0.10×0.04	0.08 × 0.06 ×0.02	0.22×0.14×0.08
Reflections collected	171268	12386	28351
Independent reflections (R _{int})	12450	12386	5657
	[R(int) = 0.0508]	[R(int) = 0.0000]	[R(int) = 0.0749]
Max. and min. transmission	0.7007 and 0.1393	0.6222 and 0.2282	0.2537 and 0.0782
Data/restraints/parameters	12450 / 39 / 495	12386/0/541	5657/0/352
Goodness-of-fit on F ²	1.166	0.902	1.140
Final R indices [I>2σ(I)]	R1 = 0.0290	R1 = 0.0435	R1 = 0.0347
	wR2 = 0.0750	wR2 = 0.1221	wR2 = 0.0896
R indices (all data)	R1 = 0.0429	R1 = 0.0642	R1 = 0.0424
	wR2 = 0.0902	wR2 = 0.1425	wR2 = 0.1093
Largest diff. peak and hole (e Å ⁻³)	2.302 and -1.320	3.650 and -5.108	2.369 and -1.913

Compound	22		
Formula	C ₃₆ H ₂₄ N ₂ O ₁₅ Os ₅ Pd		
Fw	1781.97		
Temperature (K)	103(2)K		
Crystal system	Triclinic		
Space group	P 1		
a (Å)	10.4408(4)		
b (Å)	12.5282(5)		
c (Å)	17.4046(5)		
α(°)	95.9330(10)		
β(°)	93.3810(10)		
γ(°)	101.5360(10)		
Volume (Å ³)	2213.67(14)		
Z	2		
Density (mg•m ⁻³)	2.673		
Absorption coefficient, mm ⁻¹	14.755		
F(000)	1600		
Theta range for data collection	1.67 to 28.35		
Reflections collected	10790		
Data/restraints/parameters	10790 / 0 / 538		
Goodness-of-fit on F ²	1.149		
Final R indices [I>2σ(I)]	R1 = 0.0387		
	wR2 = 0.0997		
R indices (all data)	R1 = 0.0538		
	wR2 = 0.1228		
Largest diff. peak and hole (e Å ⁻³)	7.357 and -2.562		

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CHAPTER 3 Nucleophilic attack of [Pt(NHC)] fragment on osmium carbonyl clusters

As mentioned in chapter 1, heteronuclear organometallic clusters can serve as single-source precursors for bimetallic nanoparticles which allow control over the particle size, composition and homogeneity.¹ Cluster-derived ruthenium-platinum nanoparticles are very active heterogeneous catalysts for the steam reforming of ethanol,² and ruthenium-osmium nanoparticles showed activity for CO oxidation.³ In addition, Os-Pt bimetallic systems have been shown to be active as fuel cell catalysts.⁴ In chapter 2, we have shown that the [Pd(NHC)] fragments can readily add across the metal-metal bonds in Os/Ru carbonyl clusters complexes. It is therefore of interest to investigate the extension of that synthetic methodology to obtain bimetallic OsPt or RuPt clusters with varying ratios of the metals.

3.1 Reactivity study of [Pt(NHC)] with [Os₃(CO)₁₂]

The room temperature reaction of **3'** with [Os₃(CO)₁₂] (**5**) in the presence of KO^tBu in IPA afforded several new compounds, *viz.*, [PtOs₃(CO)₁₂(NHC)] (**6'**), [Pt₂-Os₃(CO)₁₂(NHC)₂] (**7'**), [Pt₃Os₃(CO)₁₂(NHC)₃] (**8'**), and [Os₄(CO)₁₀(μ-H)₂(NHC)] (**16**), (NHC = SIPr, IPr, IMes) (Scheme 3.1). The reaction thus follows the same general course as for the Pd analogues, with the exception of cluster **16**, which was not observed in the reactions involving the Pd analogues. As may be expected, as the reaction time or amount of **3'** relative to **5** was increased, the reaction favored the formation of **8'** over **6'** and **7'**.

Scheme 3.1

All the products have been characterized spectroscopically and analytically, and in the case of **6'a**, **6'd**, **7'a**, **7'd**, **8'c**, **16c** and **16d** by single crystal structural analyses as well. ORTEP plots showing the structures of **6'd**, **7'd**, **8'c** and **16c** are given in Figures 3.1 and 3.2, respectively.

Figure 3.1. ORTEP diagram of compound **6'd** and **7'd**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 3.2. ORTEP diagram of compounds **8'c** and **16c**. Ellipsoids are drawn at 50% probability level. Organic hydrogen atoms have been omitted for clarity.

3.2 Solid-state structures of clusters 6'-8'

The overall structural features of **6'a**, **6'd**, **7'a** as well as **8'c** are similar to their corresponding Pd analogues **6a-d**, **7b-c** and **8c-d**, respectively; all the metal cores comprise a triangular arrangement of three Os atoms, with a Pt atom bridging one to three of the Os–Os edge. In contrast to the Pd analogue **7d**, which exhibited a “spike” structure, however, the solid-state structure of cluster **7'd** is the same as that for **7b-c**.

Phosphine analogues of all three clusters **6'-8'** are known (Figure 3.3).⁵ The gross structural features of **6'-8'** are similar to the reported P^tBu_3 analogues. For **A** and **B**, with each addition of a $[Pt(PR_3)]$ group, two Pt–Os bonds are formed, but only one of the two Pt–Os bonds contains a bridging CO ligand. In **6'-8'**, all the Os–Pt bonds are each bridged by a carbonyl ligand and most probably reflects the greater electron donor ability of the NHCs;^{6,7} an increase in electron density on metal clusters are known to favour carbonyls going into the bridging mode.⁸ Another major difference is while the Pt atoms lie significantly out of the Os_3 planes in the phosphine analogues (Table 3-1),⁹ the Os_3Pt_n planes are rather flat in the clusters **6'-8'**. This may be attributed to the fact that the bulky aromatic substituents on the NHC ligands tend to occupy the space above and below the metal core plane to reduce steric interactions; in the phosphine analogues there is less of such a constraint.

Figure 3.3. Structures of reported $[Pt_n Os_3 (CO)_{12} (P^tBu_3)_n]$ analogues.

Table 3-1. Mean and maximum deviation of metal atoms from the Os₃Pt_n plane in clusters **6'a**, **6'd**, **7'c-d**, **8'c** and **A-C**.

Compound	Deviation from Os ₃ Pd _n plane	
	Mean (Å)	Maximum (Å)
6'a (molecule A)	0.018	0.019
6'a (molecule B)	0.017	0.017
6'd	0.023	0.024
7'c	0.032	0.053
7'd	0.054	0.075
8'c	0.023	0.029
A	0.118	0.123
B	0.174	0.412
C	0.176	0.441

Selected bond parameters for **6'a**, **6'd**, **7'a**, **7'd** and **8'c** are given in Figures 3.4 to 3.6, respectively. As may be expected, all the Pt-bridged Os–Os bonds are significantly longer than the unbridged Os–Os bonds; the former ranges from 2.9444(4) Å in **7'd** to 2.8995(9) Å in **6'a**, while the latter ranges from 2.8570(4) Å in **7'd** to 2.8267(6) Å in **7'a**. All the Os–Pt bonds in **6'-7'** are shorter compared to those in [Os₃(CO)₁₂{Pt(P^tBu₃)_n}] (n=1–3) (from 2.7880(5) Å to 2.8602(9) Å).

Figure 3.4. Selected metal-metal and metal-carbon bond lengths (Å). Top: for **6'a** (above, molecular A, normal font type) and **6'd** (below, italics).

Figure 3.5. Selected metal-metal and metal-carbon bond lengths (Å). Top: for **7'a** (above, normal font type) and **7'd** (below, italics).

Figure 3.6. Selected bond lengths (Å) for **8'c**. There are two crystallographically independent molecules found in the asymmetric unit. Molecule A (above, normal font type) and molecule B (below, italics).

3.3 Solution structures of clusters **7'** and **8'**

Unlike their Pd analogues, clusters **7'**–**8'** are relatively stable in solution and appear not to interconvert easily. The ^1H NMR spectrum of **8'c** showed only one set of NHC signals, at both room temperature and at $-80\text{ }^\circ\text{C}$. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum taken at room temperature showed two resonances of the same intensity, at δ 195.8 and 189.2 ppm, for the carbonyl ligands and a carbene carbon signal at 212.9 ppm. No satellites due to ^{195}Pt – ^{13}C coupling were observed, although this is not uncommon.¹⁰ Bridging carbonyl resonances have been known to appear as upfield as δ 175.2 ppm, and terminal carbonyl ligands as downfield as δ 201.1 ppm (in the iridium cluster $\text{TMBA}_2[\text{Ir}_6(\text{CO})_{15}]$).¹¹ The two CO resonances for **8'c** could thus not be assigned definitively. A $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum taken at room temperature showed only one resonance, at δ -3286 ppm. All these suggest that the clusters **8'** are not fluxional.

The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of **7'c** and **7'd** showed only one signal each, which remained the same even at low temperature; $-80\text{ }^\circ\text{C}$ for **7'd** and $-60\text{ }^\circ\text{C}$ for **7'c**, which are consistent with retention of their solid-state structures. The variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7'd** showed that the CO ligands were undergoing fast exchange above about $-40\text{ }^\circ\text{C}$. As the temperature increased, all the CO peaks collapsed (Figure 3.7). That the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum showed only one resonance suggested that detachment and then reattachment of the $[\text{Pt}(\text{NHC})]$ unit was unlikely. This was also corroborated by the observation of very weak and broad satellites due to coupling to ^{195}Pt in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum over the temperature range from $-80\text{ }^\circ\text{C}$ to $-20\text{ }^\circ\text{C}$.

Figure 3.7. Variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of ^{13}C -labeled **7'd** (CO region).

Figure 3.8. “Merry-go-round” routes for CO exchange in Os_3Pt_2 .

The most likely carbonyl exchange mechanism is probably that of a “merry-go-round”.¹² If the CO ligands which bridged the Os–Pt edge were regarded as equivalent to an equatorial terminal CO in [Os₃(CO)₁₂], then the “merry-go-round” exchanges depicted in Figure 3.8 may occur.

The VT ¹H NMR spectra of both **7’c** and **7’d** showed two sets of signals for the ⁱPr–CH at 193 K, which broadened on warming, and finally collapsed into one set of sharp signals above -20 °C; that for **7’d** is shown in Figure 3.9. The VT ¹H NMR spectrum of **7’a** similarly showed two sets of signals for the ortho–CH₃ groups at -80 °C, which collapsed into one set on warming. This may be due to restricted rotation of the phenyl rings about the N–C_{ipso} bond at very low temperature (Figure 3.10).

Figure 3.9. VT ¹H NMR spectra of **7’d**.

Figure 3.10. Restricted rotation of the phenyl rings in clusters **7**.

3.4 The clusters **16**

The structure of the clusters **16** is interesting. Single-crystal X-ray crystallographic studies were carried out on **16c** and **16d**. Two bridging hydrides were located using potential energy calculations with the XHYDEX program.¹³ The solid-state structures showed general features which are similar to those for the reported cluster $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\text{IMes})]$, except that clusters **16** have one CO and two hydride ligands less (Figure 3.11). The clusters **16** therefore have a valence electron count of 56 and hence four-electron-deficient according to the EAN rule.

Figure 3.11. Solid-state structures for **16** (left) and $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\text{IMes})]$ (right).

The ^1H NMR spectra of **16a**, **16c** and **16d** in the hydride regions are all similar in that four hydride resonances were observed in the -6 to -10 ppm range. This range is unusual, and is probably related to their electron-deficient nature. For example, the ^1H NMR spectrum of **16c** in Tol- d_8 showed the presence of one set of resonances for the IPr ligand but hydride resonances at -7.57, -7.67, -8.42 and -9.17 ppm; the second and last being broad and of lower intensity, compared to the other two (Figure 3.12).

Figure 3.12. Room temperature ^1H NMR spectra for **16c** (hydride region) in Tol- d_8 .

The proton EXSY spectrum of **16c** taken at room temperature is shown in Figure 3.13 and displays exchange cross peaks for C with the two A resonances as well as with B, but there is no exchange between the A and B resonances. These suggest that three mutually exchanging isomers are present in solution, and that there is an exchange pathway that connects isomer A to isomer B, via isomer C. This presence of three isomers and the exchange pattern is reminiscent of that for the

heterotetranuclear cluster $[\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_{12}]$.¹⁴ Indeed, one may view the Os atom carrying the NHC ligand as equivalent to the Ru atom in the latter.

Figure 3.13. ^1H EXSY spectrum for **16c** taken in Tol-d_8 at room temperature.

A consistent set of assignments and exchange pathway is given in Fig. 3.14. Resonances A1 and A2 have been tentatively assigned to isomer A, which corresponds to the solid-state structure. Both isomers B and C have two equivalent hydrides bridging Os–Os edges.

Figure 3.14. Proposed isomers of **16** and the exchange pathway.

As is clear from the above, the clusters **16** are interesting as they are deficient by four electrons as required by the EAN rule. Their availability in such low yields hampered further studies. It was therefore desirable to explore alternative high yield routes to **16** and also to the Ru analogues. The mechanism of the formation of hydride-bridged cluster **16** is not clear at this moment, but we believe that the source of the hydrides may be the solvent used, i.e., isopropyl alcohol.

One possible route was through the decarbonylation (and loss of H_2) of the monosubstituted products $[\text{H}_4\text{M}_4(\text{CO})_{11}(\text{NHC})]$, which may be available from the reaction of $[\text{H}_4\text{M}_4(\text{CO})_{12}]$ ($\text{M} = \text{Ru}$ (**17(Ru)**) or Os (**17**)) with an NHC. Attempts to prepare the $[\text{H}_4\text{M}_4(\text{CO})_{11}(\text{NHC})]$ clusters were unsuccessful, however; either there were no reaction or only formation of a little of the product. Although $[\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{IMes})]$ has been reported to be generated in high yield from the reaction of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ with $\text{IMes}\cdot\text{HCl}$ (**1a**) in the presence of KO^tBu ,¹⁵ the corresponding reaction with $\text{IPr}\cdot\text{HCl}$ (**1c**) was found to lead to H^+ abstraction by the NHC to afford $[\text{IPr}\cdot\text{H}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ (**18c(Ru)**) as the only product.

A similar reaction between **17** and IMes in dry THF also led to H^+ abstraction to afford a yellow product which analyzed as the previous reported anionic cluster $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ (**18a**).¹⁶ This cluster is stable in air, insoluble in hexane but soluble in dichloromethane, THF, acetonitrile and methanol. An attempt to duplicate the report

that $[\text{H}_4\text{Os}_4(\text{CO})_{11}(\text{IMes})]$ can be generated from the reaction of **17** with $[(\text{IMes})\text{AgCl}]$ in the presence of two equivalent of TMNO,¹⁷ gave rise to many products in very low yields (spot TLC).

3.5 Conclusion

In this chapter, it was found that the heterometallic clusters $[\text{PtOs}_3(\text{CO})_{12}(\text{NHC})]$ (**6'**), $[\text{Pt}_2\text{Os}_3(\text{CO})_{12}(\text{NHC})_2]$ (**7'**) and $[\text{Pt}_3\text{Os}_3(\text{CO})_{12}(\text{NHC})_3]$ (**8'**) (NHC = SIPr, IPr, IMes) could be obtained from the reaction of $[\text{Pt}(\text{C}_4\text{H}_7)(\text{NHC})\text{Cl}]$ (**3'**) with $[\text{Os}_3(\text{CO})_{12}]$ (**5**). As in the case of the Pd analogues, the metal core of all these clusters comprised a triangular arrangement of three Os atoms, with Pt atom bridging one to three, respectively, of the Os–Os edges. Each of the Os–Pt bonds were in turn bridged by a carbonyl ligand. VT-NMR studies on clusters **7** showed that the CO ligands underwent fast exchange above $\sim -40^\circ\text{C}$, and there was restricted rotation of the phenyl rings about the N–C_{ipso} bond at low temperatures.

The clusters $[\text{Os}_4(\text{CO})_{10}(\mu\text{-H})_2(\text{NHC})]$ (**16**) were also isolated from these reactions, albeit in very low yield. The solid-state structures of **16c** and **16d** obtained from X-ray crystallographic studies indicated that they were four-electron deficient according to the EAN rule. The hydride resonances of **16** were unusually downfield for metal hydrides, occurring in the -6 to -10 ppm range. In solution, these clusters existed as an equilibrium mixture of three interconverting isomeric forms.

3.6 Experimental

The clusters $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ and $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ were prepared following the literature methods respectively.^{18,19} Di- μ -chloro-bis(η^3 -2-methylallylplatinum),²⁰ and $[\text{PtCl}(\text{C}_4\text{H}_7)(\text{IPr})]$ (**3'c**) and $[\text{PtCl}(\text{C}_4\text{H}_7)(\text{IMes})]$ (**3'a**),²¹ were prepared according to literature methods in high yields, while $[\text{PtCl}(\text{C}_4\text{H}_7)(\text{SIPr})]$ (**3'd**) was prepared using Ag transmetallation method. Other reagents were used as obtained from commercial

sources. All other general experimental procedures have been described in section 2.10.1. The elemental analyses were performed by the microanalytical laboratory at NUS. Reactions in sections 3.6.1 were carried out with the assistance of Kwan Jian Ming. The crystal structure determinations were carried out by Dr Rakesh Ganguly.

3.6.1 Reaction of [PtCl(C₄H₇)(NHC)] with [Os₃(CO)₁₂]

Compound **3'**, KO^tBu and **5** were added in IPA (10 ml). After stirring under room temperature for several hours, the solvent was removed under vacuo, the residue redissolved in the minimum volume of DCM and subjected to TLC afforded new clusters **6'-8'** and **16**. ¹³C-labeled [Pt₃Os₃(¹³CO)₁₂(IPr)₃] was synthesized using [Os₃(¹³CO)₁₂] in a similar way. The reaction conditions and yields are summarized in Table 3-2. The analytical and spectroscopic data are tabulated in Table 3-3.

3.6.2 Reaction of IMes with [H₄Os₄(CO)₁₂]

Compound **17** (30 mg, 0.027 mmol) and IMes (8 mg, 0.027 mmol) were placed in a Carius cube followed by THF (5 ml). After stirring at room temperature overnight, the solvent was removed and the residue obtained was redissolved in the minimum volume of dichloromethane and separated by TLC. Elution with hexane/dichloromethane (5/2, v/v) gave one major yellow band containing **18a**. Yield: 25 mg. R_f = 0.45.

IR (DCM): ν_{co} 2047 s, 2032 sh, 2021 s, 1999 s, 1979 m, 1958 m, 1946 w, 1916 w cm⁻¹.

¹H NMR (400 MHz, acetone-d₆): δ -19.39 (s, hydride), -19.95 (s, hydride), -21.89 (s, hydride) ppm. Organic region: 9.48 (d, *J* = 1.6 Hz, 2H), 8.23 (d, *J* = 1.6 Hz, 1H), 7.24 (s, 8H), 2.41 (s, 9H), 2.25 (s, 24H), not identified.

3.6.3 Reaction of IPr with [H₄Ru₄(CO)₁₂]

Both IPr•HCl (49 mg, 0.114 mmol) and KO^tBu (13 mg, 0.114 mmol), were placed in round-bottomed flask followed by THF (10 ml). After stirring at room temperature for

30 min, $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ (85 mg, 0.114 mmol) was added and the mixture was stirred for 2 h to give a red-orange solution. The solvent was removed under reduced pressure, and the resulting residue was separated by column chromatography. Elution with hexane afforded a small amount of the starting material $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$. Elution with hexane/dichloromethane (1/2, v/v) gave one major red-orange band containing compound **18c(Ru)**. Yield: (37 mg). IR (DCM): ν_{CO} 2067 w, 2037 s, 2032 sh, 2017 s, 1998 s, 1975 m, 1947 m, 1927 m cm^{-1} . ^1H NMR (400 MHz, acetone- d_6): δ 9.83 (t, 1H), 8.45 (d, $J = 12$ Hz, 2H), 7.73 (t, $J = 8$ Hz, 2H), 7.55 (d, $J = 8$ Hz, 4H), 2.60 (m, 4H), 1.32 (d, $J = 6.8$ Hz, 12H), 1.26 (d, $J = 6.8$ Hz, 12H), -17.01 (s, hydride) ppm.

Table 3-2. The reaction conditions and yields for reactions of **3'** with **5**.

<i>Amount of 3'</i>	<i>Amount of 5</i>	<i>Amount of KO^tBu</i>	<i>Conditions</i>	<i>Purification data</i>		<i>Product</i>	<i>Color</i>	<i>Yield</i>
3'a (20 mg, 0.033 mmol)	30 mg, 0.033 mmol	4 mg, 0.033 mmol	IPA 10 ml, 4 h	TLC Hex:DCM =3:1	R _f = 0.40	6'a	red	3 mg, 7%
					R _f = 0.31	16a	green	trace
					R _f = 0.25	7'a	purple	2 mg, 3%
3'a (98 mg, 0.170 mmol)	50 mg, 0.055 mmol	19 mg, 0.170 mmol	IPA 20 ml, overnight	TLC Hex:DCM =3:2	R _f = 0.62	6'a	red	trace
					R _f = 0.58	16a	green	3 mg, 4%
					R _f = 0.53	7'a	purple	6 mg, 5%
					R _f = 0.28	8'a	blue	3 mg, 2%
3'c (22 mg, 0.033 mmol)	30 mg, 0.033 mmol	5 mg, 0.040 mmol	IPA 10 ml, 4.5 h	TLC Hex:DCM =3:1	R _f = 0.39	6'c	red	3 mg,
					R _f = 0.30	16c	green	4 mg,
					R _f = 0.24	7'c	purple	5 mg,
3'c (134 mg, 0.200 mmol)	30 mg, 0.033 mmol	22 mg, 0.200 mmol	IPA 10 ml, 2 days	TLC Hex:DCM =3:1	R _f = 0.30	7'c	purple	10 mg, 15%
					R _f = 0.18	8'c	blue	13 mg, 15 %
3'c (89 mg, 0.130 mmol)	¹³ C-labeled 5 20 mg, 0.022 mmol	15 mg, 0.130 mmol	IPA 10 ml, 5 days	TLC Hex:DCM =2:1	R _f = 0.20	8'c	blue	16 mg, 27%
3'd (30 mg, 0.044 mmol)	20 mg, 0.022 mmol	22 mg, 0.198 mmol	IPA 10 ml, overnight	TLC Hex:DCM =3:1	R _f = 0.54	6'a	red	1 mg, 2%
					R _f = 0.42	16d	green	2 mg, 5%
					R _f = 0.30	7'd	purple	11 mg, 17%
3'd (124 mg, 0.200 mmol)	30 mg, 0.033 mmol	22 mg, 0.200 mmol	IPA 10 ml, 40 h	TLC Hex:DCM =3:1	R _f = 0.30	7'd	purple	major
					R _f = 0.20	8'd	blue	trace

Table 3-3. Analytical and spectroscopic data for **6'-8', 16**.

	IR[ν_{co} (cm^{-1})]	^1H NMR [δ /(ppm)]	$^{13}\text{C}\{^1\text{H}\}/^{195}\text{Pt}\{^1\text{H}\}$ NMR [δ /(ppm)]	Elemental Analysis	ESI-MS ⁺ m/z:
6'c	(DCM) 2112w, 2057m, 2047m, 2025s, 1999m, 1969w, 1854w, 1798w.	7.27-7.09 (m, 6H, Ar-H); 6.68 (m, 2H, Im-H), 3.01 (m, 4H, CH); 1.36 (d, $^3J_{\text{H,H}} = 6$ Hz, 12H, CH ₃); 0.98 (d, 12H, CH ₃)	--	--	1493.1[M] ⁺
7'c	(Hex) 2096w, 2041m, 2018s, 1999m, 1973w, 1882w, br, 1847w, br, 1801w.	(acetone-d ₆ , rt): 7.73 (s, 2H, Im-H), 7.42 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 2H, Ar-H); 7.27 (d, 4H, Ar-H), 2.92 (m, 4H, CH); 1.25 (d, 12H, $^3J_{\text{H,H}} = 6$ Hz, CH ₃), 1.11(d, 12H, $^3J_{\text{H,H}} = 6$ Hz, CH ₃)	$^{195}\text{Pt}\{^1\text{H}\}$ NMR: -3188 ppm.	Anal. Calcd for 6'c : C, 38.22; H, 3.50; N, 2.70. Found: C, 38.40; H, 3.98; N, 2.69.	2075.0 [M+H] ⁺ , 2047.0 [M-CO] ⁺
8'c	(DCM) 2045w, 2027m, 2003vs, 1951w, 1873m, 1795w.	(CDCl ₃ , rt): δ 7.29 (t, $^3J_{\text{H,H}} = 8$ Hz, 2H, Ar-H); 7.13 (s, 2H, Im-H), 7.11 (d, 4H, Ar-H), 2.92 (septet, $^3J_{\text{H,H}} = 6.8$ Hz, 4H, CH); 1.15 (d, 12H, CH ₃), 1.05 (d, 12H, CH ₃).	(rt): δ 212.9 (NCN), 195.8 (CO), 189.2 (CO), 146.0 (o-Ph-C), 135.8 (ipso-Ph-C), 129.6 (p-Ph-C), 123.7 (m-Ph-C), 123.6 (NCCN), 28.2 (CH), 26.5 (CH ₃), 22.6 (CH ₃). $^{195}\text{Pt}\{^1\text{H}\}$ NMR: -3286 pm.	Anal. Calcd: C, 42.03; H, 4.10; N, 3.16. Found: C, 43.22; H, 4.58; N, 3.01.	2657.5 [M] ⁺ , 2630.4 [M-CO] ⁺
6'd	(DCM) 2112w, 2057m, 2047m, 2026s, 1999m, 1969w, 1855w, 1803w.	(CD ₂ Cl ₂ , rt): 7.43-7.34 (m, Ph, 6H), 4.05 (s, Im-H, 4H), 3.35 (m, CH, 4H), 1.44 (m, CH ₃ , 12H), 1.38 (m, CH ₃ , 12H)	--	--	HRMS-ESI: m/z 1493.0918 ([M+H] ⁺). Calculated for C ₃₉ H ₃₉ N ₂ O ₁₂ ¹⁸⁸ Os ¹⁹² Os ₂ ¹⁹⁴ Pt: 1493.0918

	IR[ν_{co} (cm ⁻¹)]	¹ H NMR [δ /(ppm)] (CD ₂ Cl ₂ -40 °C)	¹³ C/ ¹⁹⁵ Pt{ ¹ H}NMR[δ /(ppm)]	Elemental Analysis or ESI-MS ⁺ m/z:
7'd	2095w, 2038m, 2014s, 1990m, 1847w, 1805w	(CD ₂ Cl ₂ , rt): 7.32 (t, ³ J _{H,H} = 8 Hz, 2H, Ar-H); 7.17 (d, 4H, Ar-H), 3.96 (s, 4H, Im-H), 3.28 (septet, ³ J _{H,H} = 6.8 Hz, 4H, CH); 1.25 (d, 12H, CH ₃), 1.21 (d, 12H, CH ₃).	¹³ C{ ¹ H}(CD ₂ Cl ₂ , -80°C): 232.7, 196.9, 195.9, 179.2, 175.8, 146.3, 134.8, 128.5, 124.1, 123.7, 27.8, 27.7, 26.1, 22.7. ¹⁹⁵ Pt{ ¹ H} (acetone-d ₆ , 0°C) -3157	Anal. Calcd: C, 38.14; H, 3.69; N, 2.70. Found: C, 38.10; H, 3.65; N, 2.72 2081.1 [M+H] ⁺ , 2050.1 [M-CO] ⁺
8'd	(DCM)2027m, 2004vs, 1878w, 1801w	(Acetone-d ₆ , rt): δ 7.22 (t, ³ J _{H,H} = 8 Hz, 2H, Ar-H); 7.11 (d, 4H, Ar-H), 4.03 (s, 4H, Im-H), 3.41 (septet, ³ J _{H,H} = 6.8 Hz, 4H, CH); 1.24 (d, 12H, CH ₃), 1.18 (d, 12H, CH ₃).	--	2666.1 [M] ⁺ , 2636.1 [M-CO] ⁺ HRMS-ESI: m/z 2664.6335 ([M+H] ⁺). Calculated for C ₉₃ H ₁₁₅ N ₆ O ₁₂ ¹⁸⁷ Os ¹⁸⁹ Os ¹⁹² Os ¹⁹⁵ Pt ¹⁹⁶ Pt ¹⁹⁸ Pt: 2664.6303
6'a	(DCM) 2111w, 2068w, 2057m, 2048m, 2025s, 1998m, 1967w, 1854w, 1797w	(C ₆ D ₆ , rt): δ 6.76 (s, 4H, Ar-H); 6.28 (s, 2H, Im-H), 2.11 (s, 6H, CH ₃), 2.07 (s, 12H, CH ₃).	--	HRMS-ESI: m/z 1407.9855 ([M+H] ⁺). Calculated for C ₃₃ H ₂₅ N ₂ O ₁₂ ¹⁸⁷ Os ¹⁹⁰ Os ¹⁹² Os ¹⁹⁸ Pt: 1407.9855
7'a	2095w, 2038m, 2014s, 1990m, 1847w, 1805w	(CD ₂ Cl ₂ , rt): δ 7.21(s, 2H, Im-H), 6.91(s, 4H, Ar-H), 2.27(s, 6H, CH ₃), 2.06 (s, 12H, CH ₃)	--	HRMS-ESI: m/z 1906.1284 ([M+H] ⁺). Calculated for C ₅₄ H ₄₉ N ₄ O ₁₂ ¹⁸⁸ Os ¹⁸⁹ Os ¹⁹⁰ Os ¹⁹⁶ Pt ¹⁹⁸ Pt : 1906.1400
8'a	(DCM) 2094w, 2027m, 2013s, 1963w, 1842m, 1796w	(C ₆ D ₆ , rt): δ 6.89 (s, 4H, Ar-H); 6.05 (s, 2H, Im-H), 2.36 (s, 6H, CH ₃), 2.15 (s, 12H, CH ₃).	--	HRMS-ESI: m/z 2406.3123 ([M+H] ⁺). Calculated for C ₇₅ H ₇₃ N ₆ O ₁₂ ¹⁸⁷ Os ¹⁸⁹ Os ¹⁹² Os ¹⁹⁵ Pt ¹⁹⁶ Pt ¹⁹⁸ Pt: 2406.3017

	IR[ν_{co} (cm^{-1})]	^1H NMR/ $^{13}\text{C}\{^1\text{H}\}$ NMR [δ /(ppm)]	ESI-MS ⁺ m/z:
16c	(DCM) 2078w, 2046s, 2013m, 1988m, 1971m, 1947w	^1H NMR(C_6D_6 , rt.): 7.28 (m, 2H, Ar-H), 7.08 (m, 4H, Ar-H); 6.38 (s, 4H, Im-H), 2.37 (m, 4H, CH); 1.24 (m, 12H, CH_3), 0.88 (m, 12H, CH_3), -7.57(hydride), -7.67 (hydride), -8.42(hydride), -9.17(hydride) $^{13}\text{C}\{^1\text{H}\}$ NMR(C_6D_6 , rt.): 205.4 (s, NCN), 144.8 (s, o-Ph-C), 136.1 (s, ipso-Ph-C), 131.5(s, p-Ph-C), 125.4(s, m-Ph-C), 124.4(s, NCCN), 29.0(s, CH), 24.9(s, CH_3), 22.9(s, CH_3)	1437.8 $[\text{M}]^+$
16d	(DCM): 2079w, 2048s, 2013m, 1992m, 1970w, 1947 w, br	(C_6D_6 , rt.): 6.97 (m, 6H, Ar-H), 3.27 (s, 4H, Im-H), 2.94 (m, 4H, CH), 1.47 (d, J = 6 Hz, 12H, CH_3), 0.98 (d, 12H, CH_3), -7.26(hydride), -7.54 (hydride), -8.32(hydride), -9.12(hydride)	1439.3 $[\text{M}]^+$
16a	(DCM): 2077w, 2043s, 2012s, 1985s, 1970w, 1951w, 1938w	(C_6D_6 , rt.): 6.77 (s, 4H, Ph-H), 5.85 (s, 2H, Im-H), 2.15 (s, 6H, CH_3), 1.74 (s, 12H, CH_3), -6.74(hydride), -8.07(hydride), -8.80(hydride), -9.52(hydride)	HRMS-ESI: m/z 1347.0073 ([M+H] ⁺). Calculated for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_{10}^{184}\text{Os}^{192}\text{Os}_3$: 1347.0035

Table 3- 4. Crystal and structure refinement data for **6'**, **7'**, **8'**, **16c** and **16d**.

Compound	6'a	6'd	7'a
Formula	C ₃₃ H ₂₄ N ₂ O ₁₂ Os ₃ Pt	C ₃₉ H ₃₆ N ₂ O ₁₂ Os ₃ Pt	C ₅₄ H ₄₈ N ₄ O ₁₂ Os ₃ Pt ₂
Fw	1406.33	1490.49	1905.85
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P $\bar{1}$	P $\bar{1}$	P2 ₁ /c
a (Å)	12.1412(6)	12.0228(10)	12.8254(13)
b (Å)	16.7748(10)	12.6612(9)	21.4283(11)
c (Å)	19.1229(10)	18.2751(14)	22.974(2)
α (°)	88.221(3)	96.983(3)	90
β (°)	89.144(3)	108.336(2)	99.358(3)
γ (°)	84.581(3)	108.426(2)	90
Volume (Å ³)	3875.1(4)	2428.7(3)	6229.8(9)
Z	2	2	4
Density (mg•m ⁻³)	2.447	2.129	2.078
Absorption coefficient, mm ⁻¹	13.465	10.752	10.630
F(000)	2602	1451	3620
Crystal size (mm ³)	0.38×0.24×0.08	0.12 × 0.10 × 0.04	0.12 × 0.08× 0.04
Reflections collected	15473	17189	66283
Independent reflections (R _{int})	15473	9922	12721
	[R(int) = 0.0000]	[R(int) = 0.0520]	[R(int) = 0.0708]
Max. and min. transmission	0.4122 and 0.0798	0.6730 and 0.3586	0.6758 and 0.3619
Data/restraints/parameters	15473/ 1038 / 959	9922/270 / 578	12721/ 5 / 712
Goodness-of-fit on F ²	1.045	1.022	1.059
Final R indices [I>2 σ (I)]	R1=0.0637	R1 = 0.0524	R1 = 0.0385
	wR2=0.1585	wR2 = 0.1319	wR2 = 0.0970
R indices (all data)	R1=0.0960	R1 = 0.0814	R1 = 0.0668
	wR2=0.1914	wR2 = 0.1583	wR2 = 0.1203
Largest diff. peak and hole (e Å ⁻³)	4.135 and -5.553	2.477 and -2.671	2.088 and -1.736

Compound	7'd	8'c	16c	16d
Formula	C ₆₆ H ₇₂ N ₄ O ₁₂ Os ₃ Pt ₂	C ₉₃ H ₁₀₈ N ₆ O ₁₂ Os ₃ Pt ₃	C ₃₇ H ₃₈ N ₂ O ₁₀ Os ₄	C ₃₇ H ₄₀ N ₂ O ₁₀ Os ₄
Fw	2074.18	2657.86	1431.49	1433.51
Temperature (K)	103(2)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$	P2 ₁ /c
a (Å)	19.2638(6)	16.1673(11)	10.6503(5)	10.1010(2)
b (Å)	12.9033(4)	27.344(2)	10.7257(5)	19.8204(4)
c (Å)	28.4540(9)	42.944(3)	18.8741(8)	20.6321(4)
α (°)	90	90	88.630(3)	90
β (°)	95.574(2)	90	82.442(3)	96.4730(10)
γ (°)	90	90	67.551(2)	90
Volume (Å ³)	7039.3(4)	18985(2)	1974.52(16)	4104.33(14)
Z	4	4	2	4
Density (mg•m ⁻³)	1.981	1.859	2.408	2.320
Absorption coefficient, mm ⁻¹	9.415	8.463	12.886	12.398
F(000)	3970	10116	1316	2640
Crystal size (mm ³)	0.20×0.18×0.04	0.22 × 0.24 × 0.34	0.40 × 0.28 × 0.26	0.38 × 0.24 × 0.14
Reflections collected	95202	298890	72312	53833
Independent reflections (R _{int})	14372	34979	8081	8389
	[R(int) = 0.0862]	[R(int) = 0.1345]	[R(int)= 0.0792]	[R(int) = 0.0552]
Max. and min. transmission	0.4122 and 0.0798	0.2600 and 0.1600	0.2757 and 0.0884	0.2757 and 0.0884
Data/restraints/parameters	14372/ 18 / 828	34979/2040 / 2154	8081/0/486	8389/ 0 / 486
Goodness-of-fit on F ²	1.115	1.137	1.239	1.200
Final R indices [I>2σ(I)]	R1=0.0383	R1 = 0.0457	R1 = 0.0298	R1 = 0.0309
	wR2=0.1006	wR2 = 0.1144	wR2 = 0.0884	wR2 = 0.0784
R indices (all data)	R1=0.0570	R1 = 0.0693	R1=0.0394	R1 = 0.0400
	wR2=0.1216	wR2 = 0.1363	wR2=0.1138	wR2 = 0.0923
Largest diff. peak and hole (e Å ⁻³)	1.814 and -2.702	2.430 and -2.611	1.492 and -3.225	1.348 and -2.840

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CHAPTER 4: Iridium complexes containing N-heterocyclic ligands

The pioneering work of Sinfelt on petroleum reforming catalysts showed that when platinum was combined with iridium, a vastly superior catalyst was produced.¹ The synthesis of iridium-platinum bimetallic clusters containing NHC ligands, as well as their palladium analogues, are therefore of interest as they can be suitable single-source precursors for the preparation of such bimetallic catalysts.

4.1 Synthesis of high nuclearity iridium-palladium/platinum clusters containing NHC ligands

The room temperature reaction of $[\text{Ir}_4(\text{CO})_{12}]$ (**25**) with three molar equivalents of $[\text{MCl}(\text{allyl})(\text{NHC})]$ ($\text{M} = \text{Pd}$, allyl = C_3H_5 , **3**; $\text{M} = \text{Pt}$, allyl = C_4H_7 , **3'**) in the presence of KO^tBu , with IPA as the solvent, afforded the clusters $[\text{M}_2\text{Ir}_4(\text{CO})_{12}(\text{NHC})_2]$ ($\text{M} = \text{Pd}$, **27**; $\text{M} = \text{Pt}$, **27'**) (Scheme 4.1). For the Pd analogues, a small amount of the clusters $[\text{PdIr}_4(\text{CO})_{12}(\text{NHC})]$ (**26**) were also obtained. The P^tBu_3 analogue of **27'**, viz., $[\text{Ir}_4(\text{CO})_{12}\{\text{Pt}(\text{P}^t\text{Bu}_3)\}_2]$ (**27' (P)**) has been reported to result from the room temperature reaction of **25** with $[\text{Pt}(\text{P}^t\text{Bu}_3)_2]$ and it has a similar IR pattern in the CO region.²

Scheme 4.1

The clusters **26** and **27** appeared to interconvert in solution as the IR and ¹H NMR spectra of both compounds showed them to be mixtures. For example, the ¹H NMR spectrum of a freshly prepared solution of **27c** in C₆D₆ showed two sets of NHC signals, with the dominant set assignable to **27c** and the weaker set to **26c**; the situation was reversed for a freshly prepared solution of **26c**. In other cases, for example, **26a** and **27a**, the interconversion occurred too rapidly to allow definitive assignment of the two sets of resonances to be made. These observations indicated that the [Pd(NHC)] unit could rapidly detach and re-attach itself to the Ir₄ cluster. Consistent with this was that a small amount of yellow **25** was precipitated during the NMR study on **26**. Integration of the ¹H NMR spectrum of the reaction crude indicated that **26** and **27** were formed in a 2:1 ratio. The ESI-MS of freshly prepared **26** also showed peaks corresponding to both [**26**+H]⁺ and [**27**+H]⁺.

Diffraction quality crystals of **27c** were obtained from hexane/dcm at 4 °C. There are two crystallographically distinct molecules in the asymmetric unit. An

ORTEP diagram of one of the molecules and selected bond parameters are shown in Figure 4.1. Repeated attempts to obtain crystals of **26** and **27'** suitable for single crystal X-ray diffraction studies proved unsuccessful.

The solid-state structure of **27c** is similar to that of **27'(P)** and consists of a central Ir₄ tetrahedron, with bridging [Pd(IPr)] units along two Ir–Ir bonds on opposite sides of the tetrahedron. Each iridium atom contains two linear terminal carbonyl ligands, and each Ir–Pd bond has a bridging carbonyl ligand. The presence of bridging CO ligands enables additional electron density from the [Pd(NHC)] to be delocalized away from the metal core.³ The cluster can be viewed as a bis-[Pd(IPr)] adduct of the parent cluster **25** as no CO ligands were lost. The Ir–Ir bonds bridged by the [Pd(NHC)] groups [Ir(1)–Ir(2) and Ir(3)–Ir(4), ranging from 2.7433(4) to 2.7522(4) Å] are significantly longer than the unbridged Ir–Ir bonds (ranging from 2.6953(4) to 2.7076(4) Å). These can also be compared to the average Ir–Ir bond length in [Ir₄(CO)₁₂] of 2.693 Å.⁴

Bond parameter	Molecule A	Molecule B
Bond distances (Å)		
Ir(1)-Ir(2)	2.7460(4)	2.7474(4)
Ir(1)-Ir(3)	2.7043(4)	2.7000(4)
Ir(1)-Ir(4)	2.6953(4)	2.7045(4)
Ir(2)-Ir(3)	2.6958(4)	2.6967(4)
Ir(2)-Ir(4)	2.7076(4)	2.6971(4)
Ir(3)-Ir(4)	2.7433(4)	2.7522(4)
Pd(5)-Ir(1)	2.7796(6)	2.7809(6)
Pd(5)-Ir(2)	2.7446(6)	2.7604(6)
Pd(6)-Ir(3)	2.7772(6)	2.7708(6)
Pd(6)-Ir(4)	2.7755(6)	2.7344(6)
Bond angles (deg)		
Ir(1)-Ir(3)- Ir(4)	59.303(11)	59.467(11)
Ir(1)-Ir(3)- Pd(6)	100.116(16)	97.607(17)
Ir(3)-Pd(6)- Ir(4)	59.213(14)	59.987(14)
Ir(4)-Ir(2)- Pd(5)	119.105(17)	117.754(18)

Figure 4.1. ORTEP drawing of molecule A of **27c** (Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity) and selected bond lengths (Å) and bond angles (°) for cluster **27c** (molecules A and B).

4.2 Attempts to generate Ir(I)/Rh(I) species containing NHC

The very electron-rich $[\text{Cp}^*\text{Ir}(\text{CO})_2]$ (**41**) and $[\text{CpIr}(\text{CO})_2]$ (**41'**) have previously been reacted with ruthenium and osmium carbonyl clusters to afford mixed-metal clusters (Scheme 4.2).^{5,6} It is therefore expected that the $[\text{Cp}^*\text{Ir}(\text{NHC})]$ fragment, with the very electron-donating Cp^* and NHC ligands, should be even more electron rich and hence should react in a similar manner to **41/41'**; this would constitute a new synthetic method towards mixed-metal clusters containing iridium. Ir(I) complexes containing both these ligands are unknown and so we sought to synthesize these *in situ*, then check their reactivity.

Scheme 4.2

As species such as $[\text{Cp}^*\text{M}(\text{CO})(\text{NHC})]$ and $[\text{Cp}^*\text{M}(\text{NHC})_2]$ ($\text{M}=\text{Ir}, \text{Rh}$) are very electron-rich, they would almost certainly be expected to undergo C-H activation of the solvent upon being formed. The reaction of $[\text{Cp}^*\text{Ir}(\text{CO})_2]$ (**41**) with IMes (**2a**) was carried out to investigate whether any such C-H activated product will be formed. It was observed, however, that the reaction of **41** with one equiv of IMes failed to proceed at room temperature, 70°C , and even on heating in decane at 150°C for 8 h; the IR spectrum showed only the signals of unreacted **41**. The reason for the failure of

this reaction is not certain but is likely to be due to the steric bulk of the IMes ligand.⁷

Another possible strategy to the Ir(I) species is through chemical reduction of the [Cp*Ir(III)(NHC)] complexes. For example, the carbonylation of [Cp*IrCl₂]₂ (**28**) was followed by reduction with zinc and further carbonylation *in situ* to give [Cp*Ir(CO)₂] (**41**) (scheme 4.3).¹³

Scheme 4.3

The complexes [Cp*M(IMe)Cl₂] (M = Ir **30**, M = Rh **30(Rh)**) could be synthesized according to the reported method by transmetalation with the silver complex of **1e** (scheme 4.4).^{8,9}

Scheme 4.4

Attempts at a similar synthesis of [Cp*M(IMes)Cl₂] (M= Ir or Rh) using the bulky mesityl-substituted NHC ligand **1a** were unsuccessful; the ¹H NMR and mass spectra of the reaction mixture indicated the presence of starting materials only. Additional attempts by reacting **1a** and KO^tBu (to generate the free NHC *in situ*) with **28** or **28(Rh)** also proved unsuccessful. The reason for the lack of success in these reactions is as yet unclear but it is possible that the steric hindrance of bulky substituents on the N atoms of NHC hinders the ligation of the NHC ligand to the metal center which already has the very bulky Cp* ligand.

On the other hand, the reaction of the silver carbene complex of **1g** with **28** and **28(Rh)** afforded the corresponding orthometalated NHC complexes **29** (38%) and **29(Rh)** (14%), respectively (Scheme 4.5). The structures of both complexes have been established unequivocally by single crystal x-ray structure analyses; the ORTEP plot for **29** is shown in Figure 4.2.

Scheme 4.5

Figure 4.2. ORTEP drawing of **29** with thermal ellipsoids drawn at 50% probability level. All hydrogen atoms were omitted for clarity.

$[\text{Cp}^*\text{Ir}]$ fragments containing an orthometalated NHC have been reported as catalyst precursors for the oxidation of water to dioxygen,¹⁰ while $[\text{Cp}^*\text{Rh}]$ analogues have not been reported yet. A comparison of the M-C bond lengths for **29** and **29(Rh)**,

together with structurally similar iridium and rhodium complexes, are given in Table 4.1.

Table 4-1. Bond lengths of **29**, **29(Rh)** and reported orthometalated NHC complexes.

Structure	Metal-carbene bond length	Metal-orthometalated carbon bond length
<p>29(Rh)</p>	2.015(2) Å	2.045(2) Å
2.052(3) Å ⁹	NA
2.014(7) Å	2.068(8) Å ¹¹
1.998(5) Å	2.047(5) Å ¹⁰
<p>29</p>	2.010(4) Å	2.051(4) Å

The observed M-NHC bond length is slightly shorter than that of the M-orthometalated carbon bond length, but the difference between the two metals for the corresponding bonds are not significant (2.015(2) and 2.045(2) Å in **29(Rh)** vs 2.010(4) and 2.051(4) Å in **29**, for M-NHC and M-C(orthometalated), respectively). The small differences between the two metals are a reflection of their similar covalent

radii (1.25 and 1.27 Å for Rh and Ir, respectively). B. A. B. Eduard has investigated two possible explanations for the shortening in the M-NHC bond: 1) multiple-bond character in the metal-carbon linkage, and 2) change in the hybridization at the NHC carbene carbon. He concluded that it is due to the latter; hybridization of the carbene carbon is intermediate between that of sp^2 and sp , obtained from an NBO analysis.¹² It is the increase in s character that leads to the observed metal-carbon bond shortening in NHC complexes.

Formation of the complex **29** is proposed to proceed via the corresponding non-orthometalated complex **30g**, which is presumably unstable towards C-H activation to form a slipped ring $[Cp^*M(NHC)(Cl)_2(H)]$ intermediate (Scheme 4.6). Evidence for such an intermediate is the observation of a small hydride resonance at -21.0 ppm in the 1H NMR spectrum shortly after the reaction in Scheme 4.5 ($M = Rh$) was initiated; this signal disappeared quickly over time. Such an upfield terminal iridium-hydride signal has been reported, for example, the terminal hydride signal of $[IrH(L)(\mu-H)_2](BArF)_2$, $L = (S)$ -1-[2-(2-adamantan-2-yl-4,5-dihydrooxazol-4-yl)-ethyl]-3-(2,6-diisopropylphenyl)-1,2-dihydroimidazol-2-ylidene was observed at -36.9 ppm.¹³ Elimination of HCl from this intermediate would result in **29**.

Scheme 4.6

Attempts at the reduction of the metal center from M(III) (**30** and **30(Rh)**) to M(I), using Zn or Mg as reducing reagents were unsuccessful. A yellow product tentatively identified as the salt $\{[Cp^*M(IME)(PPh_3)Cl]Cl\}$ ($M = Ir$, **31**, or Rh,

31(Rh)) was obtained from the reactions of **30** or **30(Rh)** with PPh₃ using Zn or Mg as reducing reagents. These salts are soluble in CH₂Cl₂ and MeOH. Their identities are proposed on the basis of their NMR and MS data: The ¹H NMR spectra showed signals corresponding to Cp*, NHC and PPh₃; the ESI-MS spectra showed very strong peaks corresponding to the ion [Cp*M(NHC)(PPh₃)Cl]⁺. Similar displacement of chloride by phosphines in complexes of the type Cp*Ir(L)Cl₂ (where L is a phosphine) has been reported.¹⁴

4.3 Reaction of N-heterocyclic carbene complexes of iridium with osmium and ruthenium carbonyl clusters

The reaction of [Cp*Rh(CO)₂] and [Cp*Ir(CO)₂] with [Ru₃(CO)₁₂] in the presence of hydrogen have been reported to yield ruthenium-iridium mixed metal clusters in moderate yields.^{6,15} Following this procedure, complex **30** was reacted with [Os₃(CO)₁₂] in the presence of hydrogen at 120 °C. This afforded the known clusters [Os₃(CO)₁₀(μ-H)(μ-Cl)] (**15**) and [Cp*IrOs₃(CO)₁₀H₂],⁶ and minor amounts of other as-yet unidentified products (Scheme 4.7). A similar reaction with [Ru₃(CO)₁₂] gave only the known cluster [H₄Ru₄(CO)₁₂].¹⁶ These observations suggest that the limitation lies in the need to reduce the Ir(III) complexes to the corresponding Ir(I) species.

Scheme 4.7

4.4 Conclusion

Heterometallic clusters containing iridium with palladium or platinum, *viz.*, [PdIr₄(CO)₁₂(NHC)], [Pd₂Ir₄(CO)₁₂(NHC)₂] and [Pt₂Ir₄(CO)₁₂(NHC)₂], could be obtained in low to moderate yields from the reaction of an [M(NHC)] (M = Pd or Pt)

fragment, generated *in situ*, with $[\text{Ir}_4(\text{CO})_{12}]$. The $[\text{Pd}(\text{NHC})]$ fragment, however, appears to be rapidly detaching and reattaching itself to the iridium cluster.

Attempts to synthesis ruthenium-iridium and osmium-iridium clusters via $[\text{Cp}^*\text{Ir}(\text{I})(\text{NHC})]$ were unsuccessful, as the reduction of the Ir(III) complexes to the corresponding Ir(I) species failed, while attempts at the synthesis of $[\text{Cp}^*\text{M}(\text{III})(\text{NHC})\text{Cl}_2]$ complexes via the reaction of $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Ir}$ or Rh) with silver complex of **1g** afforded the metallacyclic complexes **29** in which one of the mesityl ring has been orthometallated.

4.5 Experimental

Compounds **1g**,¹⁷ **1e**,¹⁸ **28**,¹⁹ **41**,¹⁹ and $[\text{Cp}^*\text{Ir}(\text{Ime})\text{Cl}_2]$ ⁹ were prepared according to the published method. Other reagents were used as obtained from commercial sources. All other general experimental procedures have been described in section 2.10.1. Reactions in sections 4.2.2 and 4.2.3 were carried out with the assistance of Toh Zhen Siew Stephanie and Huang Chung Hao. The crystal structure determinations were carried out by Dr Rakesh Ganguly.

4.5.1 Reaction of $[\text{Ir}_4(\text{CO})_{12}]$ (**25**) with $[\text{MCl}(\text{allyl})(\text{NHC})]$

To an RBF containing **25**, KO^tBu and **3** (or **3'**) was added distilled IPA (10 ml). The mixture was stirred at room temperature overnight. Some amount of unreacted **25** remained. Removal of the solvent under reduced pressure was followed by TLC separation using DCM-hexane (1:2, v/v) as eluant to give the products **26**, **27** (or **27'**). The reaction conditions used, and the yield of products obtained, are summarized in Table 4-2. The analytical and spectroscopic data are of the products are tabulated in Table 4-3.

4.5.2 Synthesis of **30** and **30(Rh)**

Ime·HI (56 mg, 0.25 mmol) and Ag₂O (35 mg, 0.15 mmol) were added into an RBF, followed by DCM (10 ml), and the mixture was stirred overnight. The resulting suspension was filtered, and the filtrate was added to a solution of [Cp*RhCl₂]₂ (77 mg, 0.13 mmol) in DCM (5 ml). The solution was stirred for 10 h, filtered, and the solvent removed via reduced pressure. The residue was washed with ether to afford a yellow solid **30(Rh)**. Yield = 72 mg (71%). ¹H NMR (CDCl₃): δ 6.98 (s, 2H, Im-H), 4.03 (s, 6H, CH₃), 1.62 (s, 15H, Cp*) ppm. ESI-MS: m/z 369 [Cp*Rh(NHC)(Cl)]⁺.

Compound **30** was prepared using a similarly procedure. Yield = 43%. ¹H NMR (CDCl₃): δ 6.91 (s, 2H, Im-H), 3.96 (s, 6H, CH₃), 1.63 (s, 15H, Cp*) ppm.

Table 4- 2. Reaction conditions and product yields for the reactions of **25** with **3** or **3'**.

Condition	Product	Color	Yield
25 (30 mg, 0.03 mmol), KO ^t Bu (10 mg, 0.09 mmol), 3a (0.08 mmol)	26a	orange	2 mg, 5%
	27a	brown	3 mg, 6%
25 (30 mg, 0.03 mmol), KO ^t Bu (10 mg, 0.09 mmol), 3c (47 mg, 0.08 mmol)	26c	orange	5 mg, 10%
	27c	brown	14 mg, 25%
25 (15 mg, 0.01 mmol), KO ^t Bu (5 mg, 0.04 mmol), 3d (25 mg, 0.04 mmol)	26d	orange	4 mg, 17%
	27d	brown	3 mg, 10%
25 (30 mg, 0.03 mmol), KO ^t Bu (9 mg, 0.08 mmol), 3'a (48 mg, 0.08 mmol)	27'a	brown	3 mg, 5%
25 (30 mg, 0.03 mmol), KO ^t Bu (9 mg, 0.08 mmol), 3'c (55 mg, 0.08 mmol)	27'c	brown	11 mg, 18%
25 (30 mg, 0.03 mmol), KO ^t Bu (6 mg, 0.05 mmol), 3'd (37 mg, 0.05 mmol)	27'd	brown	7 mg, 11%

Table 4- 3. Analytical and spectroscopic data for **26** and **27**.

Cluster	¹ H NMR (C ₆ D ₆ , δ , ppm)	IR (vCO, DCM)	ESI-MS ⁺ m/z:
26a	Set A: 6.84(s, 4H, Ph), 6.11 (s, 2H, Im-H), 2.18 (s, 4.5H, CH ₃), 2.03 (s, 12H, CH ₃); Set B: 6.77(s, 4H, Ph), 6.12 (s, 1.5H, Im-H), 2.11 (s, 4H, CH ₃), 2.01 (s, 9H, CH ₃). For freshly prepared 26a A:B = 1:1.5; that for 27a is 1:2	2091w, 2068m, 2058s, 2039s, 2014w, 2002m, 1842br, w	--
27a			1928.54
26c	7.27 (m, 2H, Ph), 7.15 (m, 4H, Ph), 6.46 (s, 2H, Im-H), 2.76 (m, 4H, CH), 1.40(d, <i>J</i> =6.8 Hz, 12H, CH ₃), 1.03 (d, <i>J</i> =6.8 Hz, 12H, CH ₃)	2091w, 2068m, 2058s, 2039s, 2031s, 2015w, 1999m, 1862br,w	1599.99
27c	7.25 (m, 2H, Ph), 7.13 (m, 4H, Ph), 6.48 (s, 2H, Im-H), 2.76 (m, 4H, CH), 1.37(d, <i>J</i> =6.8 Hz, 12H, CH ₃), 1.01 (d, <i>J</i> =6.8 Hz, 12H, CH ₃)		2096.30
26d	A: 7.25(m, 2H, Ph), 7.10 (m, 4H, Ph), 3.32(s, 4H, Im-H), 1.46 (d, 12H, CH ₃),	2092w, 2068m, 2058s, 2039s, 2028s, 2015w, 1999m, 1869br,w	1603.99
27d	1.14(d, 12H, CH ₃); B: 7.25(m, 2H, Ph), 7.10 (m, 4H, Ph), 3.30(s, 4H, Im-H), 3.11(m, 4H, CH), 1.17-1.13 (m, 12H, CH ₃); 1.49 (d, 12H, CH ₃), 1.17(d, 12H, CH ₃); Integration ration of A: B = 1:2		2098.35
27'a	---	2093w, 2062m, 2029s, 2013s, 1985m, 1960w, 1795br, w	2106.48
27'c	7.22-7.10 (m, 6H, Ph), 6.62(s, 2H, Im-H), 2.88 (m, 4H, CH), 1.36 (m, 12H, CH ₃), 0.96 (m, 12H, CH ₃)	2092w, 2063m, 2032s, 2028s, 1999m, 1974m, 1858m, 1799m	2272.46[M] ⁺ 2246.46[M-CO] ⁺ , 2218.47[M-2CO] ⁺ 2190.46[M-3CO] ⁺
27'd	7.20-7.18 (m, 2H, Ph), 7.08 (d, 4H, Ph), 3.48 (s, 4H, Im-H), 3.30 (m, 4H, CH), 1.42 (d, <i>J</i> = 6.8Hz, 12H, CH ₃), 1.07 (d, <i>J</i> = 6.8Hz, 12H, CH ₃)	2092w, 2064m, 2035s, 2027s, 2001m, 1974m, 1858m, 1800m	2275.99[M] ⁺ 2249.03[M-CO] ⁺

4.5.3 Attempted synthesis of [Cp*MCl₂(2,4,6-trimethylphenyl-NHC)]

IMes·HCl (43 mg, 0.13 mmol) and Ag₂O (18 mg, 0.08 mmol) were added into a RBF, followed by DCM (10 ml), and the reaction mixture was stirred overnight. The resulting suspension was filtered and the filtrate was then added to a solution of [Cp*RhCl₂]₂ (39 mg, 0.06 mmol) in DCM (5 ml). The solution was stirred for 10 h, filtered, and the solvent was then removed via reduced pressure. ¹H NMR and MS spectra showed only unreacted [Cp*RhCl₂]₂ and [(IMes)AgCl]. Similar observations were made on the reaction with [Cp*IrCl₂]₂.

4.5.4 Synthesis of **29**/**29**(Rh)

Compound **1g** (47 mg, 0.17 mmol) and Ag₂O (32 mg, 0.10 mmol) were added into an RBF, followed by DCM (10 ml), and the mixture stirred overnight. The resulting suspension was filtered and the filtrate was then added to a solution of **28**(Rh) (50 mg, 0.08 mmol) in DCM (5 ml). The solution was stirred for overnight, filtered, and the solvent was then removed via reduced pressure and separated by TLC using DCM:Acetone (10:1, v/v) as eluant to afford a yellow solid **29**(Rh). Yield: 12 mg (14%). ¹H NMR (CDCl₃): δ 7.93 (d, 2H, aromatic), 7.59 (s, 1H, aromatic), 7.49 (s, 1H, aromatic), 7.31 (d, 2H, aromatic), 7.16 (d, 1H, aromatic), 6.98 (d, 1H, aromatic), 6.79 (d, 1H, aromatic), 2.45 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 1.39 (s, 15H, Cp*) ppm. ESI-MS: m/z 485 [Cp*Rh(NHC)]⁺.

Similarly, **29** was synthesized as a yellow solid in 38% yield. ¹H NMR (CDCl₃, 400 MHz): δ 7.83 (d, 1H, aromatic), 7.55 (s, 1H, aromatic), 7.45 (d, 1H, aromatic), 7.31 (d, 1H, aromatic), 7.15 (d, 2H, aromatic), 7.07 (d, 1H, aromatic), 6.79 (d, 2H, aromatic), 2.44 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 1.47 (s, 15H, Cp*).

4.5.5 Attempt to synthesis of M(I) species (M=Ir, Rh)

Compound **30** (20 mg, 0.041 mmol) and PPh₃ (26 mg, 0.10 mmol) were added into an RBF, followed by DCM (10 ml). The reaction mixture was stirred at room temperature for 4 h, the solvent removed under reduced pressure, and the residue so obtained was redissolved in the minimum of dichloromethane for TLC separation, with dichloromethane/MeOH (9:1, v/v) as the mobile phase, to afford [Cp*Ir(PPh₃)(IMe)Cl]⁺Cl⁻ (yellow, 40%). ¹H NMR (CDCl₃, 400 MHz): δ 7.52-7.15 (m, 15H, PPh₃), 6.65 (s, 2H, Im-H), 3.88 (s, 3H, CH₃), 3.25 (s, 3H, CH₃), 1.55 (d, 15H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ -0.54 ppm. ESI-MS: m/z 720.92 [Cp*Ir(NHC)(PPh₃)Cl]⁺, 459.24 [Cp*Ir(NHC)Cl]⁺.

A similar reaction of **30(Rh)** (20 mg, 0.05 mmol) with PPh₃ (26 mg, 0.10 mmol) in DCM (10 ml) afforded **31(Rh)** as major product. ¹H NMR (CDCl₃, 400 MHz): δ 7.69-7.33 (m, 15H, PPh₃), 6.99 (s, 2H, Im-H), 3.88 (s, 3H, CH₃), 3.21 (s, 3H, CH₃), 1.55 (d, 15H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 32.87, 32.05 ppm. ESI-MS: m/z 630.65 [Cp*Ir(NHC)(PPh₃)Cl]⁺, 369.03 [Cp*Ir(NHC)Cl]⁺.

Table 4- 4. Crystal and structure refinement data for **27c**, **29** and **29(Rh)**.

Compound	27c	29	29(Rh)
Formula	C ₆₆ H ₇₂ N ₄ O ₁₂ Ir ₄ Pd ₂	C ₂₇ H ₃₀ ClIrN ₂	C ₂₇ H ₃₀ ClRhN ₂
Fw	2094.88	610.18	520.89
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P 1	P 1	P 1
a (Å)	18.9248(6)	8.0900(2)	8.0899(3)
b (Å)	19.5145(5)	10.9636(4)	10.9471(4)
c (Å)	19.5292(6)	13.1771(4)	13.2001(5)
α (°)	104.4700(10)	96.644(2)	97.002(2)
β (°)	90.319(2)	92.567(2)	92.032(2)
γ (°)	96.7440(10)	97.362(2)	97.128(2)
Volume (Å ³)	6930.6(4)	1149.22(6)	1149.81(7)
Z	4	2	2
Density (mg•m ⁻³)	2.008	1.763	1.505
Absorption coefficient, mm ⁻¹	8.218	5.943	0.876
F(000)	3968	600	536
Crystal size (mm ³)	0.18 × 0.14 × 0.06	0.10 × 0.04 × 0.02	0.08 × 0.06 × 0.04
Reflections collected	263614	7601	13814
Independent reflections (R _{int})	28336	7601	7918
	[R(int) = 0.0801]	[R(int) = 0.0000]	[R(int) = 0.0278]
Max. and min. transmission	0.6384 and 0.3193	0.8904 and 0.5879	0.9658 and 0.9332
Data/restraints/parameters	28336/ 853 / 1694	7601/ 0 / 287	7918/ 0 / 287
Goodness-of-fit on F ²	1.130	1.176	1.149
Final R indices [I>2 σ (I)]	R1=0.0348	R1 = 0.0316	R1 = 0.0309
	wR2=0.0814	wR2 = 0.0686	wR2 = 0.0765
R indices (all data)	R1=0.0595	R1 = 0.0443	R1 = 0.0408
	wR2=0.1070	wR2 = 0.0899	wR2 = 0.0953
Largest diff. peak and hole (e Å ⁻³)	1.691 and -2.084	1.676 and -2.342	0.943 and -1.395

4.6 References

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Chapter 5

Nucleophilic attack of N-heterocyclic carbene at a carbonyl ligand: A zwitterionic osmium carbonyl cluster

5.1 N-heterocyclic carbene derivatives of $[M_3(CO)_{12}]$ (M = Ru or Os)

We postulated in chapter 2 that the electron-rich $[Pd(NHC)]$ group should be reactive with electron-poor but not electron-rich clusters. In order to test this hypothesis, clusters with different electronic properties are needed. NHC-containing carbonyl clusters such as $[M_3(CO)_{11}(NHC)]$ (M= Os, Ru), are desirable as they contain a strongly electron-donating NHC ligand. Although it is expected that these clusters may be synthesized via the direct reaction of an NHC with the parent clusters $[M_3(CO)_{12}]$ (M= Os, **5**; M= Ru, **5(Ru)**), very different observations have been made by various research groups.¹

As early as 1977, Lappert and Pye reported the first group 8 trinuclear carbonyl cluster $[Ru_3(CO)_{11}(SiEt)]$.² This class of compounds remained unexplored for almost 30 years until Cabeza and co-workers reported that the nature of the substituent on the NHC has significant effect on the reactivity of the NHC with the parent carbonyl clusters **5** and **5(Ru)**; the more basic and less bulky the NHC ligand, the easier its reaction with the metal clusters. They found that **5(Ru)** reacted readily at room temperature with the small IMe ligand, generated *in situ* in THF, to give the trinuclear derivative $[Ru_3(CO)_{11}(IMe)]$ (Scheme 5.1). With the bulkier IMes, the reaction was slow and afforded $[Ru_3(CO)_{11}(IMes)]$ as well as the hexanuclear salt $[IMes \bullet H][Ru_6(\mu_3-CO)_2(\mu-CO)_2(CO)_{14}]$,³ while with IPr, only the hexanuclear salt was obtained. Furthermore, the reaction of **5** with IMe gave $[Os_3(CO)_{11}(IMe)]$, but it failed to react with the bulkier IMes and IPr, even at temperatures as high as 70 °C.⁴

Interestingly, Ellul reported that the very bulky $I^t\text{Bu}$ reacted with **5(Ru)** at room temperature to give the mesoionic (abnormal) NHC complex $[\text{Ru}_3(\text{CO})_{11}(mI^t\text{Bu})]$.⁵ Crittall also reported that the even bulkier carbene IAd can react with both **5** and **5(Ru)** at 70 °C to generate $[\text{M}_3(\text{CO})_{11}(m\text{IAd})]$.⁶

Scheme 5.1

On the other hand, Bruce *et al.* also reported that the treatment of **5(Ru)** with three equivalents of IMes or IPr resulted in fragmentation to afford the mononuclear ruthenium tetracarbonyl compounds $[\text{Ru}(\text{CO})_4(\text{NHC})]$,⁷ in contrast to the observations of Cabeza. Fragmentation of the ruthenium cluster has also been observed by the Whittlesey group; the reaction of **5(Ru)** with six equivalents of the small, alkyl substituted carbenes $I^i\text{Pr}_2$, $I^i\text{Pr}_2\text{Me}_2$ or IEt_2Me_2 , resulted in the formation of the bis-NHC tricarbonyl complexes $[\text{Ru}(\text{CO})_3(\text{NHC})_2]$ (Scheme 5.2).⁸

Scheme 5.2

In our attempt at the preparation of $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$ from the reaction of the free carbene IMes with **5**, we have found that the major product formed was not the

expected mono-substituted derivative but an orange complex which seemed to be an intermediate in the substitution reaction. This chapter describes the results of our investigations into the direct reaction of free NHCs with **5** and other transition metal carbonyl clusters.

5.2 Formation of $[\text{Os}_3(\text{CO})_{11}\{\text{C}(=\text{O})m\text{NHC}\}]$

Treatment of **5** with 1.5 equivalents of free IMes (**2a**) afforded orange-red $[\text{Os}_3(\text{CO})_{11}\{\text{C}(=\text{O})m\text{IMes}\}]$ (**33a'**, 39%) as the major product, as well as smaller quantities of $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$ (**12a**, 4%), $[\text{Os}_3(\text{CO})_{11}(m\text{IMes})]$ (**12a'**, 6%), $[\text{Os}_3(\text{CO})_{10}(\text{IMes})_2]$ (**13a**, trace amount) and other unknown products (Scheme 5.3). Similar reactions with IPr and *t*Bu afforded the analogous products $[\text{Os}_3(\text{CO})_{11}\{\text{C}(=\text{O})m\text{NHC}\}]$ (NHC= IPr, **33c'**, 15%; *t*Bu, **33f'**, 23%), $[\text{Os}_3(\text{CO})_{11}(\text{IPr})]$ (**12c**, trace amount) and $[\text{Os}_3(\text{CO})_{11}(m\text{NHC})]$ (NHC= IPr, **12c'**, 5%; *t*Bu, **12f'**, 14%).

Scheme 5.3

The clusters **33'** are stable in air for a few days as solids. They are not soluble in hexane but are soluble in THF, acetone and dichloromethane, although they slowly decomposed in solution to afford **5**, **12'** and other unknown species. The clusters **12'** are relatively stable; a solution of **12a'** in THF did not show any signs of decomposition even after several days. It also did not react with CO bubbled into the solution for several hours. The IR patterns of **33'** in DCM solution are quite similar to that of the related clusters **12'**; the infrared spectra of **33a'** and **12a'**, for instance, differ in that the spectrum for **33a'** exhibited two extra weak peaks at around 1577 and 1531 cm⁻¹. These have been assigned to the acyl group, although a computational study suggested that they are not pure C=O stretches but are coupled to ring deformations of the imidazole (see below and also Figure 5.1).

The ¹H NMR spectrum of **33a'** in THF-d₈ showed two doublets at δ 9.00 and 8.27 ppm in a 1:1 ratio, which is indicative of an abnormally coordinated NHC; these signals, especially the latter, are shifted significantly downfield from the corresponding resonances in **12a'** (δ 8.78 and 6.83 ppm), which indicate that the acyl group decreases the shielding of the NHC ring.

Figure 5.1. IR spectra for **33a'** (black color) and **12a'** (red color).

The $^{13}\text{C}\{^1\text{H}\}$ resonances of **33a'** in THF- d_8 at $-30\text{ }^\circ\text{C}$ were easily assigned on the basis of $^1\text{H}\text{-}^{13}\text{C}\{^1\text{H}\}$ HMQC/HMBC and DEPT-90 experiments; resonances were found at δ 139.0 and 129.3 ppm for the two C-H carbon atoms of the imidazole ring, at δ 148.4 ppm for the ring carbon atom attached to the acyl group, and at δ 203.9 ppm for the acyl group. As may be expected, a particularly large downfield shift was observed for the resonance due to the ring carbon atom attached to the acyl group compared to the corresponding resonance in $[\text{Os}_3(\text{CO})_{11}(\text{mIMes})]$ and $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$ (δ 122.9 and 123.7 ppm, respectively).

The molecular structures of **12a'**, **13a**, **33a'**, **33c'** and **33f'** have been confirmed by single-crystal X-ray crystallographic studies; ORTEP plots of **12a'**, **13a** and **33a'** are shown in Figure 5.2-5.3, and a common atomic labeling scheme together with selected bond parameters for clusters **33a'**, **33c'**, **33f'**, as well as **12a'**, are given in Table 5.1.

Figure 5.2. ORTEP diagram of **13a**. Thermal ellipsoids are drawn at 50% probability level. Organic hydrogens are omitted for clarity. Os(1)-Os(2) 2.9814(2), Os(1)-Os(3) 2.9304(3), Os(2)-Os(3) 2.9323(3), Os(1)-C(101) 2.119(5), Os(2)-C(201) 2.113(5), Os(1)-Os(2)-Os(3) 59.465(6), Os(1)-Os(3)-Os(2) 61.133(6), Os(3)-Os(1)-Os(2) 59.465(6).

Figure 5.3. ORTEP plots showing the molecular structures of **12a'** (top), **33a'** (bottom). Thermal ellipsoids are drawn at 50% probability level. Organic hydrogens are omitted for clarity.

Table 5-1. Common atomic numbering scheme and selected bond parameters for **33a'**, **33c'**, **33f'** and **12a'**.

12a' $n = 0$, R = Mes
33a' $n = 1$, R = Mes
33e' $n = 1$, R = 2,4- $i\text{Pr}_2\text{C}_6\text{H}_3$
33f' $n = 1$, R = $t\text{Bu}$

	33a'	33c'	33f'	12a'
Bond Lengths (Å)				
Os(1)-Os(2)	2.8795(4)	2.8997(4)	2.8769(3)	2.8746(10)
Os(1)-Os(3)	2.8759(4)	2.8669(4)	2.8914(3)	2.8902(9)
Os(2)-Os(3)	2.9033(4)	2.8998(4)	2.8833(4)	2.8837(9)
Os(1)-C(14)	2.081(7)	2.106(7)	2.089(6)	-
C(14)-O(14)	1.226(8)	1.222(8)	1.229(7)	-
C(14)-C(15)	1.509(9)	1.510(9)	1.513(8)	-
Os(1)-C(15)	-	-	-	2.121(13)
Bond Angles (°)				
Os(1)-Os(2)-Os(3)	59.644(9)	59.253(9)	60.259(9)	59.579(11)
Os(1)-Os(3)-Os(2)	59.767(10)	60.372(9)	59.759(8)	60.281(11)
Os(2)-Os(1)-Os(3)	60.588(9)	60.375(10)	59.981(8)	60.141(11)
Os(1)-C(14)-C(15)	120.1(4)	118.6(5)	120.9(4)	-

The clusters **12** and **13** can be regarded as derivatives of the parent cluster **5** by substitution of one and two equatorial carbonyl ligands with a carbene and a mesoionic carbene, respectively. Analogues of **12a'** which have been structurally characterized by X-ray crystallography include the *mI*^tBu and *mI*Ad analogues,⁹ and the IMes (cluster **12a** in chapter 2) and IMe analogues.⁴ As has been observed for these (with the exception of **12a**), as well as for the phosphine analogues,¹⁰ the Os–Os bond cis to the NHC ligand (2.8902(9) Å) is elongated compared to the other two (2.8746(10) Å and 2.8837(9) Å). Interestingly, the Os–Os bond lengths in **12a** are generally slightly longer than those in **12a'** (2.9232(3) - 2.8841(3) Å vs 2.8902(9) - 2.8746(10) Å), which may be attributed to the greater electron-donating ability of *m*IMes compared to IMes.

The X-ray crystal structure of **13a** reported here is the first example for a di-NHC substituted cluster. As in the well-known phosphine analogues,¹¹ the Os–Os bond flanked by the two NHC ligands is elongated (by 0.0510 Å and 0.0491 Å, respectively) compared to the other two Os–Os bond lengths. This has been attributed to a combination of steric repulsion between the equatorial carbonyl ligand (CO(12) in **13a**) and the two bulky NHC ligands, together with the cis Os–Os bond lengthening effect of the NHC ligand.^{11,12} The disubstituted phosphine derivatives [Os₃(CO)₁₀(PR₃)₂] occur as mixtures of the structural types **A** and **B** (Figure 5.4) in rapid equilibrium in solution, and examples of both structural types have also been characterized in the solid state.^{11,12} Thus although the solid state structure of **13a** corresponded to structural type **A**, the solution state ¹H NMR spectrum of **13a** at room temperature showed broad peaks for the NHC ligands, which is indicative of rapid chemical exchange, presumably corresponding to the presence of the isomers of structural types **A** and **B**.

Figure 5.4. Isomers of $[\text{Os}_3(\text{CO})_{10}(\text{PR}_3)_2]$.

The clusters **33a'**, **33c'** and **33f'** are isostructural; all three may be regarded as the result of attack of a mesoionic NHC at a carbonyl ligand on the parent cluster **5**. The osmium-acyl (Os1–C14) bond length is significantly longer than the Os–carbonyl bond lengths; the former ranges from 2.081(7) Å to 2.106(7) Å, while the latter ranges from 1.874(7) Å to 1.962(8) Å, suggesting that Os1–C14 is probably a single bond. Likewise, the C14–O14 bond length (range from 1.222(8) Å to 1.229(7) Å) is slightly longer than that for the carbonyl ligands (range from 1.119(9) Å to 1.160(9) Å). Together with electron counting rules, all these suggest that clusters **33** are best regarded as zwitterionic with a negative charge on the cluster and a positive charge at the NHC ring (Figure 5.5). It is interesting to note that the Os–Os bond lengths in **33** do not show the trend observed in **12** and **13**.

Figure 5.5. The zwitterionic bonding description of clusters **33**.

This electronic structure of **33** was examined computationally by a natural bond orbital (NBO) analysis on a simplified model (**33**) in which the substituents on the N atoms were replaced with H atoms. The charge computed for the imidazole ring summed to a total of +0.81, while that for the $[\text{Os}_3(\text{CO})_{11}]$ moiety was -0.64 (Figure

5.6). The surprising stability of **33** may be attributed to delocalization of these charges onto the imidazole ring and the cluster $[\text{Os}_3(\text{CO})_{11}]$ moiety, respectively.

Figure 5.6. Natural charges calculation for **33**.

The atom-atom overlap-weighted natural atomic orbital (NAO) bond orders for the Os–Os vectors are roughly the same (Figure 5.7). Although NAO bond orders involving heavy transition metal atoms are not expected to be very reliable, compared to that for the Os–carbonyl bond which has double bond character (with average value ~ 1.2), the NAO bond order calculated for the Os–acyl bond (0.84) suggests that it is probably a single bond. These values can also be compared to those for the acyl C=O bond (1.19) and the acyl–imidazole bond (0.90), and are consistent with the bond parameters from the crystal structures. For example, the values for **33a'** are 1.226(8) Å for the acyl C=O, 1.509(9) Å for the acyl–imidazole, and 2.081(7) Å for the osmium–acyl vectors. The bond parameters for the imidazole rings in **33a'** and **12a'** are otherwise comparable.

Figure 5.7. NBO analysis of **33'** (atom-atom overlap-weighted NAO bond order).

5.3 The relationship between the clusters $[\text{Os}_3(\text{CO})_{11}\{(\text{C}=\text{O})(m\text{NHC})\}]$ (**33**) and $[\text{Os}_3(\text{CO})_{11}(m\text{NHC})]$ (**12'**)

The reaction in Scheme 5.3 is essentially one in which a carbonyl ligand of **5** has been substituted by an NHC leading to the formation of clusters **12** and/or **12'**. As has been suggested above, cluster **33** may be an intermediate in this substitution reaction. Several experiments were carried out to investigate this idea.

A solution of **33a'** in THF was monitored by ^1H NMR spectroscopy over time, with bubbling of Ar through the reaction mixture to remove any CO released. It was observed that **33a'** slowly converted to **12a'** over a period of four days (Figure 5.8). TLC separation of the final reaction mixture afforded **12a'** as the major product. In a Carius NMR tube, the conversion was very slow (see appendix Figure 5.8). The reaction of **5** with $t\text{Bu}$ (**2f**) was also followed by NMR spectroscopy (see appendix Figure 5.9), and similarly showed that the acyl species **33f'** and some other unknown species were formed upon mixing, and **33f'** converted slowly to **12f'**. Based on all these observations, we hypothesise that **33** is likely the precursor to **12'**; the formation of NHC mono-substituted products starts from initial attack by the NHC at the carbon atom of a carbonyl ligand to form the zwitterionic acyl intermediate **33**, rather than directly at an Os atom.

Figure 5.8. ^1H NMR spectra (δ 10.0 – 6.0 ppm region) of (a) **33a'** in acetone- d_6 , and after bubbling Ar for (b) one day, (c) four days, and (d) five days. ▲ denotes residual **33a'**; ● denotes resonances assignable to **12a'**.

Carbonyl substitution reactions may occur via one or more of several competing pathways, which have been proposed over the years, and they include:

1. Dissociation of CO as the rate-determining step.^{13,14,15,16} For the reaction of **5** with PPh_3 , for example, a simple dissociation process has been suggested.¹⁷ Many ligands (L) in six-coordinate metal carbonyl compounds are also capable of labilizing the metal center towards dissociative loss of CO, and most specifically to the cis position.¹⁸

M = metal complex
L = ligand

2. An associative process.¹⁹ The substitution reactions of $[\text{Ru}_5\text{C}(\text{CO})_{14}\text{L}]$ ($\text{L} = \text{P}(\text{OPh}_3)$ and PCy_3) with a series of P-donor nucleophiles have been shown to proceed by this pathway,²⁰ and the ability of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ to undergo addition reactions under mild conditions allows associative CO substitution via isolable intermediates of the type $[\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}]$ ($\text{L} = \text{CO}, \text{PMe}_2\text{Ph}, \text{PPh}_3$ or PhCN).²¹
3. Migration of a ligand, particularly of alkyl or hydrogen, to an adjacent CO, thus exposing a vacant coordination site at the metal center.²²
4. A radical chain pathway, in which the metal center is labilized towards substitution by a radical abstraction reaction at the metal center, e.g. abstraction of H from $[\text{ReH}(\text{CO})_5]$.²³
5. Heterolytic fission of a metal–metal bond to generate a saturated 18-electron, and a unsaturated 16-electron complex fragment, respectively, is considered to be the key initial step in the substitution reactions of clusters like $[\text{Ir}_4(\text{CO})_{12-n}\text{L}_n]$, $[\text{M}_3(\text{CO})_{12}]$ and $[(\text{CO})_4\text{Fe}(\mu\text{-AsMe}_2)\text{Co}(\text{CO})_3]$.^{24,25} The heterolytic fission step is independent of the incoming ligand.
6. Nucleophilic attack at the carbonyl carbon atom. This has been demonstrated in several different chemical situations, e.g., with Grignard reagents,²⁶ organolithium compounds,²⁷ methoxide,²⁸ and hydroxide,²⁹ the reaction between nucleophiles such as primary and secondary amines and OR^- with $[\text{FeCp}(\text{CO})_2\text{L}]$,³⁰ and in the activation of cyclopentadienyl ruthenium complexes by $^t\text{BuOK}$ in the racemization of alcohols.³¹ In many cases, the base interacts with the carbon atom of a metal carbonyl ligand to form a weak acid-base adduct. For instance, in a study of different base-catalyzed substitution reactions of $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, Morris and Basolo proposed that the base catalysts functioned by attacking the carbonyl carbon (hard) and not the metal (soft).³² Kaesz and co-workers also suggested that anionic nucleophiles attacked the complexes

$[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Os}, \text{Ru}$) at the carbon atom of a CO ligand to form $\eta^1\text{-C}(\text{O})\text{Nu}$ -substituted trinuclear anions (in which Nu is the nucleophile).³³ This pathway can be represented below but to the best of our knowledge, however, no intermediate has ever been isolated.

Scheme 5.4

This last reaction pathway proposed by Basolo and Morris,²¹ is essentially identical to our proposal that the formation of the substituted clusters $[\text{Os}_3(\text{CO})_{11}(\text{NHC})]$ may start from initial nucleophilic attack of the NHC at a carbonyl carbon rather than directly at an Os atom but with a small difference. In that version, the attack of base at a CO ligand to form the acyl labilised CO loss, and the resulting vacant coordination site was taken up by the incoming ligand. In our case, we believe that the same ligand (NHC) was involved in both the acyl formation and substitution steps; we have found that the NMR scale reaction of free IMes with **33a'** was very rapid and afforded a complex mixture which did not appear to contain any of **12** or **13a** (see appendix Figure 5.12). That Basolo's mechanism was also operative, however, would account for why cluster **33** was not reported by earlier workers; they had employed NHCs that were generated *in situ* and hence the reaction mixtures would have contained reagents such as KO^tBu , $^t\text{BuOH}$ and KCl in large quantities, which would have catalysed the carbonyl substitution.

That the free NHCs can give rise to mesoionic NHC complexes is well-established,²² and mesoionic imidazolin-4/5-ylidenes are also stronger σ -electron donors than normal NHCs and they tend to cleave from the metal more easily than normal imidazolin-2-ylidene.²³ A migratory deinsertion from **33a'** would afford **12a'**, and **12a** presumably resulted through a similar pathway via attack of the NHC as a normal carbene. The parent cluster **5** is known, from all indications, to be quite inert with respect to CO dissociation. Presumably, the migratory deinsertion step from **33** is aided by the presence of the acyl ligand, which labilizes a cis CO ligand towards dissociation.

Figure 5.9. Proposed mechanism for **33** to **12'**.

The proposed mechanism was also investigated computationally for the reaction $\mathbf{33} \rightarrow \mathbf{12'} + \text{CO}$, using simplified models of the complexes in which the substituents on the imidazole ring were replaced with H atoms. The potential energy surfaces were explored using DFT; the MPW1PW91 density functional, with the LANL2DZ basis set together with an f-type polarization function were employed for

the heavy atoms, and the 6-311+G(2d,p) basis set for the light atoms. The overall change in Gibbs free energy for the reaction was -144 kJ/mol (Figure 5.11).

The first step from **33** involves the elimination of one CO ligand to form intermediate **A**. Four alternative pathways for this step, and hence structures for **A**, were calculated (Figure 5.10):

- Elimination of the equatorial CO on the Os atom carrying the acyl to intermediate **A1** and CO;
- Elimination of an equatorial CO on an adjacent Os atom to intermediate **A2**;
- Elimination of an axial CO on the Os atom carrying the acyl to either **A3** or **A4** (the orientation of the acyl ligand breaks the symmetry of the Os₃ plane).

Figure 5.10. Relative energy profile and structures involved in the formation of **A** and CO from **33**.

The computed free energies suggest that the elimination of an axial CO ligand on the Os atom carrying the acyl ligand (to **A3** or **A4**) is the most favoured. From **A4**, migratory deinsertion would give rise to **12'**. We have located a transition state (**TS**)

for this deinsertion step, however, it also appeared to us that an isomerisation of **A4** into another intermediate **B** was required, in which **A4** undergoes ligand rearrangement that moves the acyl ligand to an axial position.

Figure 5.11. Computed changes in the relative free energy (in $\text{kJ}\cdot\text{mol}^{-1}$, with respect to **33**) for the reaction $33 \rightarrow 12' + \text{CO}$. Simplified models of the complexes, in which the N substituents were replaced with H atoms, were used.

The computationally optimized geometries of intermediates **A4** and **B**, and the transition state **TS**, are given in Figure 5.12. In going from **A4** to **B**, the NHC approached closer to the cluster; the metal-acyl-NHC bond angle becomes more acute ($\angle\text{Os1-C7-C16} = 124.6^\circ$ in **A4** vs 75.3° in **B**), and the metal...NHC distance decreases ($\text{Os1}\cdots\text{C16} = 3.078 \text{ \AA}$ in **A4** vs $2.221 \text{ \AA}$ in **B**). This is accompanied by a lengthening of the associated metal-metal bonds (Os1-Os3 and $\text{Os1-Os2} = 2.783 \text{ \AA}$ and $2.784 \text{ \AA}$ in **A4** vs $2.915 \text{ \AA}$ and $2.856 \text{ \AA}$ in **B**, respectively). From **B** to **TS**, the transition state which connects **B** to **12'**, the Os-Os bond lengths changed slightly but

the NHC-acyl bond is elongated by 0.16 Å. The acyl CO is on the way to become a carbonyl; the $\angle\text{Os1-C7-O7}$ increased from 155° in **B** to 163.7° in **TS**.

Figure 5.12. Computationally optimized geometry of (top to bottom): intermediates **A4** and **B**, and the transition state **TS**.

5.4 Reaction of free carbene with other transition metal carbonyl complexes

In view of the above proposed mechanism for NHC substitution in **5**, attempts were made at the generation of the acyl intermediate in some mononuclear carbonyl complexes. The reaction of $[\text{W}(\text{CO})_6]$ (**37**) with free carbene IMes afforded, after TLC separation, the substitution product $[\text{W}(\text{CO})_5(\text{IMes})]$ (**38a**). Complex **38a** has been characterized by a single crystal X-ray crystallographic study; an ORTEP diagram showing the molecular structure, together with selected bond parameters, is given in Figure 5.14. IR monitoring of the reaction did not provide unambiguous evidence for any intermediate or product with an acyl group as absorption peaks in the region between $1600\text{--}1400\text{ cm}^{-1}$ were very weak (Figure 5.13).

Figure 5.13. Reaction of **37** with IMes in THF monitored by IR over time. (blue color—6h; black color--1 day; red color--2 days; pink color--4 days).

Figure 5.14. ORTEP diagram of **38a**. Thermal ellipsoids are drawn at 50% probability level. Organic hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): W1-C1 2.038(2), W1-C2 1.986(2), W1-C3 2.047(3), W1-C4 2.048(2), W1-C5 2.051(2), W1-C6 2.254(2), C2-W1-C1 88.50(10), C2-W1-C5 92.98(10), C2-W1-C6 177.79(8).

A similar reaction of $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ with one equivalent of IMes was very rapid and afforded a dark red solution which, after stirring overnight, changed to an orange color. The IR spectrum of the reaction mixture showed CO stretches corresponding to the complex $[\text{Ir}(\text{CO})_2(\text{IMes})\text{Cl}]$ (**40**), and two weak peaks at 1917 and 1542 cm^{-1} . Complex **40** was isolated in 40% yield by column chromatography, together with some other unidentified species. Analogues of **40** with other NHC ligands have previously been reported.³⁴

To examine the analogous reactivity with other clusters, an NMR-scale reaction of IMes with one equivalent of the cluster $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$ (**12i**) in THF-d_8 was attempted. The crude ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed the presence of one major unknown product **C**. IR monitoring of the reaction did not provide unambiguous

evidence for any intermediate or product with an acyl group as absorption peaks in the region between 1600-1400 cm^{-1} were very weak. Unfortunately, repeated attempts to obtain crystals suitable for single crystal X-ray diffraction studies proved unsuccessful. Yellow cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\text{OP}(\text{OMe})_2]$ (**34**) was obtained in 14% yield after TLC separation. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **34** were different from that of the crude product **C**, which indicated that **34** may be a decomposition product from TLC.

The x-ray crystal structure of **34** is shown in Figure 5.15 and it shows that the phosphite ligand of **12i** has lost a methyl group to afford an $\text{OP}(\text{OMe})_2$ moiety; Pentaosmium clusters containing a bridging OPR_2 have been reported previously from the pyrolysis of $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$ at 210 $^\circ\text{C}$.³⁵

Figure 5.15. ORTEP diagrams of **34**. Thermal ellipsoids are drawn at 50% probability level. Organic hydrogens are omitted for clarity.

5.5 Conclusion

We have found that the direct reaction of the heavier group 8 trinuclear carbonyl clusters **5** with a free NHC proceeded via initial attack of the NHC at the carbonyl carbon. The intermediate acyl complex **33** so-formed turned out to be a sufficiently stable zwitterion, which was isolated and completely characterized. We also demonstrated that this intermediate subsequently loses a CO ligand, and showed computationally that a migratory deinsertion of the acyl ligand led to overall carbonyl substitution.

Attempts were also made at verifying the applicability of this mechanism to mononuclear carbonyl compounds. The reactions of IMes with $[\text{W}(\text{CO})_6]$ or $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ afforded the corresponding substitution products $[\text{W}(\text{CO})_5(\text{IMes})]$ and $[\text{Ir}(\text{CO})_2(\text{IMes})\text{Cl}]$, respectively; no unequivocal evidence for acyl intermediates was found. Extension of the reaction to the substituted cluster $[\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3]$ was found to lead to C–O bond cleavage to afford the novel cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\text{OP}(\text{OMe})_2]$.

5.6 Experimental

5.6.1 General procedures

General experimental procedures have been described in chapter 2. All the free carbene was stored and handled in Glovebox. Solvents were freshly distilled and stored in flask containing dried molecular sieves. General computational details were described in chapter 2. The MPW1PW91 density-functional was used, together with an “ultrafine” numerical integration grid. The LANL2DZ (Los Alamos Effective Core Potential Double- ζ) basis set together with an f-type polarisation function, was employed for the osmium atoms. For all the other atoms, the 6-311+G(2d, p) basis set

was used. Vibrational frequencies and the enthalpy (H) and Gibbs free energy (G) calculations of the systems were performed at 298.15 K and 1 atm pressure. All geometries were fully optimized and evaluated for the correct number of imaginary frequencies, and the nature of the transition states were clarified using the pseudo-intrinsic reaction coordinates (IRC) approach.³⁶ Single crystals of **33a'**, **33f'**, **12a'** and **13a** suitable for diffraction analysis were grown by slow evaporation from hexane/dichloromethane solutions at 4 °C, those of **33c'** were grown from ether/hexane. All crystal structure determinations were carried out by Dr Rakesh Ganguly.

5.6.2 Synthesis of $[\text{Os}_3(\text{CO})_{11}\{(\text{C}=\text{O})_m\text{NHC}\}]$ (**33**)

IMes (**2a**) (51 mg, 0.17 mmol) in dry THF (20 ml) was added dropwise to the mixture of **5** (100 mg, 0.11 mmol) in THF (5 ml) in glovebox. The mixture was stirred for around 20 h, the color changing from yellow to red-orange. Volatiles were removed under reduced pressure and the residue was redissolved in the minimum volume of DCM and transferred onto a low temperature (-15 °C) silica gel chromatographic column packed in hexane. Elution with hexane-THF (3:1, v/v) afforded **12a** (4%), **12a'** (6%), **13** (trace amount) as well as other minor products. Further elution of the column with hexane-THF (1:1, v/v) gave one red-orange band which contained **33a'** (39%). THF used should be freshly distilled and kept with dry molecular sieves, otherwise the yield of desired products may decrease.

2 d reaction of **5** (100 mg, 0.11 mmol) with **2c** (65 mg, 0.17 mmol) was carried out. Some unreacted **5** (50 mg) was observed. The solvent was removed on the vacuum line and the residue obtained was redissolved in the minimum volume of dichloromethane and transferred onto a low temperature (-15 °C) silica gel chromatographic column packed in hexane. Elution with hexane/dichloromethane (3/1,

v/v) afforded trace amount of yellow colour compound **12c** as well as **12c'** (5%). Further elution of the column with hexane-DCM (1:2, v/v) gave **33c'** (15%).

Compound **5** (50 mg, 0.055 mmol) and **2f** (15 mg, 0.083 mmol) were placed in an RBF followed by THF (10 ml). The mixture was stirred at room temperature for 1 d, during which the color changed from yellow to orange. The solvent was removed in vacuo and the residue was extracted with the minimum volume of DCM and TLC separation elution with hexane/dichloromethane (1/3, v/v) afforded two major bands: **12f'** ($R_f = 0.81$, 8 mg, 14%) and **33f'** ($R_f = 0.14$, 14 mg, 23%).

The analysis data of all the products were summarized in table 5.2.

5.6.3 NMR monitor of **33a'**

Compound **33a'** (50 mg) was dissolved in AR grade of THF (20 ml) with Ar bubbled through the solution. The reaction mixture was monitored by ^1H NMR over time. (During each NMR study, the solvent was removed and the residue was dissolved in acetone- d_6 , after NMR analysis, the D-solvent was removed and the residue was redissolved in 20 ml of THF). After 5 d, TLC separation afforded **12a'** (23 mg).

Compound **33a'** (30 mg) was dissolved in acetone- d_6 (0.5 ml) placed in a carius NMR tube and the reaction mixture was monitored by ^1H NMR studies overtime.

5.6.4 Reaction of **33a'** with **2a**

To a Carius NMR tube, **33a'** (30 mg, 0.025 mmol) and free IMes (8 mg, 0.025 mmol) were added, followed by THF- d_8 (0.75 ml). The reaction mixture was monitored by ^1H NMR studies overtime.

5.6.5 Reaction of IMes with $[\text{W}(\text{CO})_6]$

$[\text{W}(\text{CO})_6]$ (50 mg, 0.14 mmol) was added in THF (5 ml). **2a** (42 mg, 0.14 mmol) in THF (10 ml) was then added dropwise. The reaction was monitored by IR overtime. After stirring at room temperature for 4d, the solvent was removed on the vacuum line and the residue was recrystallized from hexane/DCM. The red-orange solid residue contained an unknown compound. IR (hex) ν_{CO} : 2058 w, 2041 w, 1995 w, 1938 m, 1912 s, 1878 m, 1854 m, 1826 w, 1955 w, 1705 m, 1692 m cm^{-1} . ^1H NMR (400 MHz, acetone- d_6): δ 8.26 (s, 2H, Im-H), 7.10 (s, 2H, Ph-H); 2.35 (s, 6H, CH_3), 2.21 (s, 12H, CH_3) ppm.

The supernatant was separated by TLC. Elution with hexane-DCM (3:1, v/v) afforded several bands, one of which was identified as $[\text{W}(\text{CO})_5(\text{IMes})]$. IR (DCM) ν_{CO} : 2059 m, 1962 w, 1919 s, 1894 sh cm^{-1} . ^1H NMR (400 MHz, acetone- d_6): δ 7.50 (s, 2H, Im-H), 7.01 (s, 4H, Ph-H); 2.34 (s, 6H, CH_3), 2.10 (s, 12H, CH_3) ppm.

5.6.6 Reaction of **2a** with $[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$

$[\text{Cp}^*\text{Ir}(\text{CO})\text{Cl}_2]$ (100 mg, 0.23 mmol) and **2a** (71 mg, 0.23 mmol) were added into THF (15 ml). The color changed to dark red immediately. After stirring at room temperature overnight, the color changed to orange. The solvent was removed on the vacuum line and the residue redissolved in the minimum volume of DCM for separation by column chromatography. Elution with hexane/DCM (1/1, v/v) afforded an orange band, IR spectrum (DCM) of which showed no CO stretches. Elution with hexane/dichloromethane (1/2, v/v) gave one major yellow band containing $[\text{Ir}(\text{CO})_2(\text{NHC})\text{Cl}]$ (54 mg, 40%). IR (DCM) ν_{CO} : 2066 s, 1980 s cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.11 (s, 2H, Im-H), 7.01 (s, 4H, Ph-H), 2.37 (s, 6H, CH_3), 2.22 (s, 12H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 180.2 (s), 168.5 (s), 176.2 (s), 139.6 (s, Ph-C), 135.3 (s, Ph-C), 134.9 (s, Ph-C), 129.4 (s, Ph-CH), 123.8 (NCHCH), 21.3 (s, CH_3),

18.6 (s, 12H, CH₃) ppm. HRMS-ESI: m/z 560.1119. Calculated for [Ir(CO)₂(NHC)Cl+H-CO]⁺, C₂₃H₂₄O₂¹⁹³Ir 560.1094.

5.6.7 Reaction of **2a** with [Os₃(CO)₁₁P(OMe)₃] (**12i**)

A Carious NMR tube fitted with a re-sealable valve was charged with **12i** (30 mg, 0.03 mmol), **2a** (10 mg, 0.03 mmol) and THF-d₈ (0.7 ml). There was an immediate darkening of the yellow coloured solution to yellow-orange. Some yellow precipitate was observed at the bottom of the NMR tube after several hours. The crude ¹H and ³¹P{¹H} NMR remains unchanged over 4 d. It showed the presence of **12i** and one major unknown product **C**. Data for **C**: ¹H NMR (400 MHz, THF-d₈): δ 8.15 (s, 2H), 7.20 (s, 4H), 3.27 (d, 6H), 2.38 (s, 6H), 2.25 (s, 2H), 2.13 (s, 12H) ppm. ³¹P{¹H} NMR (THF-d₈): δ 49.6. ESI-MS⁺: m/z 1181.30, 932.8, 906.9. IR ν_{co} (THF): 2096 w, 2073 w, 2036 s, 2022 s, 2004 s, 1972 m, 1958 m, 1934 w, 1779 vw cm⁻¹.

[Os₃(μ-H)(CO)₁₀OP(OMe)₂] (**34**) was obtained in 14% yield after TLC separation. IR (DCM) ν_{co}: 2113 w, 2072 s, 2063 m, 2031 s, 2021 m, 2006 m, 1984 m cm⁻¹. ¹H NMR (400 MHz, C₆D₆): δ 3.09 (d, *J* = 4 Hz, CH₃), 3.06 (d, *J* = 4 Hz, CH₃), -15.59 (d, *J* = 12 Hz, hydride) ppm. ³¹P{¹H} NMR (C₆D₆): δ 52.26 ppm. ESI-MS⁺: m/z 932.86.

Table 5-2. NMR and MS data for **33**.

Cluster	^1H NMR (THF- d_8) δ	$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ	ESI-MS $^+$: m/z
33a'	(RT): 9.00 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, NCHN), 8.27 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, CCHN); 7.19 (s, 2H, Ph-H), 7.00 (s, 2H, Ph-H), 2.38 (s, 3H, CH ₃), 2.32 (s, 3H, CH ₃), 2.24 (s, 6H, CH ₃), 2.05 (s, 6H, CH ₃). (acetone- d_6): 9.22 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, NCHN), 8.43 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, CCHN); 7.21 (s, 2H, Ph-H), 7.02 (s, 2H, Ph-H), 2.40 (s, 3H, CH ₃), 2.33 (s, 3H, CH ₃), 2.29 (s, 6H, CH ₃), 2.09 (s, 6H, CH ₃)	(-30 °C): 203.9 (s, acyl-CO-), 148.4 (s, NCCH); 142.0 (s, Ph-C), 140.3 (s, Ph-C), 139.0 (s, NCHN), 135.4 (s, Ph-C), 134.5 (s, Ph-C), 133.0 (s, Ph-C), 132.1 (s, Ph-C), 130.2 (s, Ph-CH), 129.6 (s, Ph-CH), 129.3 (s, NCCHC) 21.0 (s, CH ₃), 21.0 (s, CH ₃), 17.7 (s, CH ₃), 17.3 (s, CH ₃)	1214 [M] $^+$ 1186 [M-CO] $^+$
33c'	(acetone- d_6 , RT): 9.58 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, NCHN), 8.74 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, CCHN); 7.71 (m, 2H, Ph-H), 7.54 (d, $^2J_{\text{H-H}} = 8$ Hz, 2H, Ph-H), 7.38 (d, $^2J_{\text{H-H}} = 8$ Hz, 2H, Ph-H), 2.63 (m, 2H, CH), 2.44 (m, 2H, CH), 1.34 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH ₃), 1.26 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH ₃), 1.19 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CH ₃)	--	HRMS-ESI m/z calculated for 3b , C ₃₉ H ₃₇ N ₂ O ₁₂ ¹⁸⁸ Os ¹⁹⁰ O s ¹⁹² Os [M+H] $^+$ 1295.1194, found 1265.1104
33f'	(THF- d_8 , -30 °C): 8.62 (d, $^4J_{\text{H-H}} = 2$ Hz, 1H, NCHN), 7.84 (d, $^4J_{\text{H-H}} = 2$ Hz, 1H, CCHN), 1.71 (s, 18H, CH ₃) (acetone- d_6 , RT): 8.90 (d, $^4J_{\text{H-H}} = 2$ Hz, 1H, NCHN), 7.87 (d, $^4J_{\text{H-H}} = 2$ Hz, 1H, CCHN), 1.78 (s, 9H, CH ₃), 1.75 (s, 9H, CH ₃)	(-30 °C): 212.6 (s, C=O), 153.1 (s, Im-C), 132.3 (s, Im-C), 123.6 (s, Im-C), 63.3 (s, C(CH ₃) ₃), 60.7 (s, C(CH ₃) ₃), 29.9 (s, CH ₃), 29.0 (s, CH ₃)	1087 [M] $^+$, 1059 [M-CO] $^+$, 1033 [M-2CO] $^+$

Table 5-3. Infrared and analytical data for **12**, **12'**, **13** and **33**.

Cluster	IR (DCM) $\nu(\text{CO})$ (cm^{-1})	Elemental Analysis (%) Found (Calculated)
12a	2104w, 2048m, 2025m, 2015s, 1990w, 1975w, 1963w, 1949w	$\text{C}_{32}\text{H}_{24}\text{O}_{11}\text{N}_2\text{Os}_3$: C, 32.48 (32.67); H, 2.04 (2.07); N, 2.37 (2.38)
12a'	2097w, 2040m, 2020m, 2005s, 1972m, 1961m, 1942m	$\text{C}_{32}\text{H}_{24}\text{O}_{11}\text{N}_2\text{Os}_3$: C, 32.48 (32.86); H, 2.04 (2.40); N, 2.37 (2.41)
13a	(hexane): 2080w, 2019m, 2003s, 1996vs, 1951m, 1934w, 1916w	$\text{C}_{52}\text{H}_{48}\text{O}_{10}\text{N}_4\text{Os}_3$: C, 42.79 (42.83); H, 3.31(3.23); N, 3.84 (3.80)
33a'	2097w, 2039s, 2020s, 2002vs, 1973s, 1958m, br, 1926w; $\nu(\text{C=O})$ 1578w, 1531w; $\nu(\text{imidazole})$ 1607w, 1556w, 1481w IR (KBr) 2097m, 2033vs, 2011vs, 1996vs, 1975s, 1960s, 1954s, 1940m, 1918m; $\nu(\text{C=O})$ 1575w, 1530w; $\nu(\text{imidazole})$ 1609w, 1561w, 1480w	33a .THF: C, 34.63 (34.71); H, 2.51 (2.89); N, 2.18 (2.16)
12c	2105w, 2050m, 2027m, 2017s, 1992w, 1979w, 1968w, 1946w.	--
12c'	2097w, 2068w, 2039s, 2019s, 2004vs, 1973m, 1961m, 1940w	--
33c'	2096w, 2068w, 2039s, 2017s, 2002vs, 1973m, 1958m, 1932w, 1924w; $\nu(\text{C=O})$ 1575w, 1530w; $\nu(\text{imidazole})$ 1605w, 1555w, 1467w	--
33f'	2097w, 2068m, 2038s, 2022s, 2003vs, 1972m, 1958m, 1928w; $\nu(\text{C=O})$ 1557w, br; $\nu(\text{imidiazole})$ 1605w, 1524w	$\text{Os}_3\text{C}_{23}\text{H}_{20}\text{O}_{12}\text{N}_2\cdot\text{CH}_2\text{Cl}_2$: C, 24.60 (24.75); H, 1.89 (2.19); N, 2.39 (2.45)

Table 5-4. NMR and MS data for **12**, **12'** and **13**.

Cluster	^1H NMR (CDCl_3): δ	$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ	ESI-MS $^+$:m/z
12a	7.04 (s, 4H, Ph-H), 6.92 (s, 2H, Im-H); 2.37 (s, 6H, CH_3), 2.13 (s, 12H, CH_3) (THF- d_8) 7.27 (s, 2H, Im-H), 7.07 (s, 4H, Ph-H), 2.34 (s, 6H, CH_3), 2.15 (s, 12H, CH_3)	157.6 (s, NCN), 140.8 (s, Ph-C), 137.0 (s, Ph-C), 136.4 (s Ph-C), 129.9 (s, Ph-CH), 123.7 (s, NCHCH), 21.4 (s, CH_3), 18.5 (s, CH_3).	1186 [M] $^+$
12a'	7.86 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, NCHN), 7.08 (s, 2H, Ph-H), 7.03 (s, 2H, Ph-H), 6.72 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, CCHN), 2.38 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.12 (s, 6H, CH_3), 2.10 (s, 6H, CH_3). (THF- d_8) 8.78 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, NCHN), 7.13 (s, 2H, Ph-H), 7.10 (s, 2H, Ph-H), 6.83 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, CCHN), 2.36 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.16 (s, 6H, CH_3), 2.13 (s, 6H, CH_3)	(THF- d_8):141.1 (s, Ph-C), 140.9 (s, Ph-C), 137.5 (s, Ph-C), 136.3 (s, Ph-C), 135.5 (s, Ph-C), 135.1 (s, NCHC), 134.4 (s, NCHN), 132.5 (s, Ph-C), 130.1 (s, Ph-CH), 130.0 (s, Ph-CH), 122.9 (s, NCHCH), 21.0 (s, CH_3), 20.8 (s, CH_3), 18.1 (s, CH_3), 17.0 (s, CH_3)	1186 [M] $^+$
13a	6.93 (s, br, 4H, Ph-H), 6.81 (s, 2H, Im-H); 2.34 (s, 6H, CH_3), 2.07 (s, 12H, CH_3)	159.2 (s, NCN), 139.8 (s, Ph-C), 137.4 (s, Ph-C), 136.5 (s, Ph-C), 129.5 (s, Ph-C), 123.3 (s, NCHCH), 21.4 (s, CH_3), 18.7 (s, CH_3)	1461 [M] $^+$
12c	7.53 (m, 2H, Ph-H), 7.35 (m, 4H, Ph-H), 6.97 (s, Im-H), 2.76 (m, 4H, CH), 1.42 (d, $^3J_{\text{H-H}}=6.8$ Hz, 12H, CH_3), 1.10 (d, $^3J_{\text{H-H}}=6.8$ Hz, 12H, CH_3)	---	1268 [M] $^+$
12c'	8.00 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, NCHN), 7.55 (m, 2H, Ph-H), 7.39 (d, $^3J_{\text{H-H}}=8$ Hz, 2H, Ph-H), 7.32 (d, $^3J_{\text{H-H}}=8$ Hz, 2H, Ph-H), 6.72 (d, $^4J_{\text{H-H}}=1.6$ Hz, 1H, CCHN); 2.64 (m, 2H, CH), 2.48 (m, 2H, CH), 1.43 (d, $^3J_{\text{H-H}}=6.8$ Hz, 6H, CH_3), 1.24 (d, $^3J_{\text{H-H}}=6.8$ Hz, 6H, CH_3), 1.19 (d, $^3J_{\text{H-H}}=6.8$ Hz, 6H, CH_3), 1.09 (d, $^3J_{\text{H-H}}=6.8$ Hz, 6H, CH_3).	46.3 (s, Ph-C), 145.7 (s, Ph-C), 136.1 (s, NCHC), 135.2 (s, NCHN), 134.2 (s, NCHCH), 131.6 (s, Ph-CH), 131.5 (s, Ph-CH), 130.3 (s, Ph-C), 126.4 (s, Ph-C), 124.8 (Ph-CH), 124.6 (s, Ph-CH), 28.9 (s, isopropyl-CH), 28.9 (s, isopropyl-CH), 26.7 (s, CH_3), 24.7 (s, CH_3), 24.4 (s, CH_3), 22.5 (s, CH_3).	1269 [M] $^+$

Table 5-5. Crystal data for **33a'**, **33c'**, **33f'**, **12a'**, **13a**, **38a** and **34**.

Compound	33a'	33c'	33f'
Formula	C ₃₃ H ₂₄ N ₂ O ₁₂ Os ₃ .CH ₂ Cl ₂	C ₃₉ H ₃₆ N ₂ O ₁₂ Os ₃ .0.4C ₆ H ₁₄	C ₂₃ H ₂₀ N ₂ O ₁₂ Os ₃
Fw	1211.24	1295.41	1087.01
Temperature (K)	103(2)	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a (Å)	12.1138(7)	11.7927(4)	9.9266(4)
b (Å)	16.3659(10)	18.8187(7)	22.0281(10)
c (Å)	19.7503(13)	20.5674(7)	13.0871(6)
α(°)	90	90	90
β(°)	102.654(3)	91.0210(10)	97.8530(10)
γ(°)	90	90	90
Volume (Å ³)	3820.5(4)	4563.7(3)	2834.8(2)
Z	4	4	4
Density (mg•m ⁻³)	2.253	1.935	2.547
Absorption coefficient, mm ⁻¹	10.155	8.391	13.476
F(000)	2408	2512	1984
Crystal size (mm ³)	0.34×0.32×0.26	0.28×0.28×0.12	0.08×0.08×0.16
Reflections collected	89625	109455	34368
Independent reflections (R _{int})	7817	9334	8931
	[R(int) = 0.0927]	[R(int) = 0.0929]	[R(int) = 0.0570]
Max. and min. transmission	0.1777 and 0.1297	0.4325 and 0.2022	0.4119 and 0.2217
Data/restraints/parameters	7817/0/484	9334/0/541	8931/0/367
Goodness-of-fit on F ²	1.092	1.119	1.115
Final R indices [I>2σ(I)]	R1 = 0.0315	R1 = 0.0314	R1 = 0.0315
	wR2 = 0.0797	wR2 = 0.0813	wR2 = 0.0730
R indices (all data)	R1 = 0.0412	R1 = 0.0486	R1 = 0.0474
	wR2 = 0.0839	wR2 = 0.1034	wR2 = 0.0948
Largest diff. peak and hole (e Å ⁻³)	2.202 and -2.092	1.310 and -2.155	1.851 and -2.729

Compound	12a'	13a	38a	34
Formula	C ₃₂ H ₂₄ N ₂ O ₁₁ Os ₃	C ₅₂ H ₄₈ N ₄ O ₁₀ Os ₃	C ₂₆ H ₂₄ N ₂ O ₅ W	C ₁₂ H ₇ O ₁₃ Os ₃ P
Fw	1183.13	1459.54	628.32	906.75
Temperature (K)	103(2)	103(2)	103(2)	103(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	Pbca	P $\bar{1}$	P 1 2 ₁ /c 1	P2 ₁ /c
a (Å)	19.8355(13)	12.6378(4)	11.5953	16.9654(8)
b (Å)	16.6866(11)	13.3713(4)	15.3474(9)	7.8758(4)
c (Å)	21.0956(10)	16.5127(5)	14.3173(8)	29.3341(15)
α (°)	90	79.961(2)	90	90
β (°)	90	85.802(2)	95.9672(13)	96.164(3)
γ (°)	90	64.687(2)	90	90
Volume (Å ³)	6982.4(7)	2483.84(13)	2534.1(3)	3896.8(3)
Z	8	2	4	4
Density (mg•m ⁻³)	2.251	1.952	1.647	3.272
Absorption coefficient, mm ⁻¹	10.951	7.716	4.596	19.662
F(000)	4368	1392	1232	3408
Crystal size (mm ³)	0.12×0.10×0.10	0.30×0.24×0.18	0.200×0.200×0.320	0.240×0.080×0.020
Reflections collected	80600	57563	45548	6759
Independent reflections (R _{int})	7148	10125	8168	6759
	[R(int) = 0.1054]	[R(int) = 0.0456]	[R(int) = 0.0386]	[R(int) = 0.0000]
Max. and min. transmission	0.4072 and 0.3532	0.3372 and 0.2055	0.4600 and 0.3210	0.69 and 0.30
Data/restraints/parameters	7147/0/439	10125/0/634	8168/0/313	6759/444/527
Goodness-of-fit on F ²	1.081	1.177	1.037	1.265
Final R indices [I>2 σ (I)]	R1 = 0.0318	R1 = 0.0232	R1 = 0.0229	R1 = 0.0666
	wR2 = 0.0754	wR2 = 0.0608	wR2 = 0.0494	wR2 = 0.1528
R indices (all data)	R1 = 0.0481	R1 = 0.0291	R1 = 0.0310	R1 = 0.0847
	wR2 = 0.0959	wR2 = 0.0729	wR2 = 0.0526	wR2 = 0.1646
Largest diff. peak and hole (e Å ⁻³)	1.600 and -1.689	0.928 and -1.185	1.213 and -1.306	4.138 and -3.818

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Chapter 6 Overall Conclusion

As set out in chapter 1, the primary aim of this project was to investigate the reactivity of N-heterocyclic carbene complexes of Pd/Pt with osmium, ruthenium or iridium carbonyl clusters as a new synthetic methodology towards heterometallic clusters containing these metals.

The very electron-rich $[M(\text{NHC})]$ ($M = \text{Pd}$ or Pt) fragment could be generated *in situ* either from $[M(\text{NHC})_2]$, or more conveniently, from $[M\text{Cl}(\text{allyl})(\text{NHC})]$ ($M = \text{Pd}$, **3** or Pt , **3'**) and KO^tBu in IPA or DCM, and added across the Os-Os bonds of $[\text{Os}_3(\text{CO})_{12}]$ (**5**) under mild conditions to afford heterometallic clusters of formulae $[\text{MOs}_3(\text{CO})_{12}(\text{NHC})]$, $[\text{MOs}_3(\text{CO})_{12}(\text{NHC})_2]$, $[\text{M}_2\text{Os}_3(\text{CO})_{12}(\text{NHC})_2]$ and $[\text{M}_3\text{Os}_3(\text{CO})_{12}(\text{NHC})_3]$ ($M = \text{Pd}$, **6-9**; $M = \text{Pt}$, **6'-8'**). Similar reactions with the iridium cluster $[\text{Ir}_4(\text{CO})_{12}]$ (**25**) afforded the new heterometallic clusters $[\text{PdIr}_4(\text{CO})_{12}(\text{NHC})]$ and $[\text{M}_2\text{Ir}_4(\text{CO})_{12}(\text{NHC})_2]$ ($M = \text{Pd}$, Pt) (Scheme 6.1).

As the reaction time, or amount of **3** or **3'** relative to **5**, was increased the reaction favored the formation of **8**(') over **6**(') and **7**('). This suggested that the clusters could be viewed as built up by the sequential addition of an $[M(\text{NHC})]$ unit across one to three Os–Os bonds. This was also supported by their close structural similarities; with the exception of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{SIPr})_2]$ (**7d**), the metal cores comprised a triangular arrangement of three Os atoms, with M atoms bridging the Os–Os edges. The Os_3M_n planes in these clusters were fairly planar, in contrast to the phosphine analogues such as $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{PP}^t\text{Bu}_3)_2]$, in which the Pd atoms were significantly off the Os_3 plane. All the M-bridged Os–Os bonds were significantly longer than the unbridged Os–Os bonds, pointing to loss of electron density from the Os–Os bonds to the $[M(\text{NHC})]$. Each of the Os–M bond was, in turn, bridged by a carbonyl ligand. This was again in contrast to the phosphine analogues, in which only

one of the two Pd-Os bonds of each $[\text{Pd}(\text{PR}_3)]$ group had a bridging CO ligand, and most probably reflected the greater electron donor ability of the NHCs; the presence of bridging CO ligands enabled additional electron density from the $[\text{Pd}(\text{NHC})]$ to be delocalized away from the metal core (Scheme 6.1).

Scheme 6.1 Reaction of $[\text{M}(\text{NHC})]$ with $[\text{Os}_3(\text{CO})_{12}]$ and $[\text{Ir}_4(\text{CO})_{12}]$.

The structure of **7d** was unique in that one of the [Pd(NHC)] fragments adopted a spike position on the triosmium core. A computational study using density functional theory (DFT) on **7c** and **7d**, with NHC = IPr and SIPr, respectively, indicated that the “spike” structure should be thermodynamically more stable (lower Gibbs’ free energy) than the planar structure, although the energy difference was small. The charge distribution was also the same for both structures. These implied that both structures could exist in solution, although their VT ^1H NMR spectra showed only one set of NHC resonances over the temperature range from $-80\text{ }^\circ\text{C}$ to room temperature. Similarly, the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of **7’c** and **7’d** showed only one signal each over that same temperature range. The VT $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7** and **7’**, on the other hand, pointed to fluxionality of the carbonyl ligands (most likely via a “merry-go-round” exchange mechanism), although it was found that the Pd analogues were more highly fluxional than the corresponding Pt compounds. In addition, the latter also exhibited restricted rotation of the phenyl rings about the N–C_{ipso} bond at very low temperatures (Figure 6.1).

There were also evidence which suggested that the [Pd(NHC)] unit, especially, could rapidly detach and re-attach itself to the precursor cluster. The cluster **6a**, for example, was found to be unstable and decomposed readily upon heating. At room temperature, it reacted rapidly with PPh_3 to afford the substituted triosmium clusters $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)]$, $[\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2]$ and $[\text{Os}_3(\text{CO})_{11}(\text{IMes})]$, as well as some other unknown products. Similarly, the clusters $[\text{PdIr}_4(\text{CO})_{12}(\text{NHC})]$ (**26**) and $[\text{Pd}_2\text{Ir}_4(\text{CO})_{12}(\text{NHC})_2]$ appeared to interconvert in solution, together with precipitation of a small amount of yellow **25**.

Figure 6.1. “Merry-go-round” routes for CO exchange, and restricted rotation of the phenyl rings, in clusters **7**.

We believe that the formation of these clusters involved initial attack by the [M(NHC)] group at the carbon atom of a carbonyl ligand, rather than at a metal atom or a metal–metal bond. This proposal was made on the basis of our observation that direct reaction of **5** with a free NHC afforded $[\text{Os}_3(\text{CO})_{11}\{(\text{C}=\text{O})m\text{NHC}\}]$ (**33**), which was isolated and crystallographically characterized. Cluster **33** slowly lost a CO ligand to form $[\text{Os}_3(\text{CO})_{11}(m\text{IMes})]$ (**12'**), via migratory deinsertion of the acyl ligand. The identification of **33** and its subsequent transformation to **12'** suggested that initial attack of the NHC was at the carbonyl carbon; this pathway was supported by a computational study (Scheme 6.2).

Scheme 6.2. Proposed mechanism for the initial attack by nucleophile at the carbon atom of a carbonyl ligand.

That a similar reaction pathway was followed by the $[M(NHC)]$ fragment in the formation of the heterometallic clusters was also supported by natural bond orbital (NBO) analyses on **6c** and **6d**, which showed that their osmium metal cores carried a negative charge, while the carbonyl carbons were positively charged. The proposal was also consistent with the observation that the electron-rich $[Pd(NHC)]$ fragment reacted readily with the clusters $[Os_3(CO)_{11}(ACN)]$, $[Os_3(CO)_{11}(IMes)]$, $[Os_3(CO)_{11}P(OMe)_3]$ and $[Os_3(CO)_{10}(ACN)_2]$, but not with the more electron-rich, disubstituted clusters $[Os_3(CO)_{10}L_2]$ ($L = P(OMe)_3$ or $IMes$).