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UNIVERSITY**

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SYNTHESIS OF NHC-CONTAINING
HETEROMETALLIC CARBONYL
CLUSTERS AND THEIR APPLICATION AS
HETEROGENEOUS OXIDATION
CATALYSTS

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School of Physical and Mathematical Sciences

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Abstract

The reaction of N-heterocyclic carbene (NHC) derivatives of platinum or gold with ruthenium or cobalt carbonyl clusters gave various combinations of heterometallic NHC-containing Ru_xPt_y , Ru_xAu_y and Co_xPt_y clusters. The methodologies employed for syntheses of such heteronuclear clusters allowed good control of bimetallic ratios. These clusters were used as single-source precursors for the preparation of catalysts upon deposition onto titanium dioxide. Their catalytic potential for the selective oxidation of alcohol to benzaldehyde were explored. Aspects such as the cluster-to-nanoparticle transformation, bimetallic alloying effects, surface chemical states and nanoparticle sizes, were studied.

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Abbreviations

DCM	Dichloromethane
DFT	Density functional theory
DRIFTS	Diffused reflectance infrared fourier transform spectroscopy
EDX	Energy dispersive X-ray
ESI	Electrospray ionization
FID	Flame Ionization Absorption
FTIR	Fourier transform infrared
GC	Gas chromatography
HRTEM	High resolution transmission electron microscopy
IMes	<i>N,N'</i> -bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
IPA	Isopropyl alcohol
IPr	<i>N,N'</i> -bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
LCMS	Liquid chromatography-mass spectroscopy
<i>m/z</i>	Mass-to-charge ratio
<i>m</i> NHC	Abnormally bound N-heterocyclic carbene
MS	Mass spectrometry
NBO	Natural bond orbital
NHC	N-Heterocyclic carbene
NMR	Nuclear magnetic resonance
ppm	Parts per million
<i>R_f</i>	Retention factor
RT	Room temperature
SEM	Scanning Electron Microscopy
TGA	Thermo-Gravimetric Analysis
TLC	Thin layer chromatography
TOF	Time of flight
XPS	X-ray Photoelectron Spectroscopy

Infrared (IR) spectroscopy

<i>ν</i> CO	Stretching frequency in the carbonyl region (1800-2200 cm ⁻¹)
<i>vw</i>	Very weak
<i>w</i>	Weak
<i>m</i>	Medium
<i>s</i>	Strong
<i>vs</i>	Very strong
<i>br</i>	Broad
<i>sh</i>	Shoulder

Nuclear magnetic resonance (NMR) spectroscopy

δ	Chemical shift
<i>J</i>	Coupling constant
<i>s</i>	Singlet
<i>d</i>	doublet
<i>t</i>	Triplet
<i>m</i>	Multiplet
VT	Variable temperature

Molecular Numbering Scheme

Cluster	Molecular Formula	Molecular Structure
1	$\text{Ru}_3(\text{CO})_{12}$
2	$\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$
3	$\text{Ru}_6(\mu_3\text{-H})_2(\text{CO})_{18}$
4	$\text{Pt}(\text{IPr})(\text{C}_4\text{H}_7)\text{Cl}$	<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin: 0 10px;">where IPr =</div> </div>
5	$\text{Ru}_3\text{Pt}_2(\text{L})_2(\mu\text{-CO})_4(\text{CO})_8$ L = IPr (a), IMes (b)

6

7

8a

8b

8c

33b **34a** **34b** **35a** **35b** **36**

—

Scheme 1.1

Heteronuclear carbonyl clusters are also of interest as the presence of polarized metal-metal bonds can stabilize structures that are otherwise unstable in their monometallic states. For example, tetracobalt and pentacobalt carbido carbonyl clusters such as $[\text{Co}_5\text{C}(\text{CO})_{12}]^-$, $[\text{Co}_5\text{C}(\text{CO})_{11}]^{3-}$ and $[\text{Co}_4\text{C}(\text{CO})_{10}]^{2-}$ are unknown, but they can be stabilized by adding $[\text{Au}(\text{PPh}_3)]^+$ fragments to the known hexacobalt cluster $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ to give isolable Co_4Au and Co_5Au clusters (Scheme 1.2).²⁻⁴

Scheme 1.2

1.2 Synthetic strategies to heteronuclear carbonyl clusters

Various synthetic methods have been developed for heteronuclear carbonyl clusters. This includes condensation, addition and redox condensation reactions.

1.2.1 Condensation reactions

Thermal condensation between small clusters, either through pyrolysis or thermolysis, gives clusters of higher nuclearity. The metal-metal bond formation is driven by loss of ligands. The condensation of two compounds, each having weakly coordinating ligands that could be readily lost during reaction, allows the formation of mixed-metal bonds. For example, the reaction of $\text{Pt}(\text{COD})_2$ with osmium carbonyl clusters containing acetonitrile ligands gave heteronuclear Os-Pt clusters (Scheme 1.3).^{5,6}

Scheme 1.3

The formation of mixed metal-metal bonds can also occur due to the thermal elimination of CO. The loss of CO acts as a driving force for the reaction. For example, $\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{13}$ reacts with $\text{Ru}_4\text{Pt}_2(\text{CO})_{18}$ to form the decanuclear cluster $\text{Ru}_8\text{Pt}_2(\mu_3\text{-H})_2(\text{CO})_{23}$ with the elimination of CO ligands (Scheme 1.4).⁷

Scheme 1.4

However, condensation reactions that involve the exact sum of the metal compositions of the precursors are exceedingly rare. More often than not, thermolysis and pyrolysis reactions involve both cluster fragmentation and re-condensation processes to give multiple products. Thus, the heteronuclear cluster of a desired ratio would likely be obtained in low yield.

1.2.2 Addition reactions

Some clusters 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. The addition of the nucleophilic mononuclear metal fragment $[M(P^tBu_3)_2]$ (where $M = Pt$ or Pd), which can lose one of its phosphine ligands readily in solution to give $[M(P^tBu_3)]$, across the metal-metal bonds of various metal carbonyl clusters give a variety of phosphine-containing heteronuclear carbonyl clusters.⁸⁻¹⁷ For example, $[Re_2(CO)_8(\mu-SnPh_2)_2M_2(P^tBu_3)_2]$ can be obtained by reacting $[Re_2(CO)_8(\mu-SnPh_2)_2]$ with $[M(P^tBu_3)_2]$ (Scheme 1.5).¹³

Scheme 1.5

Stepwise addition of $[M(P^tBu_3)]$ fragments onto carbonyl clusters can also occur. For example, the addition of $[Pt(P^tBu_3)_2]$ across Os-Os bonds of $Os_3(CO)_12$ gave mono-, bis- and tris- $[Pt(P^tBu_3)]$ adducts. Although the three addition products are isolable, they exist in equilibrium in solution (Scheme 1.6).¹⁵

Scheme 1.6

This synthetic methodology can be coupled with a thermal condensation reaction where the main cluster framework rearranges into higher nuclearity, stabilised by the mononuclear fragments. For example, $Ir_4(CO)_{12}$ reacts with excess $[Pt(P^tBu_3)_2]$ to give $Ir_4(CO)_{12}[Pt(P^tBu_3)_2]$ at room temperature, while the same reaction carried out in refluxing toluene gives the higher nuclearity complexes $Ir_8(CO)_{12}[Pt(P^tBu_3)]_4$ and $Ir_6(CO)_{10}[Pt(P^tBu_3)]_4$ (Scheme 1.7).¹⁷

Scheme 1.7

Thus, an advantage of this synthetic methodology is that it provides good control of the bimetallic ratio, enabling the stepwise addition of metal fragments onto neutral carbonyl clusters. However, a drawback is that the number of metal fragments that can be added onto the carbonyl clusters is limited. Moreover, some of the addition products may exist as an equilibrium in solution, making isolation more challenging.

1.2.3 Redox condensation reactions

Redox condensation involves reaction between two complexes of different metals with different oxidation states to give clusters of higher nuclearity.

Neutral clusters such as $M_3(CO)_{12}$ ($M = Fe, Ru, Os$) react with the mononuclear anionic fragments $[M'(CO)_4]^-$ ($M' = Co, Rh, Ir$) to give $[M_3M'(CO)_{13}]^-$ clusters (Scheme 1.8).¹⁸

Scheme 1.8

Anionic clusters can be coupled with mononuclear cationic fragments to form neutral clusters or anionic clusters, depending on the magnitude of the charges. The coupling of anionic carbonyl clusters with cationic fragments of the same charge form neutral clusters whereas anionic clusters can be obtained if the opposite charges are different. For example, $[Os_3(\mu_2-H)(CO)_{11}]^-$ can be coupled with $[Rh(COD)_2]^+$ to yield an Os-Rh cluster $Os_3Rh(\mu_2-H)_3(CO)_{10}(COD)$ (Scheme 1.9),¹⁹ while the reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with $[AuPPh_3]^+$ gave the anionic Os-Au cluster $[Os_{10}C(CO)_{24}Au(PPh_3)]^-$ (Scheme 1.10).^{20,21}

Scheme 1.9

Scheme 1.10

High nuclearity anionic clusters can be achieved by thermal redox condensation of ionic complexes with opposite charges. For example, reflux of the cluster $[\text{HRu}_6(\text{CO})_{18}]^-$ with the mononuclear cationic $[\text{Cu}(\text{MeCN})_4]^+$ fragment in MeCN gave the Ru-Cu cluster $[\text{H}_2\text{Ru}_{12}\text{Cu}_6\text{Cl}_2(\text{CO})_{34}]^{2-}$ (Scheme 1.11).²²

Scheme 1.11

Monometallic anionic clusters can also undergo redox condensation reaction with neutral or anionic clusters to form higher nuclearity anionic clusters. The reaction of $\text{Co}_3(\text{CO})_9\text{CCl}$ and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ afforded $[\text{Co}_6\text{Ni}_2\text{C}_2(\text{CO})_{12}]^{2-}$ (Scheme 1.12),²³ while the reaction of

$[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ afforded $[\text{Rh}_5\text{Pt}(\text{CO})_{15}]^-$. The synthesis of $[\text{Rh}_5\text{Pt}(\text{CO})_{15}]^-$ could be simplified by redox condensation of the monometallic salts in the presence of CO (Scheme 1.13).²⁴

Scheme 1.12

Scheme 1.13

Redox condensation is of greater potential for the synthesis of heteronuclear carbonyl clusters due to the fact that a large number of neutral and anionic carbonyl clusters are known. However, there is less control over the bimetallic ratio as the heteronuclear product often bears an unexpected metal composition from its monometallic precursors.

1.3 Heteronuclear carbonyl clusters as precursors of heterogeneous catalysts

Organometallic carbonyl clusters have been used as precursors for the preparation of metallic nanoparticles.²⁵ The metal carbonyl clusters are first adsorbed onto a porous material support such as an inorganic oxide via interaction between the carbonyl ligands and the hydroxyl groups present on the surface.^{26,27} This typically involves making a slurry

of the organometallic cluster with a solvent. Upon removal of the solvent, the support with the clusters anchored, is subjected to thermolysis to remove the ligand shell of the supported organometallic cluster, resulting in nano-sized metallic particles (Figure 1.2).²⁸ Bartholomew and co-workers prepared iron nanoparticles from the reduction of alumina-supported $\text{Fe}(\text{CO})_5$ under H_2 at 300-350 °C. These nanoparticles showed great improvement in metal dispersion and reduction compared to salt-derived nanoparticles, which can be accounted for by the sheath of carbonyl ligands.²⁹

Figure 1.2. (a) Cluster migration into pores of the support. (b) Cluster anchoring onto the walls. (c) Removal of ligands by thermolysis to yield denuded metal nanoparticles.³⁰

The deposition of heteronuclear carbonyl clusters onto inorganic supports as bi- or multi-heterometallic nanoparticles finds its niche as precursors of well-defined heterogeneous catalysts.³¹⁻³⁵ The use of bimetallic molecular precursors has allowed for greater control of the size, composition and homogeneity of the nanoparticles, compared to nanoparticles obtained from mixtures of the monometallic salts.³⁶ Cluster-derived nanoparticles were generally observed to be of smaller sizes, with a narrower size distribution, and tend to retain the ratio of the metallic components of their cluster precursor. This is due to the close proximity of the atoms in the precursors and the presence of metal–metal bonds, which maintain the integrity of the metallic core during the thermolytic process that removes the ligand shell. This was demonstrated in the thermal decarbonylation of $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{SnCl}_3]^-$ which gave Ru_6Sn nanoparticles (Figure 1.3).³²

Figure 1.3. An illustration of Ru_6Sn nanoparticles obtained from $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{SnCl}_3]^-$ after thermal decarbonylation.³²

Cluster-derived multi-metallic nanoparticles also have the advantage that the differences in properties of the different metal centers could lead to synergistic enhancement in the efficiency of the catalysts. For example, Siani and co-workers have shown that a $\text{Pt}_5\text{Fe}_2/\text{SiO}_2$ catalyst prepared from the cluster $\text{Pt}_5\text{Fe}_2(\text{COD})_2(\text{CO})_{12}$ supported on SiO_2 gave complete CO conversion at lower temperatures compared to both salt-derived catalysts: co-impregnated $\text{Pt}_5\text{Fe}_2/\text{SiO}_2$ catalysts and monometallic Pt/SiO_2 . The cluster-derived catalyst showed better metal dispersion and homogeneity over the wet impregnated salt-derived catalysts. HRTEM indicated that the cluster-derived nanoparticles were smaller (1-2 nm) compared to the salt-derived nanoparticles (1.5-4 nm), and an EDX analysis showed that the cluster-derived nanoparticles maintained the bimetallic stoichiometry of the precursor while the Pt/Fe atomic ratio for the salt-derived Pt_5Fe_2 nanoparticles were found to be Pt rich, in the order of 10 to 60. The presence of Fe is known to provide adsorption sites for oxygen that can subsequently react with the CO molecules adsorbed on Pt sites. As such, the catalytic activity would be enhanced with substantial Pt-Fe interactions found in the cluster-derived $\text{Pt}_5\text{Fe}_2/\text{SiO}_2$. Moreover, the presence of Pt-Fe interactions also reduces CO adsorption onto Pt, further enhancing its performance for CO oxidation.^{37,38}

1.4 NHC-containing heteronuclear transition metal carbonyl clusters

In recent years, there has been an increasing interest in the organometallic chemistry of NHCs, in both homogeneous catalysis and metal nanoparticle heterogeneous catalysis. NHCs have been used as replacements for phosphine ligands in the design of organometallic catalysts. A well-known example is that of Grubbs' catalyst for olefin metathesis (Figure 1.4). The replacement of one of the phosphine ligands with NHC gave rise to higher activity compared to the bis-phosphine complex.³⁹

Figure 1.4. Molecular structures of Grubb's catalysts.

NHC-stabilized ruthenium nanoparticles were found to increase the rate of hydrogenation of aromatics compared to phosphine-stabilized ruthenium nanoparticles. This increase in reaction rate is attributed to the stronger electron donating ability of NHC compared to phosphines.⁴⁰

NHC-derived cluster precursors of heterogeneous catalysts is also attractive because phosphine ligands are known to act as catalytic poisons; phosphorus binds strongly to transition metals, reducing the active sites and thus the catalytic activity.^{41,42} Higher calcination temperatures and conditions are required to remove phosphorus from the metal nanoparticles, making undesirable sintering of the nanoparticles more likely. An NHC-

derived cluster precursor could circumvent these problems as the NHC may be expected to be more easily burnt off.

The convenient replacement of transition metal phosphine complexes with NHCs is due to the similarity that both ligands are monodentate, two-electron donors. In general, NHCs form stronger bonds with transition metals compared to phosphines.⁴³ However, while the synthetic methodologies for phosphine substitution of heteronuclear carbonyl clusters are well-established, NHC derivatives of carbonyl clusters are more limited; there are only a handful of NHC-substituted heteronuclear carbonyl clusters currently in the literature.

As mentioned in section 1.2.2, R. D. Adams and co-workers have developed a well-established synthetic methodology to phosphine-substituted heteronuclear carbonyl clusters involving the addition of $[M(P^tBu_3)]$ (where $M = Pt$ or Pd) fragments across the M-M bonds of carbonyl clusters. This synthetic methodology has also been successfully applied to $[M(NHC)_2]$ (where $M = Pt$ or Pd). Similar to its phosphine analogues, $[M(NHC)_2]$ can lose one of its NHC ligands in solution to give the $[M(NHC)]$ fragment. For example, $[Pd(IMes)_2]$ reacts with $Os_3(CO)_{12}$ to form a variety of NHC-containing OsPd clusters (Scheme 1.14).⁴⁴ Similarly, $[Pt(IMes)_2]$ reacts with ruthenium carbonyl clusters to give NHC-containing RuPt clusters (Scheme 1.15).⁴⁵

Scheme 1.14

Scheme 1.15

Moreover, Leong and co-workers discovered that the $[\text{M}(\text{NHC})]$ (where $\text{M} = \text{Pt}$ or Pd) fragment generated *in situ* from the reduction of $[\text{MCl}(\text{allyl})(\text{NHC})]$ in the presence of a base could react directly with a carbonyl cluster. This synthetic route is more convenient as $[\text{MCl}(\text{allyl})(\text{NHC})]$ is air-stable and easily prepared, while $[\text{M}(\text{NHC})_2]$ is both air and moisture sensitive. Hence, the use of $\text{M}^{\text{II}}\text{NHC}$ salts, $[\text{MCl}(\text{allyl})(\text{NHC})]$ to generate *in situ* $[\text{M}^0(\text{NHC})]$ fragments to add across metal-metal bonds of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ gave a variety of NHC containing OsPd, OsPt, IrPd and IrPt carbonyl clusters with varying bimetallic ratios (Schemes 1.16).^{44,46}

Scheme 1.16

Another example is the reaction of $\text{Ru}_5\text{C}(\text{CO})_{15}$ with $(\text{NHC})\text{AuPh}$; the latter was found to oxidatively add to the metal carbonyl cluster to give two isolated products, $\text{Ru}_5\text{C}(\text{CO})_{13}(\mu\text{-}\eta^2\text{-Ph})[\mu\text{-Au}(\text{NHC})]$ and $\text{Ru}_5\text{C}(\text{CO})_{14}(\text{Ph})[\mu\text{-Au}(\text{NHC})]$, with different bonding modes of the phenyl ligand (Scheme 1.17).⁴⁷

Scheme 1.17

A direct substitution of weakly coordinating ligand with NHCs is also an effective synthetic route. The labile MeCN ligand in $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{Cu}\{\text{MeCN}\})_2]$ was substituted with IPr to form $[\text{Fe}_4\text{C}(\text{CO})_{12}(\text{Cu}\{\text{IPr}\})_2]$ (Scheme 1.18).⁴⁸

Scheme 1.18

1.5 Aim and objectives

That heteronuclear clusters are precursors for heterometallic nanocatalysts, affording excellent control of the bimetallic ratio, suggests that this is a good methodology for the preparation of heterogeneous selective oxidation catalysts, with the selective oxidation of benzyl alcohol to benzaldehyde as the model reaction. Salt-derived heterogeneous catalysts prepared using various metals such as Ru, Pt, Au and Co, have been shown to be active for oxidation reactions.^{49,50} However, the catalytic potential of the heterometallic combinations, i.e., RuPt, RuAu and CoPt, for the selective oxidation of benzyl alcohol to benzaldehyde have yet to be explored. The use of NHC derived heteronuclear carbonyl clusters of such bimetallic combinations as precursors would enable us to design catalysts, with good control over the bimetallic ratio. This would allow us to probe the optimal ratio for the catalytic reaction. It is therefore desirable to develop synthetic strategies to such organometallic precursors and to carry out a systematic study on their catalytic efficiency.

The aim of this project is therefore:

To explore the use of N-heterocyclic transition metal carbenes for the synthesis of heterometallic clusters as single-source precursors of bimetallic heterogeneous catalysts for the selective oxidation of benzyl alcohol to benzaldehyde.

The specific objectives are:

1. Examine the reaction of the Pt(NHC) fragment with ruthenium and cobalt carbonyl clusters.
2. Examine the reaction of the Au(NHC) fragment with ruthenium carbonyl clusters.
3. Explore the catalytic potential of the cluster products for the selective oxidation of benzyl alcohol to benzaldehyde.

1.6 References

- (1) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.
- (2) Bortoluzzi, M.; Ciabatti, I.; Femoni, C.; Funaioli, T.; Hayatifar, M.; Iapalucci, M. C.; Longoni, G.; Zacchini, S. *Dalton Trans.* **2014**, *43*, 9633.
- (3) Ciabatti, I.; Femoni, C.; Hayatifar, M.; Iapalucci, M. C.; Ienco, A.; Longoni, G.; Manca, G.; Zacchini, S. *Inorg. Chem.* **2014**, *53*, 9761.
- (4) Ciabatti, I.; Femoni, C.; Hayatifar, M.; Iapalucci, M. C.; Zacchini, S. *Inorg. Chim. Acta* **2015**, *428*, 203.
- (5) Adams, R. D.; Chen, G.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 1007.
- (6) Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1395.
- (7) Adams, R. D.; Li, Z.; Lii, J. C.; Wu, W. *Organometallics* **1992**, *11*, 4001.
- (8) Adams, R.; Boswell, E.; Captain, B.; Zhu, L. *J. Cluster Sci.* **2008**, *19*, 121.
- (9) Adams, R. D.; Captain, B. *Angew. Chem. Int. Ed.* **2005**, *44*, 2531.
- (10) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Manson, J.; Smith, M. D.; Webster, C. E. *J. Am. Chem. Soc.* **2004**, *126*, 5253.
- (11) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Smith, M. D.; Webster, C. E. *Inorg. Chem.* **2004**, *43*, 3921.
- (12) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D.; Zhu, L. *J. Cluster Sci.* **2006**, *17*, 87.
- (13) Adams, R. D.; Captain, B.; Herber, R. H.; Johansson, M.; Nowik, I.; Smith, J. L.; Smith, M. D. *Inorg. Chem.* **2005**, *44*, 6346.
- (14) Adams, R. D.; Captain, B.; Smith, M. D. *J. Cluster Sci.* **2004**, *15*, 139.
- (15) Adams, R. D.; Captain, B.; Zhu, L. *Inorg. Chem.* **2006**, *45*, 430.
- (16) Adams, R. D.; Hall, M. B.; Pearl, W. C.; Yang, X. *Inorg. Chem.* **2009**, *48*, 652.
- (17) Adams, R. D.; Captain, B.; Hall, M. B.; Smith, J. L.; Webster, C. E. *J. Am. Chem. Soc.* **2004**, *127*, 1007.

- (18) Fumagalli, A.; Bianchi, M.; Malatesta, M. C.; Ciani, G.; Moret, M.; Sironi, A. *Inorg. Chem.* **1998**, 37, 1324.
- (19) Wong, W.-T. *Organometallics* **1999**, 18, 3474.
- (20) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; McPartlin, M. J. *Organomet. Chem.* **1983**, 246, c69.
- (21) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; Henrick, K.; McPartlin, M. J. *Chem. Soc., Dalton Trans.* **1986**, 975.
- (22) Beswick, M. A.; Lewis, J.; Raithby, P. R.; de Arellano, M. C. R. *Angewandte Chemie International Edition in English* **1997**, 36, 291.
- (23) Arrigoni, A.; Ceriotti, A.; Pergola, R. D.; Longoni, G.; Manassero, M.; Masciocchi, N.; Sansoni, M. *Angewandte Chemie International Edition in English* **1984**, 23, 322.
- (24) Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Bruckner, S.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 195.
- (25) Anderson, J. R.; Elmes, P. S.; Howe, R. F.; Mainwaring, D. E. *J. Catal.* **1977**, 50, 508.
- (26) Reddy, K. P.; Brown, T. L. *J. Am. Chem. Soc.* **1995**, 117, 2845.
- (27) Fierro-Gonzalez, J. C.; Kuba, S.; Hao, Y.; Gates, B. C. *The Journal of Physical Chemistry B* **2006**, 110, 13326.
- (28) Koh, A. C. W., Msc thesis, National University of Singapore **2006**.
- (29) Rameswaran, M.; Bartholomew, C. H. *J. Catal.* **1989**, 117, 218.
- (30) Koh, A. C. W.; Chen, L.; Leong, W. K.; Ang, T. P.; Johnson, B. F. G.; Khimyak, T.; Lin, J. *Int. J. Hydrogen Energy* **2009**, 34, 5691.
- (31) Koh, A. C. W.; Leong, W. K.; Chen, L.; Ang, T. P.; Lin, J.; Johnson, B. F. G.; Khimyak, T. *Catal. Commun.* **2008**, 9, 170.
- (32) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, 36, 20.

- (33) Johnson, B. F. G. *Top. Catal.* **2003**, *24*, 147.
- (34) Johnson, B. F. G. *Coord. Chem. Rev.* **1999**, *190–192*, 1269.
- (35) Zacchini, S. *Eur. J. Inorg. Chem.* **2011**, *2011*, 4125.
- (36) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28.
- (37) Siani, A.; Alexeev, O. S.; Captain, B.; Lafaye, G.; Marécot, P.; Adams, R. D.; Amiridis, M. D. *J. Catal.* **2008**, *255*, 162.
- (38) Siani, A.; Captain, B.; Alexeev, O. S.; Stafyla, E.; Hungria, A. B.; Midgley, P. A.; Thomas, J. M.; Adams, R. D.; Amiridis, M. D. *Langmuir* **2006**, *22*, 5160.
- (39) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.
- (40) Gonzalez-Galvez, D.; Lara, P.; Rivada-Wheelaghan, O.; Conejero, S.; Chaudret, B.; Philippot, K.; van Leeuwen, P. W. N. M. *Catalysis Science & Technology* **2013**, *3*, 99.
- (41) Snelders, D. J. M.; Yan, N.; Gan, W.; Laurenczy, G.; Dyson, P. J. *ACS Catalysis* **2012**, *2*, 201.
- (42) Argyle, M.; Bartholomew, C. *Catalysts* **2015**, *5*, 145.
- (43) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2416.
- (44) Liu, Y., PhD thesis, Nanyang Technological University **2014**.
- (45) Saha, S.; Captain, B. *Inorg. Chem.* **2014**, *53*, 1210.
- (46) Liu, Y.; Ganguly, R.; Huynh, H. V.; Leong, W. K. *Organometallics* **2013**, *32*, 7559.
- (47) Adams, R. D.; Tedder, J.; Wong, Y. O. *J. Organomet. Chem.* **2015**, *795*, 2.
- (48) Della Pergola, R.; Sironi, A.; Rosehr, A.; Colombo, V.; Sironi, A. *Inorg. Chem. Commun.* **2014**, *49*, 27.
- (49) Davis, S. E.; Ide, M. S.; Davis, R. J. *Green Chemistry* **2013**, *15*, 17.
- (50) Guo, Z.; Liu, B.; Zhang, Q.; Deng, W.; Wang, Y.; Yang, Y. *Chem. Soc. Rev.* **2014**, *43*, 3480.

Chapter 2: Reactions of [Pt(NHC)] fragment with ruthenium carbonyl clusters

2.1 Cluster precursors to RuPt catalysts

The ruthenium-platinum bimetallic system is an effective electrocatalyst for methanol oxidation in the Direct Methanol Fuel Cell (DMFC).¹⁻³ Metallic ruthenium mitigates CO poisoning of the platinum, thus preventing catalyst deactivation. Furthermore, it was found that a cluster-derived catalyst, prepared by decarbonylation of $\text{Ru}_4\text{Pt}_2(\text{CO})_{18}$, was more active compared to commercial catalysts due to the higher metal dispersion and smaller particle size.⁴

The ruthenium-platinum catalyst is also highly efficient for ethanol steam reforming, an oxidation process for hydrogen generation. The RuPt/ Al_2O_3 catalyst prepared from the decarbonylation of $[\text{Ru}_5\text{Pt}(\mu_6\text{-C})(\text{CO})_{15}]^{2-}$ gave better selectivity and overall ethanol conversion compared to that prepared by salt-impregnation and commercial Ru/ Al_2O_3 , again due to higher metal dispersion and the smaller particle size. The platinum was found to reduce coking.^{5,6}

Cluster-derived RuPt catalysts have also been found to be effective for a variety of hydrogenation reactions, most notably for the hydrogenation of nitrobenzene, alkenes and C=O bonds.⁷ For the hydrogenation of nitrobenzene, the platinum readily activated H_2 while the ruthenium activated the nitrobenzene via the NO_2 group.⁸

The binary Ru-Pt carbonyl cluster $\text{Ru}_4\text{Pt}_2(\text{CO})_{18}$ can be synthesized by the condensation reaction between $\text{Pt}(\text{COD})_2$ and $\text{Ru}(\text{CO})_5$.^{9,10} This cluster can also serve as precursor to other Ru-Pt clusters by reaction with other clusters or ligands.^{11,12} Ru-Pt carbonyl clusters have also been obtained by the ionic coupling of cationic Pt fragments such as $[\text{Pt}(\text{COD})]^{2+}$, generated via chloride abstraction by silica gel from $\text{Pt}(\text{COD})\text{Cl}_2$, with anionic ruthenium carbonyl clusters like $[\text{Ru}_5(\mu_5\text{-C})(\mu\text{-CO})_2(\text{CO})_{12}]^{2-}$ to give neutral $\text{Ru}_5\text{Pt}(\mu_6\text{-C})(\text{COD})(\mu\text{-CO})_2(\text{CO})_{12}$, which could give $[\text{Ru}_5\text{Pt}(\mu_6\text{-C})(\mu\text{-CO})_3(\text{CO})_{12}]^{2-}$ after

CO ligand exchange with COD and subsequently reductive elimination of CO in the presence of base.¹³⁻¹⁵ The addition of unsaturated fragments such as $[\text{Pt}(\text{P}^t\text{Bu}_3)]$, generated from the elimination of one P^tBu_3 ligand from $\text{Pt}(\text{P}^t\text{Bu}_3)_2$, to ruthenium carbonyl clusters has also been used. Thus, the reaction of $\text{Ru}_3(\text{CO})_{12}$, **1** and $\text{Ru}_6(\mu_6\text{-C})(\mu\text{-CO})(\text{CO})_{16}$ with $\text{Pt}(\text{P}^t\text{Bu}_3)_2$ gave Ru-Pt adducts of various nuclearities (Scheme 2.1).^{16,17}

The addition of unsaturated Pt fragments to ruthenium carbonyl clusters could also be applied to prepare NHC derivatives, using $\text{Pt}(\text{IMes})_2$ in place of $\text{Pt}(\text{P}^t\text{Bu}_3)_2$ (Scheme 2.2).¹⁸ Recent work from Leong, *et. al.* have shown that the $[\text{Pt}(\text{NHC})]$ fragment, generated *in situ* from $\text{Pt}(\text{NHC})(\text{allyl})\text{Cl}$,¹⁹ could also react directly with metal carbonyl clusters.²⁰

Scheme 2.2

Condensation reaction

Ionic coupling reaction

Addition reaction

Scheme 2.1

2.2 Reaction of Ru₃(CO)₁₂, **1** with [Pt(IPr)]

The reduction of Pt(IPr)(C₄H₇)Cl, **4** in the presence of KO^tBu as a base and IPA as the reducing agent generates the [Pt(IPr)] fragment *in situ* (scheme 2.3). The 12-electron [Pt(IPr)] species could be stabilized by interaction with IPA solvent while the solution was kept under inert atmosphere. The [Pt(IPr)] fragment was subsequently reacted with Ru₃(CO)₁₂, **1**, Ru₄(μ-H)₄(CO)₁₂, **2**, and Ru₆(μ₃-H)₂(CO)₁₈, **3**. Previously, we would carry out a one-pot synthesis in which all reactants were added at the beginning of the reaction.^{20,21} This methodology was found to be effective for both Os₃(CO)₁₂ and Ir₄(CO)₁₂, but resulted in decomposition with ruthenium carbonyl clusters. We attributed this to the presence of KO^tBu, which reacts readily with ruthenium carbonyl clusters. Thus, the [Pt(IPr)] fragment was first generated *in situ* before addition of the cluster.

Scheme 2.3

The reaction of three equivalents of [Pt(IPr)] with cluster **1** at room temperature gave an air-stable, red-brown solid, which has tentatively been identified on the basis of spectroscopic evidence as Ru₃Pt₂(μ-CO)₄(CO)₈, **5a** as the only product. Cluster **5a** showed

a similar IR pattern to that of the reported IMes analogue $\text{Ru}_3\text{Pt}_2(\text{IMes})_2(\mu\text{-CO})_4(\text{CO})_8$, **5b** (Figure 2.1).¹⁸ Its ^1H NMR spectrum showed one set of resonances for the IPr carbene and a set of peaks corresponding to the molecular ion was also observed in the mass spectrum.

Figure 2.1. IR spectrum of cluster **5a**.

Unlike in the similar reaction with the IMes analogue,¹⁸ however, a cluster corresponding to $\text{Ru}_3\text{Pt}(\text{IMes})_2(\mu\text{-CO})_2(\text{CO})_9$, **6**, viz., the cluster $\text{Ru}_3\text{Pt}(\text{IPr})_2(\text{CO})_{11}$, was not observed even with one molar equivalent of $[\text{Pt}(\text{IPr})]$; only a reduced yield of **5a** and unreacted **1** were obtained (Scheme 2.4). This may be attributed to the different Pt source used. Presumably, an unstable Ru_3Pt cluster was initially formed in the reaction; with $\text{Pt}(\text{IMes})_2$, the IMes ligand that was lost to generate the $[\text{Pt}(\text{IMes})]$ fragment could have substituted one of the CO ligands on this Ru_3Pt cluster product and possibly stabilising it as **6**, while with the $[\text{Pt}(\text{IPr})]$ fragment generated in the procedure adopted here, no excess IPr ligand was generated that could lead to the formation of $\text{Ru}_3\text{Pt}(\text{IPr})_2(\text{CO})_{11}$.

The reaction of cluster **1** with six equivalents of $\text{Pt}(\text{P}^t\text{Bu}_3)_2$ has been reported to give $\text{Ru}_3\text{Pt}_3(\text{P}^t\text{Bu}_3)_3(\mu\text{-CO})_3(\text{CO})_9$, **7b** as the only product.¹⁷ An attempt at an analogous reaction between **1** and six equivalents of $[\text{Pt}(\text{IPr})]$ at room temperature afforded two isolable

compounds; cluster **5a** and a green solid tentatively identified as $\text{Ru}_3\text{Pt}_3(\text{IPr})_3(\mu\text{-CO})_3(\text{CO})_9$, **7a**, on the basis of its IR spectral pattern which is very similar to that reported for cluster **7b** (Figure 2.2).¹⁷ Unfortunately, cluster **7a** decomposed fairly quickly (30–60 min) on standing in solution, similar to cluster **7b**. This has hampered further spectroscopic characterization; attempts at growing diffraction-quality crystals in the glovebox also resulted in decomposition.

Scheme 2.4

Figure 2.2. IR spectrum of cluster **7a**.

2.3 Reaction of Ru₄(μ-H)₄(CO)₁₂, **2** with [Pt(IPr)]

The reaction of cluster **2** with various molar equivalents of [Pt(IPr)] at room temperature resulted in decomposition during chromatographic separation, likely due to the instability of the addition products. Reaction at elevated temperature afforded many products upon chromatographic separation, among which two products, viz., Ru₄(μ-H)₄(*m*IPr)(CO)₁₁, **8a**, and RuPt₂(IPr)₂(μ-CO)₃(CO)₃, **9a**, were isolated and characterized, including by single crystal X-ray crystallography; both were obtained in low yields (Scheme 2.5). In both cases, it was believed that addition products were initially formed, however their instability might have resulted in decomposition or cluster fragmentation.

Scheme 2.5

The ORTEP diagram showing the molecular structure of cluster **8a** is given in Figure 2.3. It comprises a tetrahedral Ru₄ core, and may be regarded as a substituted derivative of **2** in which one of the CO ligands is replaced with an abnormal carbene (*m*NHC). The ¹H NMR spectrum at room temperature showed two sets of ⁱPr resonances for the asymmetric abnormal carbene, and only one broad hydride resonance (-17.25 ppm). However, when the temperature was lowered to -80 °C, three hydride resonances in a 1:1:2 ratio were observed (Figure 2.4). Thus the hydrides are highly fluxional and the solid state

structure persisted in solution at low temperature, with the hydrides bridging Ru(1)-Ru(2) and Ru(1)-Ru(3) being equivalent.

The positions of the bridging hydrides in the X-ray structure, located using potential energy calculations with the XHYDEX program,²² are corroborated by the lengthening of the corresponding Ru-Ru bonds (Ru(2)-Ru(3) = 2.9497(15) Å, Ru(1)-Ru(2) = 2.9938(14) Å, Ru(1)-Ru(3) = 2.9877(14) Å and Ru(1)-Ru(4) = 2.9876(13) Å) compared to the other Ru-Ru bonds (Ru(2)-Ru(4) = 2.7984(14) Å and Ru(3)-Ru(4) = 2.791(1) Å).

Figure 2.3. ORTEP diagram of cluster **8a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms on the carbene have been omitted for clarity. Selected bond lengths (Å):

Ru(2)-Ru(3) = 2.9497(15), Ru(1)-Ru(2) = 2.9938(14), Ru(1)-Ru(3) = 2.9877(14), Ru(1)-Ru(4) = 2.9876(13), Ru(2)-Ru(4) = 2.7984(14), Ru(3)-Ru(4) = 2.791(1).

Figure 2.4. Varying temperature ^1H NMR of cluster **8a** in toluene- d_8 (Hydride region).

It is unprecedented for an Ru_4 cluster to be substituted with an abnormal carbene; it has been observed earlier that the reaction of **2** with IPr.HCl in the presence of KO^tBu resulted in abstraction of a hydride to give $[\text{IPr.H}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$,²¹ while the corresponding reaction with IMes.HCl was reported to give the normal NHC-substituted product $\text{Ru}_4(\mu\text{-H})_4(\text{IMes})(\text{CO})_{11}$, **8c**.^{18,23} Cluster **8a** is structurally similar to its $\text{Os}(m\text{IMes})$ analogue, *viz.*, $\text{Os}_4(\mu\text{-H})_4(m\text{IMes})(\text{CO})_{11}$, **8b**, obtained from the thermolysis of its normal carbene analogue $\text{Os}_4(\mu\text{-H})_4(n\text{IMes})(\text{CO})_{11}$.²⁴ All the clusters **8** exhibit C_s rather than D_{2d} symmetry for the M_4H_4 core (Figure 2.5).^{18,24} While the ^1H NMR spectrum of **8b** showed four non-fluxional hydrides in a 1:2:1 ratio at room temperature, the hydrides of both **8a** and **8c** were found to

be fluxional.^{23,24} Since the formation of **8c** is obtained by the thermolysis of the normal carbene isomer, it is possible that the formation of **8a** is resulted from the isomerization of an undetected normal carbene isomer.

Figure 2.5. Two possible geometries of the tetranuclear M_4H_4 ($M = Ru, Os$) cores for clusters with the formulation of $[M_4(\mu-H)_4(L)_n(CO)_{12-n}]$.

The ORTEP diagram showing the molecular structure of **9a** is shown in Figure 2.6. Cluster **9a** is electron-precise with a valence electron count of 44, with each ruthenium atom having an 18-electron configuration and each platinum atom a 16-electron configuration. It comprises an $RuPt_2$ triangular planar core, with an IPr ligand on each of the platinum atoms, and three symmetric CO ligands bridging each of the metal-metal bonds. The other three terminal CO ligands are bonded to ruthenium. The Pt-Pt bond (2.6507(7) Å) is slight shorter than the Ru-Pt bonds (2.6938(7) - 2.6959(7) Å). Cluster **9a** is structurally similar to its IMes analogue, $RuPt_2(IPr)_2(\mu-CO)_3(CO)_3$, **9b**.

Figure 2.6. ORTEP diagram of cluster **9a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)-Pt(2) = 2.6507(7) , Pt(1)-Ru(3) = 2.6938(7) , Pt(2)-Ru(3) = 2.6959(7), Pt(2)-Pt(1)-Ru(3) = 60.579(15), Pt(1)-Pt(2)-Ru(3) = 60.501(15), Pt(1)-Pt(2)-Ru(3) = 60.501(15).

The isolation of **9a** suggests that the harsh reaction conditions resulted in fragmentation of the Ru₄ cluster. Although the crystal of **9a** was obtained from the brown solid that was isolated after preparative TLC, spectroscopic evidence (IR and NMR) showed that more than one species was present in the TLC band. Since the IMes analogue RuPt₂(IMes)₂(CO)₆, **9b** has previously been reported to be available via the reaction of Ru(CO)₅ and Pt(IMes)₂,¹⁸ it may be possible to obtain **9a** via a similar synthetic route. Indeed, the reaction of Ru(CO)₅ with [Pt(IPr)] afforded two products which, based on spectroscopic evidence (IR, ¹H NMR and ESI-MS), have been identified as **9a** and Ru₂Pt(IPr)(μ-CO)₃(CO)₆, **10a** (Scheme 2.6).

Scheme 2.6

The identity of **10a** was proposed on the basis of the similarity of its IR pattern to that of the reported IMes analogue $\text{Ru}_2\text{Pt(IMes)(}\mu\text{-CO)}_3(\text{CO})_6$, **10b** that was also obtained from the reaction between Ru(CO)_5 and Pt(IMes)_2 (Figure 2.7).¹⁸ The formation of **10** could be explained by the stabilization of the transient $\text{Ru}_2(\text{CO})_9$ species, which was present in the solution of Ru(CO)_5 at low temperature,²⁵ by $[\text{Pt(NHC)}]$. Its ^1H NMR spectrum showed one set of resonances for the IPr carbene and its mass spectrum also showed a cluster of peaks corresponding to the molecular ion.

Figure 2.7. IR spectra of cluster **10a**.

2.4 Reaction of Ru₆(μ₃-H)₂(CO)₁₈, **3** with [Pt(IPr)]

The room temperature reaction of **3** with one equivalent of the [Pt(IPr)] fragment readily formed the mono adduct Ru₆Pt(μ₃-H)₃(IPr)(CO)₁₈, **11** as the major product in 71 % yield (Scheme 2.7). Cluster **3** was found to be insoluble in IPA and was found to readily fragment into smaller clusters in oxygen-containing solvents, as such the solvent was switched from isopropyl alcohol to dichloromethane before the addition of **3**.²⁶ Cluster **11** reacted with one equivalent of the [Pt(IPr)] fragment in toluene at 70 °C to afford Ru₆Pt₂(μ-H)₂(μ₃-H)₄(IPr)₂(CO)₁₆, **12**. Cluster **12** could also be obtained directly from cluster **3** via the reaction in toluene with two equivalents of [Pt(IPr)]; the reaction mixture was stirred until it turned a dark blue, indicating the formation of **11**, before it was heat at 70 °C for 2 h to afford a dark brown solution from which **12** could be isolated in 56% yield. It was found that heating the reaction mixture before it turned dark blue led to a complicated mixture of products, as did a change in the solvent to DCE instead of toluene.

Scheme 2.7

The molecular structure of **11** consists of a bicapped tetrahedron Ru₆ core, an edge-bridging [Pt(IPr)(CO)₂] fragment, and two capping hydrides (Figure 2.8). This is in contrast to **3** in which the Ru₆ core is an octahedron, and two carbonyl ligands have been transferred to the platinum metal center. If we consider the [Pt(IPr)(CO)₂] moiety as a two-electron

donor, then **11** contains 84 cluster valence electrons, which is predicted to adopt a *mono-capped closo* trigonal bipyramid structure on the basis of the Polyhedral Skeletal Electron Pair theory (PSEPT). All the CO ligands are terminal, as confirmed also by its IR spectrum. The capping hydrides are chemically equivalent; the ^1H NMR spectrum showed only one hydride resonance at -20.02 ppm. The positions of the hydrides in the crystal structure were calculated using the XHYDEX program.²² The presence of capping hydrides is also evident from the lengthening of Ru-Ru bonds (2.977(2) Å to 3.015(2) Å) for the face capped by the hydrides compared to the other Ru-Ru bonds (2.696(2) Å to 2.836(2) Å). However, the only exception is the length of the Ru(2)-Ru(3) bond (2.732(2) Å) bridged by both a Pt fragment and a hydride, is within the range of an unbridged Ru-Ru bond.

The molecular structure of **12** is shown in Figure 2.9. It also contained only terminal CO ligand, as confirmed by its IR spectrum. The metal core has C_2 rotational symmetry; the symmetry axis passes through the midpoints of the Ru(4)-Ru(6) and Ru(2)-Ru(5) bonds (Figure 2.10). The presence of this rotational symmetry rendered both the [Pt(IPr)] fragments equivalent.

Figure 2.8. ORTEP diagram of cluster **11**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms for the IPr carbene have been omitted for clarity. Selected bond lengths (Å): Pt(1)-Ru(2) = 2.8846(16), Pt(1)-Ru(3) = 2.9193(16), Ru(2)-Ru(4) = 2.701(2), Ru(2)-Ru(3) = 2.732(2), Ru(2)-Ru(5) = 2.977(2), Ru(2)-Ru(6) = 3.012(2), Ru(3)-Ru(7) = 2.696(2), Ru(3)-Ru(6) = 2.994(2), Ru(3)-Ru(5) = 3.015(2), Ru(4)-Ru(6) = 2.800(2), Ru(4)-Ru(5) = 2.830(2), Ru(5)-Ru(6) = 2.790(2), Ru(5)-Ru(7) = 2.836(2), Ru(6)-Ru(7) = 2.822(2).

Figure 2.9. ORTEP diagram of cluster **12**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)-Ru(4) = 2.844(3), Ru(1)-Ru(5) = 3.004(3), Ru(1)-Ru(6) = 3.032(4), Ru(2)-Ru(5) = 2.968(4), Ru(2)-Ru(3) = 3.005(3), Ru(2)-Ru(6) = 3.009(5), Ru(3)-Ru(6) = 2.823(3), Ru(3)-Ru(4) = 3.001(4), Ru(4)-Ru(6) = 2.835(4), Ru(4)-Ru(5) = 2.983(5), Ru(5)-Pt(8) = 2.720(3), Ru(3)-Pt(8) = 2.924(4), Ru(2)-Pt(7) = 2.690(3), Ru(1)-Pt(7) = 2.893(3), Ru(3)-Ru(5) = 2.831(3), Ru(1)-Ru(2) = 2.832(4).

Figure 2.10. Position of the C₂-axis of the Ru₆Pt₂ metal core of cluster **12**.

However, the ¹H NMR spectrum showed two sets of resonances due to the isopropyl groups but only one for the imidazole protons. This may be attributed to restricted rotation of the isopropyl groups at room temperature. Indeed, a V-T ¹H NMR experiment showed that at 80 °C, the protons of the isopropyl groups simplified into one set of resonances, while the resonance for the imidazole protons remained unchanged throughout.

There is ambiguity in the number and location of the hydrides in **12** but if the [Pt(IPr)(CO)] fragment is considered a two-electron donor as with **11** above, then it would be electron-precise with a total cluster valence electron count of 86 if it contained six hydride ligands. The room temperature ¹H NMR spectrum showed three sets of broad hydride resonances which coalesced at higher temperatures; they were well-defined at low temperatures and integration with respect to the imidazole proton resonances suggested an integration ratio of 2:2:2 (Figure 2.11). The spectrum at - 60 °C, for example, showed that the hydride resonances at -8.30 ppm and -12.19 ppm with satellites due to ¹⁹⁵Pt coupling,²⁷ with ¹J(Pt-H) = 588 Hz and ²J(Pt-H) = 120 Hz, respectively. The assignments of the

coupling constants were made on the basis of comparisons with the reported values for $\text{Ru}_5\text{Pt}(\mu\text{-H})_3(\mu_5\text{-C})(\text{GePh}_3)(\text{P}^t\text{Bu}_3)(\text{CO})_{13}$ ($^1J(\text{Pt-H}) = 558 \text{ Hz}$),²⁸ and $\text{Ru}_5\text{Pt}(\mu\text{-H})_2(\mu_5\text{-C})(\mu_3\text{-PhC}_2\text{H})(\text{P}^t\text{Bu}_3)(\text{CO})_{12}$ ($^2J(\text{Pt-H}) = 42 \text{ Hz}$).²⁹ The third hydride resonance at -14.57 ppm was a singlet. Thus **12** probably possesses six hydride ligands, and it is very likely that the source of the additional hydrides is the solvent (IPA). Unfortunately, because of twinning in the crystal, not all the positions of the hydrides could be located with certainty using potential energy calculations with the XHYDEX program.²² However, the positions shown in Figure 2.9, i.e., comprising four capping hydrides and two bridging Ru-Pt edges, are in good agreement with the NMR data and the potential energy calculations.

Figure 2.11. VT ^1H NMR of **12** in toluene- d_8 (hydride region).

2.5 Concluding remarks

In general, it was found that [Pt(IPr)] fragments could react with ruthenium carbonyl clusters to give heteronuclear ruthenium-platinum clusters via addition reaction. The [Pt(IPr)] fragments gave products by adding across Ru-Ru bonds. In some cases, further additions can occur, giving multiple adducts (such as **5a**, **7a** and **12**); whereas in other cases, fragmentation occurs (such as **8a** and **9a**), probably due to instability of the addition products (Scheme 2.8). Nevertheless, this synthetic methodology could be a useful for building NHC-containing heteronuclear clusters as it has good control over the addition of [Pt(NHC)] fragments onto carbonyl clusters.

Scheme 2.8

2.6 Experimental

All reactions were performed under an argon atmosphere using standard Schlenk techniques or in the glove box. Solvents used in reactions were of AR grade, and were dried under the appropriate drying agent and distilled under nitrogen; and stored in flasks fitted with Teflon valves prior to use. Toluene was dried over sodium/benzophenone, IPA over Mg/I₂ and DCM over CaH₂. The products were separated by thin-layer chromatography (TLC), using Merck silica gel 60 Å F 254 20 × 20 cm² plates. ¹H NMR spectra were collected using a Bruker BBFO 400 or AV 300 NMR spectrometer, with chemical shifts referenced to the solvent residual peaks. 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. High resolution mass spectra were recorded in electrospray ionization (ESI) mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by the microanalytical laboratory at NTU. Single crystal X-ray crystallographic analyses were performed by Dr Rakesh Ganguly and/or Dr Li Yongxin from the NTU. Ru₃(CO)₁₂ were purchased from Oxkem. Ru₄(μ-H)₄(CO)₁₂,³⁰ Ru₆(μ₃-H)₂(CO)₁₈³¹ and Pt(C₄H₇)(IPr)Cl¹⁹ were prepared according to the published methods. All other reagents were used as received from commercial suppliers.

Reaction of cluster 1 with three equivalents of [Pt(IPr)]

Complex **4** (38.9 mg, 0.0578 mmol) and KO^tBu (6.5 mg, 0.058 mol) were heated at 80 °C in IPA (5 mL) for 1 h. The initial colourless solution turned yellow. Solvent was removed under vacuum to give a yellow oil which was re-dissolved in toluene and then cluster **1** (13.3 mg, 0.0188 mmol) subsequently added. The reaction mixture was left to stir for 15 mins during which the solution turned red-brown. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by preparative TLC with hexane/DCM (2:1, v/v) as the eluent, to give a red-brown solid upon removal of solvent. The red-brown solid is believed to be Ru₃Pt₂(IPr)₂(μ-CO)₄(CO)₈, **5a**.

Yield = 16.0 mg (47%)

IR (DCM) : ν_{CO} 2053 (w), 2015 (s), 1989 (m), 1972 (w), 1945 (m), 1864(w), 1811 (m), 1741 (m) cm^{-1}

^1H NMR (400 MHz, C_6D_6) : δ 7.03 (d, 4H, *meta*-Ar-**H**), 6.51 (s, 2H, Imidazole **H**) , 2.81 (sept, 4H, **CH**(CH_3)₂), 1.41 (dd, 12H, **CH**(CH_3)₂), 0.81 (dd, 12H, **CH**(CH_3)₂)

ESI-MS⁺ m/z: 1806.97 [M]⁺, 1779.98 [M - CO]⁺

Hi-res MS⁺: calcd for $\text{C}_{46}\text{H}_{73}\text{N}_4\text{O}_{12}^{96}\text{Ru}^{99}\text{Ru}^{104}\text{Ru}^{198}\text{Pt}_2$ 1808.1772; found 1808.1783.

Reaction of cluster **1** with six equivalents of [Pt(IPr)]

Complex **4** (79.7 mg, 0.118 mmol) and KO^tBu (6.5 mg, 0.12 mol) were heated at 80 °C in IPA (5 mL) for 1 h. The initial colourless solution turned yellow. Solvent was removed under vacuum to give a yellow oil which was re-dissolved in toluene and then cluster **1** (12.0 mg, 0.0188 mmol) was subsequently added. The reaction mixture was left to stir for 2 h during which the solution turned dark brown. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by preparative TLC with hexane/DCM (4:1, v/v) as the eluent. Two products were isolated; a red-brown solid believed to cluster **5a** (R_f = 0.45; yield = 13 mg, 37 %) and a green solid, believed to be $\text{Ru}_3\text{Pt}_3(\text{IPr})_3(\mu\text{-CO})_3(\text{CO})_9$, **7a** (R_f = 0.55; yield = 4.0 mg, 8 %).

For cluster **7a**,

IR (DCM) : ν_{CO} 2045 (w), 2013 (m), 1999 (vs), 1868(m), 1848(m), 1784 (m) cm^{-1}

Reaction of cluster **2** with three equivalents of [Pt(IPr)]

Complex **4** (54.3 mg, 0.00806 mmol) and KO^tBu (8.7 mg, 0.0078 mol) were heated in IPA (5 mL) at 80 °C for 1 h, followed by 25 °C overnight to generate [Pt(IPr)]. The initial colourless solution turned bright yellow. Solvent was removed under vacuum to give a yellow oil. The yellow oil was redissolved in toluene to give a yellow solution. Cluster **2** (20.0 mg, 0.00269 mmol) was subsequently added. The reaction mixture was then left to stir at 80 °C for 2 h, in which the initial yellow solution gradually turned dark brown. After

removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by TLC with DCM/hexane (1:1, v/v) as the eluent. Two bands were isolated and characterized.

The first yellow band was identified as $\text{Ru}_4(\mu\text{-H})_4(m\text{IPr})(\text{CO})_{11}$, **8a** ($R_f = 0.66$; yield = 3.0 mg, 11 %). Red crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

IR (DCM) : ν_{CO} 2080 (w), 2044 (vs), 2022 (s), 1995 (m), 1979 (m) cm^{-1}

^1H NMR (300 MHz, C_6D_6) : δ 6.74 – 7.04 (m, 8H , aromatic H & Im-H), 2.58 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.29 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, 6H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.04 (d, 6H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.92 (d, 6H, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.85 (d, 6H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), -17.25 (s, hydride) ppm

ESI- MS^+ m/z: 1105.37 $[\text{M}]^+$, 1075.58 $[\text{M} - \text{CO}]^+$.

The second brown band was identified as $\text{RuPt}_2(\text{IPr})_2(\mu\text{-CO})_3(\text{CO})_3$, **9a** ($R_f = 0.66$; yield = 1.0 mg, 12 %). Yellow crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

IR (DCM) : ν_{CO} 2078 (vw), 2057 (vw), 2045 (s) , 2027 (m), 2011 (m), 2000 (vs), 1966 (m), 1804 (w), 1789 (m) cm^{-1}

Reaction of $\text{Ru}(\text{CO})_5$ with $[\text{Pt}(\text{IPr})]$

Complex **4** (62.7 mg, 0.0930 mmol) and KO^tBu (10.4 mg, 0.0930 mol) were heated in IPA (5 mL) at 80 °C for 1 h, followed by 25 °C overnight to generate $[\text{Pt}(\text{IPr})]$. The initial colourless solution turned bright yellow. Solvent was removed under vacuum to give a yellow oil. $\text{Ru}_3(\text{CO})_{12}$ (7.5 mg, 0.012 mmol) was dissolved in 10 mL of Hexane in a 100 mL carius tube. After three cycles of freeze-pump-thaw, CO gas was introduced into the carius tube and sealed. The reaction vessel was placed in an ice bath and irradiated using a

60 W light bulb. After 3 h, the orange solution turned colourless, indicative for the formation of Ru(CO)₅. The generated [Pt(IPr)] was dissolved in 10 mL of toluene and was introduced into the hexane solution of Ru(CO)₅ at 0 °C via cannula. The solution was left to warm to room temperature and left to stir for 1 h in which a yellow solution was obtained. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by TLC with DCM/hexane (1:3, v/v) as the eluent. Two bands were isolated and characterized.

The first yellow-orange band was identified as Ru₂Pt(μ -CO)₃(CO)₆, **10a** (R_f = 0.52, Yield = 1.8 mg, 4 %).

IR (DCM) : ν_{CO} 2102 (w), 2066 (m), 2025 (vs), 1977 (m), 1837 (m), 1818 (m) cm⁻¹

¹H NMR (400 MHz, C₆D₆) : δ 6.72 – 7.05 (m, 8H , aromatic and Imidazole H), 3.09 (m, 2H, CH(CH₃)₂), 1.31 (d, 12H, *J* = 6.4 Hz, CH(CH₃)₂), 0.98 (d, 12H, *J* = 6.8 Hz, CH(CH₃)₂) ppm

ESI-MS⁺ *m/z*: 1039.01 [M]⁺, 1012.01 [M - CO]⁺, 983.02 [M - 2CO]⁺, 927.03 1012.01 [M - 4CO]⁺

Hi-res MS⁺: calcd for C₃₆H₃₇N₂O₉¹⁰⁴Ru₂¹⁹⁰Pt 1039.0207; found 1039.0118.

The second yellow band was identified as RuPt₂(IPr)₂(μ -CO)₃(CO)₃, **9a** (R_f = 0.25, Yield = 11.0 mg, 22 %).

IR (DCM) : ν_{CO} 2075 (w), 2001 (s), 1952 (m), 1880 (vw), 1802 (s), 1788 (vs) cm⁻¹

¹H NMR (400 MHz, C₆D₆) : δ 7.01 - 7.14 (m, 12H , aromatic H), 6.73 (s, 4H , Imidazole H), 3.31 (broad s, 4H, CH(CH₃)₂), 3.14 (broad s, 4H, CH(CH₃)₂), 1.22 (broad s, 24H, CH(CH₃)₂), 1.06 (d, 24H, *J* = 6.4 Hz, CH(CH₃)₂) ppm

ESI-MS⁺ *m/z*: 1381.39 [M - 2CO]⁺, 1352.38 [M - 3CO]⁺, 1324.39 [M - 4CO]⁺

Hi-res MS⁺: calcd for C₆₀H₃₇N₂O₉¹⁰⁴Ru¹⁹²Pt¹⁹⁵Pt 1436.3843; found 1436.3842.

Synthesis of cluster 11

Complex **4** (65.6 mg, 0.00972 mmol) and KO^tBu (10.9 mg, 0.00972 mol) were heated at 80 °C in IPA (5 mL) for 1 h. The initial colourless solution turned yellow. Solvent was removed under vacuum to give a yellow oil. The yellow oil was redissolved in DCM to give a yellow solution. Cluster **3** (72.4 mg, 0.00651 mmol) was subsequently added. The reaction mixture was then left to stir at rt for 15 h, in which the initial dark purple solution gradually turned dark blue-green. Solvent was removed and re-dissolve in chloroform and loaded onto a column of silica gel. The column first eluted with Hexane to remove some impurities. Elution with chloroform afforded a dark blue solution. Solvent was removed and the dark blue solid washed with methanol to give pure Ru₆Pt(μ₃-H)₂(IPr)(CO)₁₈, **11**. Dark blue crystals were obtained by slow evaporation of a DCM/Chloroform solution at 4 °C.

Yield = 78.0 mg (71 %)

IR (DCM) : ν_{CO} 2071 (m), 2053 (vs), 2035 (s), 2012 (w), 1997 (w), 1986 (w), 1937 (vw) cm⁻¹.

¹H NMR (400 MHz, CDCl₃) : δ 7.59 (t, 2H, *para*-Ar-**H**), 7.43 (s, 2H, Imidazole **H**), 7.38 (d, 4H, *meta*-Ar-**H**), , 2.79 (sept, 4H, CH(CH₃)₂), 1.40 (d, 12H, *J* = 6.8 Hz, CH(CH₃)₂), 1.26 (d, 12H, *J* = 6.8 Hz, CH(CH₃)₂) , -20.02 (s, hydride) ppm

ESI-MS⁺ m/z: 1696.38 [M]⁺, 1669.40[M - CO]⁺

Hi-res MS⁺: calcd for C₄₅H₃₉N₂O₁₈⁹⁶Ru⁹⁹Ru¹⁰⁰Ru₂¹⁰⁴Ru₂¹⁹⁸Pt 1697.6232; found 1697.6234.

Elemental Analysis (%) calcd for C₄₅H₃₉N₂O₁₈Ru₆Pt: C 31.86, H 2.26, N 1.65; found: C 31.85, H 2.41, N 1.62.

Synthesis of cluster 12

Complex **4** (58.9 mg, 0.00874 mmol) and KO^tBu (9.8 mg, 0.0087 mol) were heated in IPA (5 mL) at 80 °C for 1 h, followed by 25 °C overnight to generate [Pt(IPr)]. The initial colourless solution turned bright yellow. Solvent was removed under vacuum to give a yellow oil. The yellow oil was redissolved in toluene to give a yellow solution. Cluster **3** (24.3 mg, 0.00218 mmol) was subsequently added and the mixture immediately turned dark blue-green. The reaction mixture was heated at 70 °C for 2 h, in which the initial dark blue-green solution gradually turned dark brown. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by TLC with hexane/chloroform (2:1, v/v) as the eluent. The major dark brown band gave a brown solid after work-up. The dark brown solid was washed with hexane to give pure Ru₆Pt₂(μ-H)₂(μ₃-H)₄(IPr)₂(CO)₁₆, **12**. Dark brown crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

Yield = 27.0 mg (56 %)

IR (DCM) : ν_{CO} 2068 (vw), 2049 (m), 2043 (m), 2021 (s), 2007 (vs), 1989 (w, sh), 1960 (w), 1944 (w) cm⁻¹.

¹H NMR (400 MHz, C₆D₆, 25 °C) : δ 7.09 -7.24 (m, 12H, Ar-**H**), 7.28 (s, 4H, Imidazole **H**), 2.87 (sept, 4H, CH(CH₃)₂), 2.78 (sept, 4H, CH(CH₃)₂), 1.39 (dd, 24H, CH(CH₃)₂), 0.93 (dd, 24H, CH(CH₃)₂), -8.27 (t, hydride, ¹J_{Pt-H} = 587 Hz), -12.33 (m, hydride), -14.50 (s, hydride) ppm

¹H NMR (400 MHz, toluene-d₈, -60 °C) : δ 7.06 -7.20 (m, 12H, Ar-**H**), 6.30 (s, 4H, Imidazole **H**), 2.84 (broad m, 4H, CH(CH₃)₂), 2.72 (broad m, 4H, CH(CH₃)₂), 1.39 (dd, 24H, CH(CH₃)₂), 0.93 (dd, 24H, CH(CH₃)₂), -8.30 (t, 2H, hydride, ¹J_{Pt-H} = 588 Hz), -12.19 (t, 2H, hydride, ²J_{Pt-H} = 120 Hz), -14.57 (s, 2H, hydride) ppm

ESI-MS⁺ m/z: 2226.82 [M]⁺, 2202.82 [M - CO]⁺

Hi-res MS⁺: calcd for C₇₀H₇₉N₄O₁₆¹⁰¹Ru¹⁰²Ru₅¹⁹⁰Pt¹⁹⁵Pt 2226.9011; found 2226.9011.

X-Ray crystallographic analyses

X-ray data was collected at 103 K on a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the SMART suite of programs.³² The data was processed and corrected for Lorentz and polarisation effects with SAINT,³³ and for absorption effects with SADABS.³⁴ Structural solution and refinement were carried out with the SHELXTL suite of programs.³⁵ The structures were solved by direct methods or Patterson methods to locate the heavy atoms, followed by successive difference maps for the light, non-hydrogen atoms. The crystal of **12** were found to be twinned; the twin law and cell parameters were determined using the program CELL_NOW,³⁶ and the reflection data were processed and corrections applied using the program TWINABS.³⁷ All non-hydrogen atoms were refined with anisotropic thermal parameters in the final model. All hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, and refined with a riding model. The metal hydrides were placed by potential energy calculations using the XHYDEX program, with fixed isotropic thermal parameters.²² For cluster **12**, five of the hydride positions were located by potential energy calculations using the XHYDEX program;²² one of them (H2) was placed in a calculated position in accord with the symmetry implied in the NMR data.

DCM solvates found in the crystal of cluster **11** were disordered. A common U[iso] was used for the C atoms and another for all the Cl atoms. These were modeled with two alternative sites of equal occupancies (totalling 0.5 molecule) with appropriate bond and distance restraints. There were also disorder of the isopropyl groups. Both disordered groups have been modelled with two sites for each of the methyl groups only, of equal occupancies. Crystal and refinement data are summarized in Table 2.1.

Table 2.1. Crystal and structure refinement data for **8a**, **9a**, **11** and **12**.

Complex	8a	9a	11.(0.5CH₂Cl₂)	12
Empirical formula	C ₃₈ H ₃₆ N ₂ O ₁₁ Ru ₄	C ₆₀ H ₇₂ N ₄ O ₆ Pt ₂ Ru	C ₄₅ H ₃₈ N ₂ O ₁₈ Ru ₆ Pt.0.5CH ₂ Cl ₂	C ₇₀ H ₇₈ N ₄ O ₁₆ Pt ₂ Ru ₆
Formula weight	1100.97	1436.46	1738.74	2227.96
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
a (Å)	14.4526(12)	12.5512(3)	10.7776(9)	19.86(3)
b (Å)	14.5434(14)	24.8654(6)	19.1465(14)	20.36(3)
c (Å)	20.482(2)	18.3948(4)	27.137(2)	19.44(3)
α (deg)	90	90	90	90
β (deg)	90	91.9115(14)	90	97.28(3)
γ (deg)	90	90	90	90
Volume, Å ³	4305.2(7)	5737.6(2)	5599.7(8)	7794(21)
Z	4	4	4	4
Density (calculated), Mg/m ³	1.699	1.663	2.062	1.899
Absorption coefficient, mm ⁻¹	1.432	11.451	4.178	4.768
F(000)	2168	2832	3316	4296
Crystal size, mm ³	0.12 x 0.18 x 0.28	0.26 x 0.16 x 0.01	0.06 x 0.06 x 0.02	0.12 x 0.14 x 0.20
Reflections collected	29525	49077	59524	224172
Independent reflections	10670 [R(int) = 0.1363]	10121 [R(int) = 0.0656]	9905 [R(int) = 0.1376]	19197 [R(int) = 0.1766]
Max. and min. transmission	0.85 and 0.44	0.89 and 0.52	0.92 and 0.79	0.75 and 0.46
Data / restraints / parameters	10670 / 0 / 504	10121 / 18 / 674	9905 / 433 / 693	19197 / 840 / 899
Goodness-of-fit on F ²	1.016	1.234	1.034	1.116
Final R indices [I>2s(I)]	R1 = 0.0745 wR2 = 0.1809	R1 = 0.0492 wR2 = 0.1347	R1 = 0.0513 wR2 = 0.0821	R1 = 0.0773 wR2 = 0.1903
R indices (all data)	R1 = 0.0943 wR2 = 0.2011	R1 = 0.0540 wR2 = 0.1375	R1 = 0.0824 wR2 = 0.0936	R1 = 0.1299 wR2 = 0.2253
Largest diff. peak and hole, e.Å ⁻³	1.983 and -1.676	2.171 and -2.661	1.070 and -1.096	2.089 and -3.784

2.7 References

- (1) Gasteiger, H. A.; Markovic, N.; Ross, P. N.; Cairns, E. J. *The Journal of Physical Chemistry* **1993**, *97*, 12020.
- (2) Iwasita, T.; Hoster, H.; John-Anacker, A.; Lin, W. F.; Vielstich, W. *Langmuir* **2000**, *16*, 522.
- (3) Park, K.-W.; Sung, Y.-E.; Han, S.; Yun, Y.; Hyeon, T. *The Journal of Physical Chemistry B* **2004**, *108*, 939.
- (4) García, B. L.; Captain, B.; Adams, R. D.; Hungria, A. B.; Midgley, P. A.; Thomas, S. J. M.; Weidner, J. W. *J. Cluster Sci.* **2007**, *18*, 121.
- (5) Koh, A. C. W.; Leong, W. K.; Chen, L.; Ang, T. P.; Lin, J.; Johnson, B. F. G.; Khimyak, T. *Catal. Commun.* **2008**, *9*, 170.
- (6) Koh, A. C. W.; Chen, L.; Leong, W. K.; Ang, T. P.; Johnson, B. F. G.; Khimyak, T.; Lin, J. *Int. J. Hydrogen Energy* **2009**, *34*, 5691.
- (7) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28.
- (8) Manzoli, M.; Shetti, V. N.; Blaine, J. A.; Zhu, L.; Isrow, D.; Yempally, V.; Captain, B.; Coluccia, S.; Raja, R.; Gianotti, E. *Dalton Trans.* **2012**, *41*, 982.
- (9) Adams, R. D.; Barnard, T. S.; Cortopassi, J. E.; Wu, W.; Li, Z.; Shapley, J. R.; Lee, K. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 2007, p 280.
- (10) Antonucci, V.; Aricò, A. S.; Calderazzo, F.; Labella, L.; Marchetti, F. *J. Cluster Sci.* **2001**, *12*, 293.
- (11) Adams, R. D.; Li, Z.; Lii, J. C.; Wu, W. *Organometallics* **1992**, *11*, 4001.
- (12) Adams, R. D.; Alexander, M. S.; Arafa, I.; Wu, W. *Inorg. Chem.* **1991**, *30*, 4717.
- (13) Hermans, S.; Khimyak, T.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **2001**, 3295.
- (14) Hermans, S.; Khimyak, T.; Feeder, N.; Teat, S. J.; Johnson, B. F. G. *Dalton Trans.* **2003**, 672.

- (15) Johnson, Brian F. G.; Hermans, S.; Khimyak, T. *Eur. J. Inorg. Chem.* **2003**, 2003, 1325.
- (16) Adams, R. D.; Captain, B.; Fu, W.; Hall, M. B.; Manson, J.; Smith, M. D.; Webster, C. E. *J. Am. Chem. Soc.* **2004**, 126, 5253.
- (17) Adams, R.; Boswell, E.; Captain, B.; Zhu, L. *J. Cluster Sci.* **2008**, 19, 121.
- (18) Saha, S.; Captain, B. *Inorg. Chem.* **2014**, 53, 1210.
- (19) Fantasia, S.; Nolan, S. P. *Chem. Eur. J.* **2008**, 14, 6987.
- (20) Liu, Y.; Ganguly, R.; Huynh, H. V.; Leong, W. K. *Organometallics* **2013**, 32, 7559.
- (21) Liu, Y., PhD thesis, Nanyang Technological University **2014**.
- (22) Orpen, G. *XHYDEX: A Program for Locating Hydrides in Metal Complexes*; School of Chemistry, University of Bristol: UK, 1997.
- (23) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Organometallics* **2009**, 28, 1832.
- (24) Cooke, C. E.; Jennings, M. C.; Pomeroy, R. K.; Clyburne, J. A. C. *Organometallics* **2007**, 26, 6059.
- (25) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.
- (26) McCarthy, D. A.; Krause Bauer, J.; Hong, F.-E.; Ran Oh, J.; Deng, H.; Liu, J.; Shore, S. G. *J. Organomet. Chem.* **1998**, 550, 309.
- (27) Still, B. M.; Kumar, P. G. A.; Aldrich-Wright, J. R.; Price, W. S. *Chem. Soc. Rev.* **2007**, 36, 665.
- (28) Khimyak, T.; Johnson, B. F. G.; Hermans, S.; Bond, A. D. *Dalton Trans.* **2003**, 2651.
- (29) Adams, R. D.; Captain, B.; Zhu, L. *J. Organomet. Chem.* **2006**, 691, 3122.
- (30) Bruce, M. I.; Jensen, C. M.; Jones, N. L.; Süß-Fink, G.; Herrmann, G.; Dase, V. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 2007, p 216.

- (31) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.
- (32) *SMART Version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.*
- (33) *SAINT+ Version 6.22a, Bruker AXS Inc, Madison, Wisconsin, USA, 2001.*
- (34) *Sheldrick, G.M. SADABS; University of Göttingen, Göttingen, Germany, 1996.*
- (35) *SHELXTL Version 5.1, Bruker AXS Inc, Madison, Wisconsin, USA, 1997.*
- (36) *Sheldrick, G.M. CELL_NOW; University of Göttingen, Göttingen, Germany, 2008.*
- (37) *Sheldrick, G.M. TWINABS; University of Göttingen, Göttingen, Germany, 2008.*

Chapter 3: Reactions of the [Pt(NHC)] fragment with cobalt carbonyl clusters

3.1 Cluster precursors to CoPt catalysts

The cobalt-platinum bimetallic system has been reported to be effective oxidation catalysts for methanol electro-oxidation, toluene combustion and preferential CO oxidation reactions.¹⁻⁵ However, cluster-derived cobalt-platinum catalysts have yet to be used for any oxidation reactions. The only reported cluster-derived cobalt-platinum bimetallic catalysts were tested for the hydrogenolysis and demethylation of methylcyclopentane.⁶

The high nuclearity cobalt-platinum cluster $[\text{Co}_8\text{Pt}_4(\mu_6\text{-C})_2(\text{CO})_{24}]^{2-}$ can be obtained in good yield by a redox condensation reaction of $[\text{Co}_6(\mu_6\text{-C})(\text{CO})_{15}]^{2-}$ with two equivalents of $\text{PtCl}_2(\text{Et}_2\text{S})_2$. With a lower equivalent of $\text{PtCl}_2(\text{Et}_2\text{S})_2$, however, a mixture of species that were tentatively formulated as $[\text{Co}_9\text{Pt}_3(\mu_6\text{-C})_2(\text{CO})_{24}]^{n-}$ ($n = 2, 3$) was obtained.⁷ Control of the bimetallic composition is thus an issue.

A more convenient and controlled synthetic methodology is the addition of unsaturated [Pt(L)] fragments to cobalt carbonyl clusters. For example, the reaction of $\text{Co}_3(\mu_3\text{-CH})(\text{CO})_9$, **21** and $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPr}^i_3)_2$ gave $\text{Co}_3\text{Pt}_2(\mu_2\text{-H})(\mu_5\text{-C})(\text{PPr}^i_3)_2(\text{CO})_9$, **24** and $\text{Co}_3\text{Pt}_3(\mu_2\text{-H})(\mu_6\text{-C})(\text{PPr}^i_3)_3(\text{CO})_9$, **25** (Scheme 3.1).⁸

Scheme 3.1

While the chemistry of $[\text{Pt}(\text{PR}_3)]$ fragments are known, the addition of $[\text{Pt}(\text{NHC})]$ fragments onto cobalt carbonyl clusters have yet to be explored. Thus, it is interesting to

explore analogous reactions with [Pt(NHC)], which can be generated *in situ* from Pt(NHC)(allyl)Cl as described in Chapter 2.

3.2 Synthesis of Co₂Pt₂(IPr)₂(μ₂-CO)₄(CO)₄, **23a**

The cluster Co₂Pt₂(IPr)₂(μ₂-CO)₄(CO)₄, **23a** can be obtained as an air-stable purple solid from the room temperature reaction of two equivalents of [Pt(IPr)] with either Co₂(CO)₈, **20** or Co₄(CO)₁₂, **22** (Scheme 3.2). In the former reaction, two units of [Pt(IPr)] has been added onto cluster **20**. In the latter reaction, cluster **23a** was the only isolated product, and no Co₄Pt_x cluster was observed even with one molar equivalent of [Pt(IPr)].

Scheme 3.2

The molecular structure of cluster **23a** has been confirmed by an X-ray crystallographic analysis. An ORTEP plot showing the molecular structure, together with selected bond parameters, is given in Figure 3.1. The crystal of cluster **23a** exhibited disorder about a mirror passing through the two Pt atoms. The molecule itself possesses crystallographically-imposed symmetry as it is located at a special position with 2/m symmetry, with the 2-fold rotation axis through the Pt atoms. The IR spectrum confirmed the presence of both terminal and bridging CO ligands, while the NMR spectrum showed one set of resonances for the IPr carbene ligand.

Figure 3.1. ORTEP diagram of cluster **23a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)-Pt(1A) = 2.7570(6), Pt(1)-Co(1) = 2.526(2) / 2.58226(2)*, Pt(1)-Co(1A) = 2.5918(19) / 2.5672(19)*, Co(1A)-Pt(1)-Co(1) = 114.83(5) / 115.26(5)*, Co(1)-Pt(1)-Pt(1A) = 58.56(4) / 57.89(4)*, Co(1)-Pt(1)-Pt(1A) = 56.27(5) / 57.37(4)*. *values for the other half of the disorder.

The valence electron count for cluster **23a** is 58, which is in accord with the EAN rule if Pt adopts an expected 16-electron configuration. There is a Pt-Pt bonding interaction (Pt(1)-Pt(1A) = 2.7570(6) Å), but no Co-Co bond (Co(1)...Co(1A) ~ 4.349 Å). This contrasts with its phosphine analogue Co₂Pt₂(PPh₃)₂(μ₂-CO)₃(CO)₅, **23b**, which has a butterfly Co₂Pt₂ core, an intact Co-Co bond (2.498(3) Å) and a Pt...Pt distance of 2.987(4) Å (Figure 3.2).⁹ In comparison, The Co₂Pt₂ core is constrained by the 2/m symmetry to be planar, unlike that of any known phosphine derivatives of CoPt clusters. This difference in

skeletal arrangement is not uncommon in heteronuclear clusters, however. For example, with Mo_2Pt_2 clusters, while $\text{Mo}_2\text{Pt}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{PEt}_3)_2(\mu_2\text{-CO})_6$ has a planar Mo_2Pt_2 core, $\text{Mo}_2\text{Pt}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)_2(\mu_2\text{-CO})_4(\text{CO})_2$ has a butterfly core.^{10,11} Moreover, interconversion in solution between skeletal isomers is also possible, for example, the bulkier phosphine analogues $\text{Mo}_2\text{Pt}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{PR}_3)_2(\text{CO})_6$ ($\text{R} = \text{Cy}$ or Pr^i) can exist in solution with both a planar or a tetrahedral core.¹² There is no evidence for such skeletal rearrangement in solution in cluster **23a**, however.

Figure 3.2. Molecular structure of cluster **23a** and **23b**.

3.3. Synthesis of $\text{Co}_4\text{Pt}_2(\mu_6\text{-C})(\text{IPr})_2(\mu_2\text{-CO})_5(\text{CO})_6$, **26a**

The reaction of $[\text{Pt}(\text{IPr})]$ with cluster **21** at room temperature gave multiple products, of which two were identified as **23a** and the new cluster $\text{Co}_4\text{Pt}_2(\mu_6\text{-C})(\text{IPr})_2(\mu_2\text{-CO})_5(\text{CO})_6$, **26a** which was isolated as an air-stable green solid (Scheme 3.3). Interestingly, the IPr analogues of **24** and **25** shown in Scheme 3.1 were not observed, even with various molar equivalents of $[\text{Pt}(\text{IPr})]$.

Scheme 3.3

The molecular structure of **26a** has been confirmed by a single-crystal X-ray crystallographic analysis; the ORTEP plot showing its molecular structure, together with selected bond parameters, is given in Figure 3.3. IR analysis confirmed the presence of both terminal and bridging CO ligands, while the NMR spectrum showed one set of resonances for the IPr carbene, consistent with the symmetry of the cluster. The molecular structure of cluster **26a** shows a distorted octahedral $\text{Co}_4\text{Pt}_2(\mu_6\text{-C})$ core. The basal plane made up by the four cobalt atoms is puckered, with the two $[\text{Pt}(\text{IPr})]$ fragments at the axial positions. There are no hydride ligands present, and the cluster valence electron count of 86 is in accord with PSEPT for a *closo* octahedron.

Figure 3.3. ORTEP diagram of cluster **26a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Co(1)-C(1) = 1.880(13), Co(2)-C(1) = 1.846(12), Co(3)-C(1) = 1.846(13), Co(4)-C(1) = 1.869(12), Pt(1)-C(1) = 2.123(12), Pt(2)-C(1) = 2.142(12), Co(1)-Co(2) = 2.705(3), Co(1)-Co(4) = 2.518(3), Co(2)-Co(3) = 2.698(2), Co(3)-Co(4) = 2.692(3), Co(1)-Pt(2) = 2.6359(19), Co(2)-Pt(2) = 2.9791(18), Co(3)-Pt(2) = 2.6322(19), Co(4)-Pt(2) = 3.0428(19), Co(2)-Pt(1) = 2.6389(19), Co(3)-Pt(1) = 2.8972(18), Co(4)-Pt(1) = 2.6401(19), Co(1)-Pt(1) = 3.1303.

The molecular geometry of **26a** closely resembles that of the only known [Pd(PPh₃)] analogue, Co₄Pd₂(μ₆-C)(PPh₃)₂(μ₂-CO)₅(CO)₆, **26b** (Figure 3.4).¹³

Figure 3.4. Molecular structure of cluster **26a** and **26b**.

The Co-C_{carbide} and Co-Co bond lengths (1.846(12) - 1.869(12) and 2.518(3) - 2.705(3) Å, respectively) in **26a** are comparable to those in the octahedral cluster [Co₆(μ₆-C)(CO)₁₃]²⁻ (1.852(3) - 1.880 and 2.4618(8) - 2.926(1) Å, respectively).¹⁴ The Pt-C_{carbide} and the Co-Pt bond lengths (2.123(12) - 2.142(12) and 2.6322(19)Å - 3.1303(2) Å, respectively) in **26a** are also comparable to those found in **25** (2.04(1) - 2.16(1) and 2.598(3) - 3.060(3) Å, respectively).⁸ One of the Co-Pt bonds (Pt(1)-Co(1) = 3.1303(2) Å) is unusually long, which we believe may be due to the effects of crystal packing forces. An attempt was made to corroborate this via a natural bond orbital (NBO) analysis on **26a** with density functional theory (DFT) at the def2SVP/6-31G* level of theory. The Wiberg bond indices and metal-metal bond lengths for the optimised geometry are given in Figure 3.5.

Figure 3.5. Wiberg bond indices (left) and (ii) calculated metal-metal bond lengths in Å(right) of **26a**.

The bond indices for the Co-Pt bonds can be divided into two sets, with values in the ranges 0.13-0.16 (Pt(1)-Co(1), Pt(1)-Co(3), Pt(2)-Co(4) and Pt(2)-Co(2)), and 0.21-0.24 (Pt(1)-Co(4), Pt(1)-Co(2), Pt(2)-Co(1) and Pt(2)-Co(2)). They correlate well with both the calculated and experimental bond lengths; those with shorter bond lengths correspond to higher bond indices, in accord with the trend reported for metal-metal bonds.¹⁵ Although there are no reports of bond indices for Co-Pt bonds, it has been reported that homonuclear metal-metal bonds such as the single Ru-Ru bond has a bond index ~ 0.2 ,^{16,17} and that for a single Fe-Fe bond has a bond index ~ 0.1 .¹⁸ The bond indices calculated here thus suggest that the Pt(1)-Co(1) vector corresponds to a single metal-metal bond.

The formation of **23a** and **26a** requires a change in the nuclearity of the reactant **21** and may be attributed to the ease with which cobalt carbonyl clusters undergo cluster fragmentation/rearrangement. Moreover, **23a** and **26a** do not contain any hydrides; the fate of the hydrogen atom in **21** has not been traced. A change in nuclearity is not unprecedented; as has been described in section 1.1, the reaction of the cluster $[\text{Co}_6(\mu_6\text{-C})\text{CO}]_{15}]^{2-}$ with a lower molar equivalent of $\text{Au}(\text{PPh}_3)\text{Cl}$ afforded a Co_6Au_x cluster, while

use of a larger molar equivalent resulted in a reduction in nuclearity to afford Co_4Au_x and Co_5Au_x clusters.¹⁹ The formation of **26a** can thus be viewed as the stabilisation of the unobserved neutral $\text{Co}_4(\mu_4\text{-C})(\text{CO})_{11}$ cluster by two $[\text{Pt}(\text{IPr})]$ fragments, and is reminiscent of the reported $\text{Co}_4\text{Au}_2(\mu_6\text{-C})(\text{PPh}_3)_2(\text{CO})_{10}$, which has been regarded as a stabilized form of the unobserved anionic cluster $[\text{Co}_4(\mu_4\text{-C})(\text{CO})_{10}]^{2-}$ by two $[\text{Au}(\text{PPh}_3)]^+$ fragments.¹⁹

3.4 Concluding remarks

In this chapter, it was found that the $[\text{Pt}(\text{IPr})]$ fragment can react with a variety of cobalt carbonyl clusters to give heteronuclear cobalt-platinum clusters; these are summarised in Scheme 3.4.

Scheme 3.4

In all cases, the Co_2Pt_2 cluster **23a** was obtained, through an addition reaction in **20** and cluster fragmentation in **21** and **22**. The reaction of the tricobalt cluster **21** also afforded the Co_4Pt_2 cluster **26a**, which may be viewed as the $\text{Pt}(\text{NHC})$ -stabilised product of the unobserved neutral cluster $\text{Co}_4(\mu_4\text{-C})(\text{CO})_{11}$ formed via cluster fragmentation and

condensation. The Co_2Pt_2 core in **23a** is planar, unlike the butterfly core observed in the only known, isoelectronic, cluster **23b**.

3.5 Experimental

All reactions were performed under an argon atmosphere using standard Schlenk techniques or in the glove box. Solvents used in reactions were of AR grade, and were dried under the appropriate drying agent and distilled under nitrogen; and stored in flasks fitted with Teflon valves prior to use. Toluene was dried over sodium/benzophenone, IPA over Mg/I_2 and DCM over CaH_2 . The products were separated by thin-layer chromatography (TLC), using Merck silica gel 60 Å F 254 $20 \times 20 \text{ cm}^2$ plates. ^1H NMR spectra were collected using a Bruker BBFO 400 or AV 300 NMR spectrometer, with chemical shifts referenced to the solvent residual peaks. 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. High resolution mass spectra were recorded in electrospray ionization (ESI) mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by the microanalytical laboratory at NTU. Single crystal X-ray crystallographic analyses were performed by Dr Rakesh Ganguly and/or Dr Li Yongxin from the NTU. $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ were purchased from Alfa Aesar. $\text{Co}_3(\mu_3\text{-CH})(\text{CO})_9$ ^{20,21} and $\text{Pt}(\text{C}_4\text{H}_7)(\text{IPr})\text{Cl}$ ²² were prepared according to the published methods. All other reagents were used as received from commercial suppliers.

Reaction of cluster **20** with $[\text{Pt}(\text{IPr})]$

$\text{Pt}(\text{IPr})(\text{C}_4\text{H}_7)\text{Cl}$ (30.0 mg, 0.0445 mmol) and KO^tBu (5.0 mg, 0.045 mol) were heated at 80°C in IPA (5 mL) for 1 h. The initial colourless solution turned yellow. Solvent was removed under vacuum to give a yellow oil. The yellow oil was re-dissolved in toluene to give a yellow solution, in which cluster **20** (7.6 mg, 0.022 mmol) was subsequently added. The reaction mixture turned red-purple and was left to stir at rt for 3 h. After removal of

the solvent, the residue was re-dissolved in minimal amount of toluene and filtered through a thin pad of silica gel. Solvent was removed, washed with hexane, and the product is extracted with diethyl ether. Removal of solvent afforded $\text{Co}_2\text{Pt}_2(\text{IPr})_2(\mu_2\text{-CO})_4(\text{CO})_4$, **23a** as a purple solid. The purple solid was crystallized in a DCM/hexane mixture at 4 °C to give purple crystals. Yield = 27.4 mg (82 %)

IR (Et₂O) : ν_{CO} 2034 (w), 2018 (s), 2002 (w), 1978 (vs), 1942 (vw), 1837 (m), 1817 (s), 1796 (w) cm^{-1} .

¹H NMR (400 MHz, C₆D₆) : δ 7.08 (d, 4H, *meta*-Ar-**H**), 6.52 (t, 2H, Imidazole **H**), 2.97 (sept, 4H, **CH**(CH₃)₂), 1.44 (dd, 12H, CH(**CH**₃)₂), 0.92 (dd, 12H, CH(**CH**₃)₂)

ESI-MS⁺ m/z: 1285.39 [M-8CO]⁺

Hi-res MS⁺ : calcd for C₆₂H₇₃N₄O₈⁵⁹Co₂¹⁹⁴Pt₂ 1507.3318; found 1507.3346.

Elemental Analysis (%) calcd for C₆₂H₇₂Co₂N₄O₈Pt₂·0.5CH₂Cl₂: C 48.38, H 4.74, N 3.61; found: C 48.16, H 4.98, N 3.53.

Reaction of cluster **22** with [Pt(IPr)]

Pt(IPr)(C₄H₇)Cl (21.1 mg, 0.0329 mmol) and KO^tBu (3.5 mg, 0.033 mol) were heated to 80 °C in IPA (5 mL) for 1 h. The initial colourless solution turned yellow. Solvent was removed under vacuum to give a yellow oil. The yellow oil was re-dissolved in toluene to give a yellow solution, in which a dark brown toluene solution of cluster **22** (6.0 mg, 0.010 mmol) was subsequently added. The reaction mixture was subsequently left to stir for 15 h in which the solution turned purple-brown. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by silica gel column chromatography with hexane:DCM (1:1, v/v) as the eluent, gave cluster **23a** as the major product. Yield = 17.8 mg (56 %)

Reaction of cluster **21** with [Pt(IPr)]

A solution of Pt(IPr)(C₄H₇)Cl (19.5 mg, 0.0289 mmol) and KO^tBu (3.3 mg, 0.029 mmol) in IPA (10 mL) were heated at 80 °C for 1 h to give a yellow solution. Solvent was removed under vacuum to give a yellow oil. The yellow oil was redissolved in DCM to give a yellow solution, to which cluster **21** (6.2 mg, 0.014 mmol) was added. The reaction mixture was stirred at rt for 15 h during which the solution turned dark brown. After removal of the solvent, the residue was re-dissolved in a minimal amount of DCM and separated by TLC with hexane:DCM (5:2, v/v) as the eluent. Two major bands were isolated and characterized.

The first major green band was isolated as a green solid, which was identified as Co₄Pt₂(μ₆-C)(IPr)₂(μ₂-CO)₅(CO)₆, **26a**. (Yield = 5.4 mg, 29 %) The green solid was crystallized in a diethyl ether solution at 4 °C to give dark green crystals.

IR (DCM): ν_{CO} 2047 (vw), 2010 (vs), 1846 (m), 1819 (m, sh) cm⁻¹.

¹H NMR (400 MHz, CDCl₃) : δ 7.05 (d, 4H, *meta*-Ar-**H**), 6.73 (t, 2H, Imidazole **H**) , 2.97 (sept, 4H, CH(CH₃)₂), 1.43 (dd, 12H, CH(CH₃)₂), 0.89 (dd, 12H, CH(CH₃)₂)

ESI-MS⁺ m/z: 1723.25 [M]⁺, 1695.26 [M-CO]⁺, 1639.25 [M-3CO]⁺

Hi-res MS⁺ : calcd for C₆₆H₇₃N₄O₁₁⁵⁹Co₄¹⁹⁵Pt¹⁹⁶Pt 1724.1901; found 1724.1995.

The second purple-brown band, which gave a purple solid when dried, was identified to be cluster **23a** by its IR spectrum. (Yield = 3.3 mg, 20 %)

IR (Et₂O): ν_{CO} 2034 (w), 2018 (s), 2002 (w), 1978 (vs), 1942 (vw), 1837 (m), 1817 (s), 1796 (w) cm⁻¹.

Computational studies

Computational studies were carried out with the Gaussian 09W suite of programs, with the M06L density functional, utilizing def2SVP basis set for Pt atoms, while the 6-31G* basis set is used for the remaining atoms.²³ Natural Bond Orbital (NBO) analysis was carried out with the NBO 3.1 program implemented within Gaussian 09W.²⁴

X-Ray crystallographic analyses

X-ray data was collected at 103 K on a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the SMART suite of programs.²⁵ The data was processed and corrected for Lorentz and polarisation effects with SAINT,²⁶ and for absorption effects with SADABS.²⁷ Structural solution and refinement were carried out with the SHELXTL suite of programs.²⁸ The structures were solved by direct methods or Patterson methods to locate the heavy atoms, followed by successive difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final model.

The crystal of cluster **23a** was found that have disordered at all the diisopropylphenyl groups, CO ligands and the cobalt atoms. These were modeled with two alternative sites of equal occupancies (totalling 0.5 molecule) with appropriate bond and distance restraints. A diethyl ether solvate was found in the asymmetric unit of the crystal of cluster **26a**. Crystal and refinement data are summarized in Table 3.1.

Table 3.1. Crystal and structure refinement data for complexes

Complex	23a	26a.Et₂O
Empirical formula	C ₆₂ H ₇₂ Co ₂ N ₄ O ₈ Pt ₂	C ₇₀ H ₈₂ Co ₄ N ₄ O ₁₂ Pt ₂
Formula weight	1509.28	1797.29
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/n
Unit cell dimensions	a = 13.048(2) Å b = 14.253(2) Å c = 16.460(3) Å α = 90° β = 98.476(12) ° γ = 90°	a = 12.5072(15) Å b = 31.460(4) Å c = 18.748(3) Å α = 90° β = 102.637(5) ° γ = 90°
Volume, Å ³	3027.8(8)	7198.3(15)
Z	2	4
Density (calculated), Mg/m ³	1.655	1.658
Absorption coefficient, mm ⁻¹	5.200	4.832
F(000)	1492	3560
Crystal size, mm ³	0.22 x 0.12 x 0.10	0.34 x 0.14 x 0.06
Reflections collected	47666	119217
Independent reflections	6186 [R(int) = 0.1315]	14704 [R(int) = 0.1698]
Max. and min. transmission	0.6244 and 0.3942	0.76 and 0.29
Data / restraints / parameters	6186 / 566 / 473	14704 / 516 / 847
Goodness-of-fit on F ²	1.094	1.197
Final R indices [I>2σ(I)]	R1 = 0.0417 wR2 = 0.0986	R1 = 0.0792 wR2 = 0.1679
R indices (all data)	R1 = 0.0676 wR2 = 0.1257	R1 = 0.1264 wR2 = 0.1893
Largest diff. peak and hole, e.Å ⁻³	1.362 and -1.534	2.772 and -3.165

References

- (1) Nouralishahi, A.; Rashidi, A. M.; Mortazavi, Y.; Khodadadi, A. A.; Choolaei, M. *Appl. Surf. Sci.* **2015**, *335*, 55.
- (2) Kepenienė, V.; Tamašauskaitė-Tamašiūnaitė, L.; Jablonskienė, J.; Semaško, M.; Vaičiūnienė, J.; Vaitkus, R.; Norkus, E. *Mater. Chem. Phys.* **2016**, *171*, 145.
- (3) Yang, H.; Deng, J.; Liu, Y.; Xie, S.; Xu, P.; Dai, H. *Chinese Journal of Catalysis* **2016**, *37*, 934.
- (4) Yu, X.; Li, H.; Tu, S.-T.; Yan, J.; Wang, Z. *Int. J. Hydrogen Energy* **2011**, *36*, 3778.
- (5) López, A.; Navascues, N.; Mallada, R.; Irusta, S. *Appl. Catal., A* **2016**, *528*, 86.
- (6) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28.
- (7) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Wolowska, J.; Zacchini, S.; Zanello, P.; Fedi, S.; Riccò, M.; Pontiroli, D.; Mazzani, M. *J. Am. Chem. Soc.* **2010**, *132*, 2919.
- (8) Jeffery, J. C.; Parrott, M. J.; Stone, F. G. A. *J. Organomet. Chem.* **1990**, *382*, 225.
- (9) Fischer, J.; Mitschler, A.; Weiss, R.; Dehand, J.; Nennig, J. F. *J. Organomet. Chem.* **1975**, *91*, C37.
- (10) Bender, R.; Braunstein, P.; Dusauso, Y.; Protas, J. *J. Organomet. Chem.* **1979**, *172*, C51.
- (11) Gordon, F.; Stone, A. *Inorg. Chim. Acta* **1981**, *50*, 33.
- (12) Braunstein, P.; De Meric de Bellefon, C.; Bouaoud, S. E.; Grandjean, D.; Halet, J. F.; Saillard, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 5282.
- (13) Ciabatti, I.; Fabrizi de Biani, F.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Zacchini, S. *ChemPlusChem* **2013**, *78*, 1456.
- (14) Albano, V. G.; Braga, D.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1986**, 981.
- (15) Singh, V.; Dixit, M.; Kosa, M.; Major, D. T.; Levi, E.; Aurbach, D. *Chemistry – A European Journal* **2016**, *22*, 5269.

- (16) Fowe, E. P.; Therrien, B.; Süss-Fink, G.; Daul, C. *Inorg. Chem.* **2008**, *47*, 42.
- (17) Oh, S. P.; Chor, B. Y.; Fan, W. Y.; Li, Y.; Leong, W. K. *Organometallics* **2011**, *30*, 6774.
- (18) Wang, H.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11376.
- (19) Ciabatti, I.; Femoni, C.; Hayatifar, M.; Iapalucci, M. C.; Zacchini, S. *Inorg. Chim. Acta* **2015**, *428*, 203.
- (20) Sugihara, T.; Wakabayashi, A.; Nagai, Y.; Takao, H.; Imagawa, H.; Nishizawa, M. *Chem. Commun.* **2002**, 576.
- (21) Nestle, M. O.; Hallgren, J. E.; Seyferth, D.; Dawson, P.; Robinson, B. H. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 1980, p 226.
- (22) Fantasia, S.; Nolan, S. P. *Chem. Eur. J.* **2008**, *14*, 6987.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; E., P. J. J.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, revision D.01*, Gaussian, Inc., Wallingford CT **2009**.

- (24) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *The NBO 3.1 program*
- (25) *SMART Version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.*
- (26) *SAINT+ Version 6.22a, Bruker AXS Inc, Madison, Wisconsin, USA, 2001.*
- (27) *Sheldrick, G.M. SADABS; University of Göttingen, Göttingen, Germany, 1996.*
- (28) *SHELXTL Version 5.1, Bruker AXS Inc, Madison, Wisconsin, USA, 1997.*

Chapter 4: Reactions of the [Au(NHC)] fragment with ruthenium carbonyl clusters

4.1 Cluster precursors to RuAu catalysts

The ruthenium-gold bimetallic system has been reported to be effective catalysts for the oxidation of glycerol,¹ octanol,² and preferential CO oxidation.³ However, cluster-derived ruthenium-gold has yet to be used for any catalytic reactions.

A well-established synthetic route to ruthenium-gold clusters is the ionic coupling of anionic ruthenium carbonyl clusters with the [Au(PPh₃)]⁺ fragment.⁴⁻⁷ Thus the reaction between [H₃Ru₄(CO)₁₂]⁻ and [(AuPPh₃)₃O][BF₄], **32** gave three clusters, *viz.*, Ru₄Au_n(μ-H)_{4-n}(PPh₃)_n(CO)₁₂ (n = 1-3), through the sequential replacement of hydride ligands by Au(PPh₃) moieties.⁸ An alternative synthetic equivalent for the [Au(PPh₃)]⁺ fragment is Au(PPh₃)Me, which can be used with neutral metal hydrido carbonyl clusters. Thus the reaction of Ru₃(μ-H)₃(μ-COMe)(CO)₉ with Au(PPh₃)Me gave three clusters, *viz.*, Ru₃Au_n(μ-H)_{3-n}(PPh₃)_n(μ-COMe)(CO)₉ (n = 1-3) (Scheme 4.1).^{9,10}

Scheme 4.1

While the chemistry of $[\text{Au}(\text{PR}_3)]^+$ fragments are well-known, the addition of $[\text{Au}(\text{NHC})]^+$ fragments onto ruthenium carbonyl clusters have only recently been explored; the sole example is the oxidative addition of $\text{Au}(\text{NHC})\text{Ph}$ to $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$ to give the two clusters $\text{Ru}_5\text{Au}(\mu_5\text{-C})(\text{NHC})(\mu\text{-}\eta^2\text{-Ph})(\text{CO})_{13}$ and $\text{Ru}_5\text{Au}(\mu_5\text{-C})(\text{NHC})(\text{Ph})(\text{CO})_{14}$, which differ in their bonding mode of the phenyl ligand (Scheme 4.2).¹¹

Scheme 4.2

4.2 Preliminary Study: Reaction of $[\text{Ru}_6(\mu_6\text{-H})(\text{CO})_{18}]^-$, **30 with $[\text{Au}(\text{PPh}_3)]^+$ fragments**

As a preliminary study, reactions of the well-known gold synthons $[\text{Au}(\text{PPh}_3)][\text{NO}_3]$, **31a**. NO_3 and $[(\text{AuPPh}_3)_3\text{O}][\text{BF}_4]$, **32** with the hexaruthenium cluster anion $[\text{Ru}_6(\mu_6\text{-H})(\text{CO})_{18}]^-$, **30** were carried out. The reaction with **31a**. NO_3 gave $\text{Ru}_6\text{Au}(\mu_3\text{-H})(\text{PPh}_3)(\text{CO})_{17}$, **33a** as the only product while that with **32** gave $\text{Ru}_6\text{Au}_3(\mu_6\text{-H})(\text{PPh}_3)_3(\mu_2\text{-CO})_3(\text{CO})_{14}$, **34a** as the major product isolated (Scheme 4.3).

Scheme 4.3

The structures of both products have been characterized crystallographically. The ORTEP plot showing the molecular structure of **33a** is given in Figure 4.1. Unfortunately, the poor quality of the dataset precludes meaningful detailed structural discussion but the gross structure comprising a bicapped tetrahedron Ru_6 core capped by an $[\text{Au}(\text{PPh}_3)]$ fragment is clear. A hydride resonance at -17.4 ppm, corresponding to a capping hydride, was observed in the ^1H NMR spectrum. All the CO ligands are terminal, in accord with its IR spectrum. With a cluster valence electron count of 84, it is isoelectronic to the known cluster $\text{Ru}_6(\mu_3\text{-H})_2(\mu\text{-CO})(\text{CO})_{16}$, **33b**, which also comprises a bicapped tetrahedron Ru_6 core.^{12,13} The structure of **33a** can thus be regarded as an isolobal replacement of one hydride in **33b** with an $[\text{AuPPh}_3]$ moiety; the main structural difference between them is that **33b** contains one bridging CO ligand, while the CO ligands in **33a** are all terminal (Figure 4.2).

Figure 4.1. ORTEP diagram of cluster **33a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms from the phenyl groups have been omitted for clarity. Unit cell dimensions: $a = 8.592(4) \text{ \AA}$, $b = 13.620(6) \text{ \AA}$, $c = 18.350(8) \text{ \AA}$, $\alpha = 97.384(14)^\circ$, $\beta = 92.907(14)^\circ$, $\gamma = 105.082(14)^\circ$.

Figure 4.2. Molecular structures of **33a** and **33b**.

The ORTEP plot showing the molecular structure of **34a**, together with selected bond parameters, is given in Figure 4.3. It comprises an Ru_6 octahedron core, with a digold

$[\text{Au}_2(\text{PPh}_3)_2]$ and a mononuclear $[\text{Au}(\text{PPh}_3)]$ fragments capping diametrically opposite Ru_3 faces. Presence of the bridging CO ligands is also reflected in the IR spectrum.

Based on the valence electron count, a hydride ligand is expected. While the room temperature ^1H NMR spectrum of **34a** showed a resonance at 9.71 ppm that could be assigned as an interstitial hydride, similar to the interstitial hydride resonance of **30** at 16.4 ppm,¹⁴ the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed only one resonance at 33.4 ppm. At -80°C , however, the ^1H NMR spectrum showed an additional resonance at 15.3 ppm while three additional resonances at 41.0, 66.0 and 69.0 ppm (with a 1:1:1 integration ratio) appeared in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure 4.4). These resonances broadened and finally collapsed at increasing temperatures. It may therefore be proposed that **34a** existed as two isomers; the resonances that did not show any temperature-dependent broadening may be assigned to a major isomer in which all three $[\text{Au}(\text{PPh}_3)]$ ligands are equivalent, while the minor isomer is fluxional and has the structure corresponding to that in the solid-state, i.e., with three non-equivalent $[\text{Au}(\text{PPh}_3)]$ ligands (Figure 4.5).

Figure 4.5. Molecular structures of isomers of cluster **34a**.

Figure 4.3. ORTEP diagram of cluster **34a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) : Au(1)-Ru(1) = 2.7932(13), Au(1)-Ru(2) = 2.9442(15), Au(1)-Ru(3) = 2.9904(17), Au(2)-Au(3) = 2.8951(11), Au(2)-Ru(4) = 2.9045(15), Au(2)-Ru(6) = 2.9146(14), Au(2)-Ru(5) = 2.9476(17), Au(3)-Ru(5) = 2.8331(14), Au(3)-Ru(4) = 2.8549(13), Ru(1)-Ru(3) = 2.9812(15), Ru(1)-Ru(2) = 3.0327(15), Ru(2)-Ru(3) = 2.8464(14), Ru(4)-Ru(5) = 3.062(2), Ru(4)-Ru(6) = 2.973(2), Ru(5)-Ru(6) = 2.929(1), Ru(1)-Ru(4) = 2.8549(18), Ru(1)-Ru(5) = 2.8751(16), Ru(2)-Ru(6) = 2.8560(17), Ru(2)-Ru(5) = 2.8630(15), Ru(3)-Ru(4) = 2.8674(15), Ru(3)-Ru(6) = 2.8850(16).

Figure 4.4. Variable temperature ^1H (top) and $^{31}\text{P}\{^1\text{H}\}$ (bottom) NMR spectra of **34a**.

Cluster **34a** is structurally very similar to the previously reported $\text{Ru}_6\text{Au}_3(\mu_6\text{-B})(\text{PPh}_3)_3(\mu\text{-CO})_2(\text{CO})_{14}$, **34b**.⁵ Since $[\text{Au}(\text{PPh}_3)]$ is isolobal to H, both have a cluster valence electron count of 86, which corresponds to an octahedral geometry based on PSEPT. The main structural difference between them is that the $[\text{Au}(\text{PPh}_3)]$ fragment bridges an Ru-Ru edge in **34b** but caps an Ru_3 face in **34a** (Figure 4.6).⁵ The Ru-Au and Au-Au bond lengths (2.793(1) – 2.990(2) and 2.895(1) Å, respectively) in **34a** are comparable to those in **34b** (2.755(3) – 3.328(3) and 2.902(2) Å, respectively).⁵

Figure 4.6. Molecular structures of **34a** and **34b**.

4.3 Reaction of $[\text{Ru}_6(\mu_6\text{-H})(\text{CO})_{18}]^-$, **30** with $\text{Au}(\text{IPr})\text{Cl}$, **31b.Cl**

The compound $[\text{Au}(\text{IPr})][\text{BF}_4]$, **31b.BF₄** can be obtained through salt metathesis of $\text{Au}(\text{IPr})\text{Cl}$, **31b.Cl** with AgBF_4 , should have similar reactivity to **31a.NO₃**. It was generated in-situ, and its reaction with cluster **30** gave $\text{Ru}_6\text{Au}(\mu_6\text{-H})(\text{IPr})(\text{CO})_{18}$, **35a** (Scheme 4.4).

Scheme 4.4

The molecular structure of **35a** has been confirmed by a single-crystal X-ray crystallographic analysis; the ORTEP plot showing its molecular structure, together with selected bond parameters, is given in Figure 4.7. An $[\text{Au}(\text{IPr})]$ fragment caps one of the faces of the Ru_6 octahedron core. Since the $[\text{Au}(\text{IPr})]^+$ fragment is isolobal to H^+ , the octahedron core is consistent with that predicted from PSEPT for a cluster valence electron count of 86. The Ru-Au bond lengths (2.8264(5) - 2.9149(5) Å) are comparable to those in clusters containing capping $[\text{AuL}]$ fragments, such as, cluster **34a** (2.7932(13) - 2.9904(17) Å). The Ru-Ru bonds associated with the gold-capped faces (range = 2.9105(7) - 2.9692(6) Å, mean = 2.9403 Å) are lengthened compared to the other Ru-Ru bonds (range = 2.8637(7) - 2.9202(7) Å), similar to that in **34a** (range = 2.847(2) - 3.062(2) Å, mean = 2.9658 Å for Ru-Ru bond lengths associated with the gold-capped faces, and range = 2.8549(18) - 2.8850(16) Å for the other Ru-Ru bonds).

Figure 4.7. ORTEP diagram of cluster **35a**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru1-Au7 = 2.8834(5), Ru2-Au7 = 2.9149(5), Ru3-Au7 = 2.8264(5), Ru1-Ru3 = 2.9692(7), Ru2-Ru3 = 2.9412(7), Ru1-Ru2 = 2.9105(6), Ru1-Ru4 = 2.8926(7), Ru1-Ru5 = 2.9202(7), Ru2-Ru4 = 2.8637(7), Ru2-Ru6 = 2.8653(7), Ru3-Ru6 = 2.8691(7), Ru3-Ru5 = 2.8909(7), Ru4-Ru5 = 2.8576(7), Ru4-Ru6 = 2.9202(7), Ru5-Ru6 = 2.9033(7).

The presence of an interstitial hydride ($\mu_6\text{-H}$) is indicated by a singlet resonance at 14.67 ppm. On standing the solution in the fridge for a few weeks, a new hydride resonance at -17.14 ppm developed, which is very similar to that for the capping hydride in **33a**. It is therefore postulated that **35a** spontaneously decarbonylated to form $\text{Ru}_6\text{Au}(\mu_3\text{-H})(\text{IPr})(\text{CO})_{17}$, **35b**. This decarbonylation resulted in a change in the interstitial hydride to a capping hydride, and a change in the geometry of the Ru_6 core from the octahedron to the bi-capped tetrahedron (Scheme 4.5). This is in accordance with PSEPT for a change of the cluster valence electron count from 86 to 84.

Scheme 4.5

This decomposition process is presumably much slower for the “ $\text{Au}(\text{PPh}_3)$ ” analogue as $\text{Ru}_6\text{Au}(\mu_3\text{-H})(\text{PPh}_3)(\text{CO})_{17}$ is unknown. The ν_{CO} patterns for clusters **35a** and **35b** in their IR spectra are also similar (Figure 4.8), suggesting that it would be difficult to differentiate between an $\text{Ru}_6\text{Au}(\mu_6\text{-H})(\text{IPr})(\text{CO})_{18}$ and an $\text{Ru}_6\text{Au}(\mu_3\text{-H})(\text{IPr})(\text{CO})_{17}$ cluster on the basis of their IR spectra.

Figure 4.8. IR spectra of clusters **35a** and **35b**.

Similar spontaneous decarbonylative rearrangement of carbonyl clusters have been reported. For example, the decarbonylation of **3** to **33b** resulted in a change in geometry but the clusters were indistinguishable by their IR spectra (Scheme 4.6).^{12,13}

Scheme 4.6

4.4 Reaction of Ru₄(μ-H)₄(CO)₁₂, **2** with Au(IPr)OH, **31b.OH**

An alternative synthetic equivalent for the Au(NHC) synthon is the NHC-derived gold(I) hydroxide complexes which were recently reported by Nolan and co-workers.^{15,16} These are easily synthesized and highly air stable, and may react with neutral hydrido metal carbonyl clusters with the elimination of a water molecule. The reaction of cluster **2** with two equivalents of Au(IPr)OH, **31b.OH** afforded three products. Of these, two have been structurally characterized as red Ru₄Au₂(μ₃-H)₂Au₂(IPr)₂(CO)₁₂, **37** and yellow-green Ru₃Au₂(IPr)₂(μ-CO)₃(CO)₆, **38**. Diffraction-quality crystals of the last product were not obtained but spectroscopic evidence suggests it to possibly be an Ru₄Au cluster, tentatively formulated as Ru₄AuH₃(IPr)(CO)₁₂, **36** (Scheme 4.7).

Scheme 4.7

Clusters **36** and **37a** may be regarded as resulting from the substitution of hydride ligands with [Au(IPr)] units. The possibility that **38** resulted from thermal decomposition of **37a** has been ruled out; heating **37a** in toluene did not produce **38**. Instead, the yield of **38** increased when the amount of Au(IPr)OH used was increased to 3.5 equivalents, indicating that **38** probably originated directly from the reaction of **2**.

Cluster **36** was isolated as an orange solid. Although the ν_{CO} pattern of its IR spectrum did not match any known M₄Au clusters (where M = group 8), the mass spectrum showed a cluster of peaks assignable to the molecular ion of the proposed molecular

formula. The ^1H NMR spectrum showed resonances which were assignable to two sets of IPr moieties, in a 2:1 intensity ratio; the same was observed for the hydride region, indicating the presence of two isomers (Figure 4.9).

Figure 4.9. ^1H NMR spectrum of **36**.

The ORTEP plot showing the molecular structure, and selected bond parameters, for **37a** are given in Figure 4.10. There are two crystallographically independent molecules and four dichloroethane solvates found in the asymmetric unit; two of the solvates exhibited disorder. The molecular structure of **37a** consists of a *closo* Ru_4 tetrahedron core with two bridging $[\text{Au}(\text{IPr})]$ ligands; each ruthenium vertex carries three CO ligands. This cluster core geometry is in accord with PSEPT for a cluster valence electron count of 60 and is unlike the PPh_3 analogue $\text{Ru}_4\text{Au}_2(\mu\text{-H})(\mu_3\text{-H})(\text{PPh}_3)_2(\text{CO})_{12}$, **37b**, which has a capping digold $[\text{Au}_2(\text{PPh}_3)_2]$ moiety instead of two edge-bridging $[\text{Au}(\text{IPr})]$ moieties (Figure 4.11).¹⁷

Figure 4.10. ORTEP diagram of cluster **37a**. Ellipsoids are drawn at 50% probability level.

Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1-Ru1 = 2.9011(16) / 2.9501(15)*, Au1-Ru2 = 2.9516(16) / 2.9584(15)*, Au2-Ru3 = 2.9350(16) / 2.9247(16)*, Au2-Ru4 = 3.0436(17) / 2.9292(15)*, Ru1- Ru2 = 3.037(2) / 3.0269(19)*, Ru1-Ru3 = 2.791(2) / 2.788(2)*, Ru1-Ru4 = 2.790(2) / 2.8052(19)*, Ru2-Ru3 = 2.802(2) / 2.9247(16)*, Ru2-Ru4 = 2.790(2) / 2.787(2)*, Ru3-Ru4 = 3.041(2) / 3.0615(19)*.

*Values for second molecule in the asymmetric unit.

Figure 4.11. Molecular structures of **37a** and **37b**.

The molecule of **37a** has C_2 symmetry, which renders the IPr ligands chemically equivalent. This is evident in the ^1H NMR spectrum which shows one set resonances for the IPr ligands. There is a major singlet resonance at - 15.73 ppm for the hydrides, and potential energy calculations with the XHYDEX program suggest that they are capping the faces indicated.¹⁸ Their locations are also corroborated by the lengthening of the Ru-Ru bonds associated with the capped faces ($\text{Ru1-Ru2} = 3.037(2) / 3.0269(19)^* \text{ \AA}$, $\text{Ru3-Ru4} = 3.041(2) / 3.0615(19)^* \text{ \AA}$) compared to the other Ru-Ru bonds ($\text{Ru1-Ru3} = 2.791(2) / 2.788(2)^* \text{ \AA}$, $\text{Ru1-Ru4} = 2.790(2) / 2.8052(19)^* \text{ \AA}$, $\text{Ru2-Ru3} = 2.802(2) / 2.9247(16)^* \text{ \AA}$, $\text{Ru2-Ru4} = 2.790(2) / 2.787(2)^* \text{ \AA}$). The ^1H NMR spectrum also showed, however, the presence of another set of IPr and hydride resonances (-15.70 ppm) of much lower intensities, suggesting the presence of another isomer, in ~1:7 ratio with respect to the major isomer (Figure 4.12). The proposed structure of the minor isomer is given in figure 4.13.

Figure 4.12. ^1H NMR spectrum of cluster **37a**.

Figure 4.13. Molecular structures of the isomers of cluster **37a**.

The ORTEP plot showing the molecular structure of **38**, together with selected bond parameters, is given in Figure 4.14. Each ruthenium vertex carries two terminal CO ligands and there is a CO ligand bridging each of the Ru-Ru edges; the presence of both CO bonding modes is corroborated by the IR spectrum. The NMR spectrum shows one set of resonances for the IPr ligands, consistent with the symmetry of the cluster. The Ru-Au bond lengths (2.8052(5) - 2.8536(5) Å) are comparable to those in clusters containing capping [AuL] fragments such as those found in clusters **34a** (2.7932(13) - 2.9904(17) Å) and **35a** (2.8264(5) - 2.9149(5) Å).

The Ru₃Au₂ metal core of **38** is trigonal bipyramidal. The total valence electron count is 68, which is four less than that expected on the basis of PSEPT for a trigonal bipyramidal cluster with five metal atoms.¹⁹ It is, however, isoelectronic to the reported cluster Pt₂Os₃(P^tBu₃)₂(CO)₁₀, for which the two platinum atoms were assumed to have 16-electron configurations.²⁰ In analogy, the two gold atoms of **38** may also be regarded to adopt 16-electron configurations. It thus appears that the two gold atoms in **38** should be considered as part of the cluster core, i.e., that the isolobality between [Au(IPr)]⁺ and H⁺ cannot be employed; the latter assumes the usual 14-electron configuration at the gold atom.²¹

An attempt was made to examine if there is any difference in the Ru-Au bonding about the [Au(IPr)]⁺ moiety in **35a** and **38** via a natural bond orbital (NBO) analysis with density functional theory (DFT) at the def2SVP/6-31G* level of theory. The Wiberg bond indices for the Ru-Au bonds did not show significant differences: 0.09 - 0.10 for **35a**, and 0.13 - 0.14 for **38**. The second-order perturbative energy (E₂) analysis, however, provided insights into the donor-acceptor interactions of these Ru-Au bonds; E₂ values have been used as a quantitative measure of the donor-acceptor ability of various ligands with regards to their metal-to-ligand back bonding.²² The E₂ values summed over all interactions containing an Ru-Au component (ΣE₂) may thus serve as good indicators of the net electron

flow between the donor and acceptor components for each of the metal atoms (Figure 4.15). The values suggest that Ru→Au donation is very large ($\Sigma E_2 \sim 900$ kcal/mol), at least for two of the three Ru atoms, in **35a** while the reverse Au→Ru donation is much smaller ($\Sigma E_2 \sim 440$ kcal/mol). This is consistent with the picture of an $[\text{AuL}]^+$ fragment acting primarily as an acceptor, i.e., an isolobal analogue to H^+ , in **35a**. In contrast, most of the Ru→Au and Au→Ru interactions in **38** have comparable values ($\Sigma E_2 \sim 240$ and 280 kcal/mol, respectively), which is consistent with participation of the Au in cluster bonding in which the electrons are delocalised over all the metal atoms. It is also noteworthy that the ΣE_2 values for Ru1→Au8 and its reverse Au8→Ru1, in **35a** seem to suggest an overall, albeit weaker, Au→Ru donation; a similar situation occurs for Ru4→Au1 and Ru4→Au2 in **38**. The bonding interactions in the metal cores may thus be interpreted as depicted in Figure 4.15.

Ru1 → Au8 = 199	Ru3 → Au1 = 257	Ru3 → Au2 = 221
Ru2 → Au8 = 867	Ru4 → Au1 = 534	Ru4 → Au2 = 537
Ru3 → Au8 = 931	Ru5 → Au1 = 244	Ru5 → Au2 = 257
Au8 → Ru1 = 533	Au1 → Ru3 = 297	Au2 → Ru3 = 244
Au8 → Ru2 = 444	Au1 → Ru4 = 287	Au2 → Ru4 = 268
Au8 → Ru3 = 441	Au1 → Ru5 = 296	Au2 → Ru5 = 284

Figure 4.15. Bonding and ΣE_2 values between the metal centers in **35a** and **38**. ΣE_2 is a summation over all interactions containing an Ru-Au component, including Lewis lone pairs, bonds, antibonds and 3-centre bonds for the donor.

Figure 4.14. ORTEP diagram of cluster **38**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1-Ru4 = 2.8195(5), Au1-Ru5 = 2.8357(5), Au1-Ru3 = 2.8379(5), Au2-Ru4 = 2.8052(5), Au2-Ru5 = 2.8298(5), Au2-Ru3 = 2.8536(5), Ru3-Ru5 = 2.7154(6), Ru3-Ru4 = 2.7155(6), Ru4-Ru5 = 2.7180(6).

4.5 Concluding remarks

In this chapter, heteronuclear ruthenium-gold clusters containing [Au(L)] fragments were synthesized via two methodologies (Scheme 4.8):

- Ionic coupling between an anionic ruthenium carbonyl cluster with a cationic [Au(L)]⁺ or [(AuL)₃O]⁺ synthon to afford mono-gold or tri-gold coupled clusters, respectively.
- Condensation reaction between a neutral ruthenium cluster and a gold(I) hydroxide complex to afford mono- and di-gold substituted clusters.

Scheme 4.8

These synthetic methodologies afforded good control over the introduction of [Au(L)] fragments, with the ionic coupling reactions giving specifically one product. The primary limitation would be in the number of [Au(L)] fragments that could be introduced; higher ratios of Au could not be achieved.

The use of Au(NHC)OH as an [Au(NHC)] synthon bears further exploration as its phosphine analogue is not known. A rich chemistry with other hydrido metal carbonyl clusters may be expected. In addition, extended to non-hydrido metal carbonyl clusters may also be worth exploring as the nucleophilic OH group may activate a CO ligand via the Hieber base reaction to generate an anionic hydrido metal carbonyl cluster *in-situ*.^{23,24} This could subsequently undergo ionic coupling reaction with the [Au(NHC)]⁺.

Some of the RuAu clusters were found to exist as isomeric mixtures. In particular, cluster **34a** comprised a major isomer with three equivalent [Au(PPh₃)] moieties, and a minor isomer with three fluxional, non-equivalent [Au(PPh₃)] moieties. A consideration of the valence electron counts for clusters **35a** and **38** suggested that it was more appropriate to regard the [AuL]⁺ fragment as an isolobal analogue to H⁺ in the former, and the two gold atoms should be regarded as part of the cluster metal core in the latter, i.e., whether the gold atoms satisfied a 14- or 16-electron configuration, respectively. An attempt was made to differentiate between these two bonding descriptions in terms of the Ru-Au donor-acceptor interactions, and it was found that NBO second-order perturbative energy (E₂) analysis may be employed satisfactorily for that purpose.

4.6 Experimental

All reactions were performed under an argon atmosphere using standard Schlenk techniques or in the glove box. Solvents used in reactions were of AR grade, and were dried under the appropriate drying agent and distilled under nitrogen; and stored in flasks fitted with Teflon valves prior to use. Toluene was dried over sodium/benzophenone, IPA over Mg/I₂ and DCM over CaH₂. The products were separated by thin-layer chromatography (TLC), using Merck silica gel 60 Å F 254 20 × 20 cm² plates. ¹H NMR spectra were collected using a Bruker BBFO 400 or AV 300 NMR spectrometer, with chemical shifts referenced to the solvent residual peaks. 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. High resolution mass spectra were recorded in electrospray ionization (ESI) mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by the microanalytical laboratory at NTU. Single crystal X-ray crystallographic analyses were performed by Dr Rakesh Ganguly and/or Dr Li Yongxin from the NTU. Au(PPh₃)Cl, Au(IPr)Cl and AgBF₄ were purchased from Sigma Aldrich. [Au(PPh₃)] [NO₃],²⁵ or [(AuPPh₃)₃O] [BF₄],²⁶ Ru₄(μ-H)₄(CO)₁₂,²⁷ and [PPN][Ru₆(μ₆-H)(CO)₁₈],²⁸ were prepared according to the published methods. All other reagents were used as received from commercial suppliers.

Synthesis of Ru₆Au(μ₃-H)(PPh₃)(CO)₁₇, **33a**

Cluster **30** (7.4 mg, 0.0045 mmol) and **31a.NO₃** (8.9 mg, 0.018 mmol) were stirred in DCM (5 mL) for 10 mins. The reaction mixture was loaded onto a short column of silica gel. Elution with hexane gave a dark red solid (Yield = 5.6 mg, 81 %). Dark red crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

IR (DCM): ν_{CO} 2089 (vw), 2062 (w), 2044 (vs), 2036 (m), 2021 (w), 2005 (vw), 1986 (vw) cm⁻¹.

^1H NMR (400 MHz, C_6D_6): δ 6.99 – 7.55 (m. aromatic H), -17.4 (s, hydride) ppm

^{31}P { ^1H } NMR (400 MHz, C_6D_6): 73.1 (s) ppm

Synthesis of $\text{Ru}_6\text{Au}_3(\mu_6\text{-H})(\text{PPh}_3)_3(\mu\text{-CO})_3(\text{CO})_{14}$, **34a**

Cluster **30** (9.0 mg, 0.0042 mmol) and **32** (16.5 mg, 0.0109 mmol) were stirred in DCM (5 mL) for 2 h. The mixture was separated by TLC with DCM/Hexane (1:1, v/v) as the eluent. The product was isolated from the major brown band to give a brown solid (Yield = 4.8 mg, 36 %). Dark brown crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

IR (DCM) : ν_{CO} 2056 (w), 2044 (w), 2025 (vs), 2007 (vs), 1985 (m), 1809 (vw), 1787 (vw), 1725 (vw) cm^{-1} .

^1H NMR (400 MHz, Toluene- d_8 , 25 °C): δ 9.73 (s, hydride), 6.84 – 7.86 (m. aromatic H) ppm

^1H NMR (400 MHz, Toluene- d_8 , -80 °C): δ 15.30 (s, hydride), 9.69 (s, hydride), 6.70 – 7.63 (m. aromatic H) ppm

^{31}P { ^1H } NMR (400 MHz, Toluene- d_8 , 25 °C): δ 33.6 (s) ppm

^{31}P { ^1H } NMR (400 MHz, Toluene- d_8 , -80 °C): δ 69.0 (s), 61.0 (s), 44.0 (s), 32.4 (s) ppm

Synthesis of $\text{Ru}_6\text{Au}(\mu_6\text{-H})(\text{IPr})(\text{CO})_{18}$, **35a**

Complex **31b.Cl** (22.2 mg, 0.00358 mmol) and AgBF_4 (8.4 mg, 0.0043 mol) were stirred in THF (5 mL) for 30 mins. The initial colourless solution turned cloudy. Cluster **30** (29.5 mg, 0.0179 mmol) was subsequently added and the reaction mixture was stirred for 1 h. The reaction mixture was loaded onto a short column of silica gel. Elution with hexane gave a dark red-brown solid (Yield = 15.6 mg, 51 %). Dark brown crystals were obtained by slow evaporation of a DCM/Hexane solution at 4 °C.

IR (DCM): ν_{CO} 2090 (vw), 2087 (vw), 2060 (w), 2042 (vs), 2034 (m), 2019 (w), 2002 (vw), 1986 (vw), 1978 (vw), 1962 (vw) cm^{-1} .

^1H NMR (400 MHz, C_6D_6): δ 14.7 (s, 1H, hydride), 7.14-7.22 (m, 6H, Ar-H), 6.52 (s, 2H, Imidazole H), 2.90 (sept, 4H, $\text{CH}(\text{CH}_3)_2$), 1.39 (dd, 12H, $\text{CH}(\text{CH}_3)_2$), 0.96 (dd, 12H, $\text{CH}(\text{CH}_3)_2$) ppm

ESI-MS⁺ m/z: 1729.22 $[\text{M}+\text{MeOH}]^+$, 1702.23 $[\text{M}+\text{MeOH}-\text{CO}]^+$

Hi-res MS⁺: calcd for $\text{C}_{46}\text{H}_{42}\text{N}_2\text{O}_{19}\text{Au}^{100}\text{Ru}_2^{101}\text{Ru}^{102}\text{Ru}_3^{197}\text{Au}$, 1729.6318; found 1729.6215.

Synthesis of Au(IPr)OH, 31b.OH

KO^tBu (63.2 mg, 0.564 mmol) was added to complex **31b.Cl** (100 mg, 0.161 mmol) and stirred in THF/toluene mixture (1:1, v/v, 30 ml) at room temperature for 3 h. The crude mixture was then filtered through celite and washed with THF (3 x 5 ml). Water (1 ml) was added to the filtrate and left to stir for 15 min which caused the solution to turn cloudy. The solvent was then removed in vacuo, affording **1** as a white solid.

Reaction of cluster **2** with Au(IPr)OH, 31b.OH

A solution of **2** (30.0 mg, 0.0403 mmol) and Au(IPr)OH (46.4 mg, 0.0770 mmol) in toluene (15 ml) was stirred for 6 h, after which the solvent was removed in vacuo, and the crude mixture separated by TLC plate with DCM/Hexane (1:1, v/v) as the eluent. Three bands were isolated and characterized.

The first orange band was believed to be $\text{H}_3\text{Ru}_4\text{Au}(\text{IPr})(\text{CO})_{12}$, **36** (R_f = 0.68; yield = 5.0 mg, 10 %)

IR (DCM): ν_{CO} 2083 (vs), 2055 (s), 2035 (vs), 2016 (s), 1998 (m), 1971 (w) cm^{-1}

^1H NMR (400 MHz, C_6D_6) of major isomer: δ 7.23 – 6.96 (m, 6H, aromatic H), 6.30 (s, 2 H, imidazole H), 2.71 (sept, 3 H, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.39 (d, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.03 (d, J = 6.9 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), -16.8 (s, hydride) ppm.

^1H NMR (400 MHz, C_6D_6) of minor isomer: δ 7.23 – 6.96 (m, 6H, aromatic H), 6.23 (s, 2 H, imidazole H), 2.53 (sept, 3 H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.37 (d, 12 H, $\text{CH}(\text{CH}_3)_2$), 0.99 (d, $J = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), -16.9 (s, hydride) ppm.

ESI-MS+ m/z: 1385.39 $[\text{M}+\text{MeOH}+\text{Na}]^+$

Hi-res MS+: calcd for $\text{C}_{40}\text{H}_{43}\text{N}_2\text{O}_{13}^{23}\text{Na}^{101}\text{Ru}^{102}\text{Ru}_3^{197}\text{Au}$, 1385.8515; found 1385.8442.

The second red band was identified as $\text{Ru}_4(\mu_3\text{-H})_2\text{Au}_2(\text{IPr})_2(\text{CO})_{12}$, **37a** ($R_f = 0.59$; yield = 9.0 mg, 11%). Red crystals were obtained by slow evaporation of a dichloroethane solution at 4 °C.

IR (DCM): ν_{CO} 2007 (vs), 1990 (m), 1956 (w,br) cm^{-1}

^1H NMR (400 MHz, C_6D_6) of major isomer: δ 7.23 – 7.00 (m, 6H, aromatic H), 6.30 (s, 2 H, imidazole H), 2.74 (sept, 4 H, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.51 (d, 12 H $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.00 (d, $J = 7.2$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), -15.73 (s, hydride) ppm.

^1H NMR (400 MHz, C_6D_6) of minor isomer: δ 7.23 – 7.00 (m, 6H, aromatic H), 6.23 (s, 2 H, imidazole H), 2.54 (sept, 4 H, $J = 7.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, 12 H $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.04 (d, $J = 7.2$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), -15.70 (s, hydride) ppm.

ESI-MS+ m/z: 1916.14 $[\text{M}+\text{H}]^+$

Elemental Analysis (%) calcd for $\text{C}_{66}\text{H}_{74}\text{Au}_2\text{N}_4\text{O}_{12}\text{Ru}_2\cdot 2\text{C}_6\text{H}_{14}$: C 44.91, H 4.93, N 2.69; found: C 44.95, H 5.26, N 2.54.

The third yellow-green band was identified as $\text{Ru}_3\text{Au}_2(\text{IPr})_2(\mu\text{-CO})_3(\text{CO})_6$, **38** ($R_f = 0.50$; yield = 8.4 mg, 12 %). Dark green crystals were obtained by slow evaporation of a DCM/hexane solution at 4 °C.

IR (DCM): ν_{CO} 2035 (w), 2007 (vs), 1958 (s) cm^{-1}

^1H NMR (300 MHz, CDCl_3): δ 7.21 (s, 2H, aromatic H), 7.06 (d, 4 H, $J = 7.5$ Hz, aromatic H), 5.91 (s, 2 H, imidazole H), 2.18 (sept, 4 H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.43 (d, 12 H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.77 (d, 12 H, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$) ppm.

ESI-MS+ m/z: 1728.01 [M+H]⁺

Elemental Analysis (%) calcd for C₆₃H₇₂Au₂N₄O₉Ru₃·0.5C₇H₈: C 45.06, H 4.32, N 3.16; found: C 45.15, H 4.65, N 3.22.

Computational studies

Single point calculations were performed with the crystal structures obtained for **35a** and **38** using the Gaussian 09W suite of programs, with the RM06L density functional, the def2SVP basis set for the Ru and Au atoms, and the 6-31G* basis set for the remaining atoms.²⁹ Natural Bond Orbital (NBO) analysis was carried out with the NBO 6.0 program implemented within Gaussian 09W.³⁰

X-Ray crystallographic analyses

X-ray data was collected at 103 K on a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the Apex II suite of programs.³¹ The data was processed and corrected for Lorentz and polarisation effects with SAINT,³² and for absorption effects with SADABS.³³ Structural solution and refinement were carried out with the SHELXTL suite of programs.³⁴ The structures were solved by direct methods or Patterson methods to locate the heavy atoms, followed by successive difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final model. The metal hydrides were placed by potential energy calculations using the XHYDEX program, with fixed isotropic thermal parameters.¹⁸

The crystal of cluster **37a** was found that have disordered at two of its dichloroethane solvates. These were modeled with two alternative sites of equal occupancies (totalling 0.5 molecule) with appropriate bond and distance restraints. A dichloromethane solvate was found in both the asymmetric unit of the crystals of clusters **34a** and **38**. Crystal and refinement data are summarized in Table 4.1.

Table 4.1. Crystal and structure refinement data for **34a**, **35a**, **37a** and **38**.

Complex	34a .CH ₂ Cl ₂	35a	37a .2C ₂ H ₄ Cl ₂	38 .CH ₂ Cl ₂
Empirical formula	C ₇₂ H ₄₈ Au ₃ Cl ₂ O ₁₇ P ₃ Ru ₆	C ₄₅ H ₃₇ AuN ₂ O ₁₈ Ru ₆	C ₁₄₀ H ₁₆₄ Au ₄ C ₁₈ N ₈ O ₂₄ Ru ₈	C ₆₄ H ₇₄ Au ₂ Cl ₂ N ₄ O ₉ Ru ₃
Formula weight	2546.23	1697.15	4222.81	1811.31
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /n	P $\bar{1}$	P2 ₁ /c
a (Å)	13.618(7)	14.6552(7)	17.827(3)	20.3125(6)
b (Å)	21.903(12)	19.9292(9)	20.302(3)	18.0913(5)
c (Å)	24.972(14)	19.0629(9)	21.496(3)	18.0088(5)
α (deg)	90	90	81.007(3)	90
β (deg)	90.298(17)	112.2380(14)	86.733(3)	95.2996(16)
γ (deg)	90	90	89.094(3) ^o	90
Volume, Å ³	7448(7)	5153.5(4)	7671.6(19)	6589.6(3)
Z	4	4	2	4
Density (calculated), Mg/m ³	2.271	2.187	1.828	1.826
Absorption coefficient, mm ⁻¹	7.268	4.619	4.776	14.812
F(000)	4784	3232	4112	3528
Crystal size, mm ³	0.12 x 0.08 x 0.04	0.26 x 0.18 x 0.14	0.42 x 0.11 x 0.04	0.18 x 0.14 x 0.02
Reflections collected	238113	114596	127229	52193
Independent reflections	15209 [R(int) = 0.1432]	10517 [R(int) = 0.0805]	27022 [R(int) = 0.0671]	11888 [R(int) = 0.0592]
Max. and min. transmission	0.7598 and 0.4759	0.56 and 0.40	0.0151 and 0.0017	0.76 and 0.25
Data / restraints / parameters	15209 / 0 / 931	10517 / 15 / 660	27022 / 1941 / 1783	11888 / 0 / 773
Goodness-of-fit on F ²	1.160	1.034	1.089	1.093
Final R indices [I>2s(I)]	R1 = 0.0329 wR2 = 0.0890	R1 = 0.0279 wR2 = 0.0606	R1 = 0.0818 wR2 = 0.2359	R1 = 0.0451 wR2 = 0.1207
R indices (all data)	R1 = 0.0593 wR2 = 0.1140	R1 = 0.0387 wR2 = 0.0655	R1 = 0.0988 wR2 = 0.2483	R1 = 0.0501 wR2 = 0.1265
Largest diff. peak and hole, e.Å ⁻³	1.442 and -1.770	1.249 and -0.945	3.411 and -1.539	4.261 and -2.297

4.7 References

- (1) Chinchilla, L. E.; Olmos, C. M.; Villa, A.; Carlsson, A.; Prati, L.; Chen, X.; Blanco, G.; Calvino, J. J.; Hungría, A. B. *Catal. Today* **2015**, 253, 178.
- (2) Chinchilla, L. E.; Olmos, C.; Kurttepel, M.; Bals, S.; Van Tendeloo, G.; Villa, A.; Prati, L.; Blanco, G.; Calvino, J. J.; Chen, X.; Hungría, A. B. *Particle & Particle Systems Characterization* **2016**, 33, 419.
- (3) Kirichenko, O. A.; Redina, E. A.; Davshan, N. A.; Mishin, I. V.; Kapustin, G. I.; Brueva, T. R.; Kustov, L. M.; Li, W.; Kim, C. H. *Applied Catalysis B: Environmental* **2013**, 134–135, 123.
- (4) Adams, R. D.; Pellechia, P. J.; Smith, M. D.; Zhang, Q. *J. Organomet. Chem.* **2012**, 706–707, 20.
- (5) Housecroft, C. E.; Matthews, D. M.; Waller, A.; Edwards, A. J.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **1993**, 3059.
- (6) Bruce, M. I.; Nicholson, B. K. *Organometallics* **1984**, 3, 101.
- (7) Mueting, A. M.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, A. L.; Ito, L. N.; Johnson, B. J.; Pignolet, L. H.; Leeaphon, M.; Meyer, K. E.; Walton, R. A.; Heinekey, D. M.; Harper, T. G. P. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 2007, p 279.
- (8) Bruce, M. I.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, 252, 243.
- (9) Bateman, L. W.; Green, M.; Howard, J. A. K.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 773.
- (10) Batsman, L. W.; Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2599.
- (11) Adams, R. D.; Tedder, J.; Wong, Y. O. *J. Organomet. Chem.* **2015**, 795, 2.
- (12) McCarthy, D. A.; Krause Bauer, J.; Hong, F.-E.; Ran Oh, J.; Deng, H.; Liu, J.; Shore, S. G. *J. Organomet. Chem.* **1998**, 550, 309.
- (13) McCarthy, D. A.; Krause, J. A.; Shore, S. G. *J. Am. Chem. Soc.* **1990**, 112, 8587.

- (14) Duer, M. J.; Wales, D. J. *Polyhedron* **1991**, *10*, 1749.
- (15) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742.
- (16) Gomez-Suarez, A.; Ramon, R. S.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2012**, *41*, 5461.
- (17) Freeman, M. J.; Orpen, A. G.; Salter, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 379.
- (18) Orpen, G. *XHYDEX: A Program for Locating Hydrides in Metal Complexes*; School of Chemistry, University of Bristol: UK, 1997.
- (19) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
- (20) Adams, R. D.; Captain, B.; Zhu, L. *J. Am. Chem. Soc.* **2007**, *129*, 2454.
- (21) Raubenheimer, H. G.; Schmidbaur, H. *Organometallics* **2012**, *31*, 2507.
- (22) Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. N. *Organometallics* **2007**, *26*, 2637.
- (23) Hieber, W.; Becker, E. *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1930**, *63*, 1405.
- (24) Heiber, W.; Vetter, H. *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1931**, *64*, 2340.
- (25) Malatesta, L.; Naldini, L.; Simonetta, G.; Cariati, F. *Coord. Chem. Rev.* **1966**, *1*, 255.
- (26) Nesmeyanov, A. N.; Perevalova, E. G.; Struchkov, Y. T.; Antipin, M. Y.; Grandberg, K. I.; Dyadhenko, V. P. *J. Organomet. Chem.* **1980**, *201*, 343.
- (27) Bruce, M. I.; Jensen, C. M.; Jones, N. L.; Süß-Fink, G.; Herrmann, G.; Dase, V. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 2007, p 216.
- (28) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; E., P. J. J.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, revision D.01, Gaussian, Inc., Wallingford CT 2009*.
- (30) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *The NBO 6.0 program*
- (31) *SMART Version 5.628, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.*
- (32) *SAINT+ Version 6.22a, Bruker AXS Inc, Madison, Wisconsin, USA, 2001.*
- (33) *Sheldrick, G.M. SADABS; University of Göttingen, Göttingen, Germany, 1996.*
- (34) *SHELXTL Version 5.1, Bruker AXS Inc, Madison, Wisconsin, USA, 1997.*

Chapter 5: Selective oxidation of benzyl alcohol to benzaldehyde

5.1 Background

Benzaldehyde is a key molecule in the food and flavourings, and pharmaceutical industries. It is the main component in almond-based flavourings, and an essential precursor for the synthesis of stimulants like ephedrine and of antibiotics such as ampicillin.^{1,2} Although it is commercially synthesized by the hydrolysis of benzyl chloride, this process is limited by the poor selectivity for benzaldehyde and the undesirable production of chlorine. As such, the dehydrogenative oxidation of benzyl alcohol is a more viable, chlorine-free alternative.^{3,4}

Traditionally, to convert benzyl alcohol to benzaldehyde, stoichiometric amounts of oxidizing reagents including CrO_3 , KMnO_4 , MnO_2 and SeO_2 have been employed, but these oxidants have serious setbacks such as their high cost and the production of large quantities hazardous and toxic wastes.^{5,6} Liquid-phase oxidation of primary alcohols by O_2 , H_2O_2 or t-butyl hydroperoxide (TBHP), which are considered green oxidants, with viable catalysts have proven to be viable for aldehyde production.⁷

As mentioned in the previous chapters, the three bimetallic combinations - ruthenium-platinum,⁸⁻¹² ruthenium-gold,¹³⁻¹⁵ and cobalt-platinum,¹⁶⁻²⁰ - have been found to be effective catalysts for various oxidation reactions. They have, however, yet to be applied to the selective oxidation of benzyl alcohol to benzaldehyde. In this chapter, the use of these heteronuclear clusters as precursors for the preparation of bimetallic catalysts supported on titania, and the evaluation of their catalytic performance in the selective oxidation of benzyl alcohol to benzaldehyde under the given reaction conditions is described (Scheme 5.1). Titania provides strong metal support interactions with transition metals,²¹⁻²³ and has often been used as a metal oxide support for oxidation reactions.^{24,25}

Reaction Conditions : 2g of benzyl alcohol, 1g of diglyme (Internal standard), 2.38 mL of tBuOOH (70% wt. in water), 50 mg of catalyst, Heated at 95 °C for 6h

Scheme 5.1

5.2 Catalytic performance in the selective oxidation of benzyl alcohol

The heteronuclear clusters used for each of the bimetallic systems, viz., ruthenium-platinum, ruthenium-gold and cobalt-platinum, are listed in Table 5.1.

Table 5.1. Cluster numbering, organometallic precursors and acronyms used for each catalyst.

<i>Cluster Number</i>	<i>Organometallic precursor</i>	<i>Catalyst acronyms</i>
1	$\text{Ru}_3(\text{CO})_{12}$	Ru/TiO ₂
4	$\text{Pt}(\text{IPr})(\text{C}_4\text{H}_7)\text{Cl}$	Pt/TiO ₂
20	$\text{Co}_2(\text{CO})_8$	Co/TiO ₂
31b.Cl	$\text{Au}(\text{IPr})\text{Cl}$	Au/TiO ₂
9a	$\text{RuPt}_2(\text{IPr})_2(\mu\text{-CO})_3(\text{CO})_3$	RuPt ₂ /TiO ₂
5a	$\text{Ru}_3\text{Pt}_2(\text{IPr})_2(\mu\text{-CO})_4(\text{CO})_8$	Ru ₃ Pt ₂ /TiO ₂
11	$\text{Ru}_6\text{Pt}(\mu_3\text{-H})_2(\text{IPr})(\text{CO})_{18}$	Ru ₆ Pt/TiO ₂
12	$\text{Ru}_6\text{Pt}_2\text{H}_6(\text{IPr})_2(\text{CO})_{16}$	Ru ₆ Pt ₂ /TiO ₂
35a	$\text{Ru}_6\text{Au}(\mu_6\text{-H})(\text{IPr})(\text{CO})_{18}$	Ru ₆ Au/TiO ₂
37a	$\text{Ru}_4\text{Au}_2(\mu_3\text{-H})_2(\text{IPr})_2(\text{CO})_{12}$	Ru ₄ Au ₂ /TiO ₂
38	$\text{Ru}_3\text{Au}_2(\text{IPr})_2(\mu_3\text{-CO})_3(\text{CO})_6$	Ru ₃ Au ₂ /TiO ₂
23a	$\text{Co}_2\text{Pt}_2(\text{IPr})_2(\mu_2\text{-CO})_4(\text{CO})_4$	Co ₂ Pt ₂ /TiO ₂

The catalytic reactions with Ru₆Pt/TiO₂, Ru/TiO₂ and Pt/TiO₂ were repeated thrice and the results were found to have a deviation of $\pm 2\%$; the results are summarised in Figure

5.1. The bimetallic $\text{Ru}_x\text{Pt}_y/\text{TiO}_2$ catalysts gave higher % conversion and overall yield of benzaldehyde compared to the monometallic Pt/TiO_2 catalyst but comparable to those for Ru/TiO_2 . The selectivity for benzaldehyde appeared to be lower with the bimetallic catalysts than with either of the monometallic catalysts and, as with the overall yield of benzaldehyde, decreased slightly with a higher Pt content (from right to left).

Figure 5.1. Conversion and selectivity in the oxidation of benzyl alcohol using 3% $\text{Ru}_x\text{Pt}_y/\text{TiO}_2$ and its monometallic counterparts.

The results for the bimetallic RuAu and CoPt catalysts are summarised in Figures 5.2 and 5.3, respectively. For the RuAu system, the bimetallic catalysts gave higher % conversion and overall yield of benzaldehyde than the monometallic Au/TiO_2 catalyst but were comparable to those for Ru/TiO_2 . The yield of benzaldehyde also decreased with an increase in the Au content. It thus appears that the RuAu system does not incorporate the advantages of both metals.

The CoPt catalyst also did not show any signs of synergistic effects of the metals as its performance was intermediate between those of the monometallic counterparts. In comparison with the other two bimetallic combinations, i.e., RuPt and RuAu , the CoPt catalyst gave the worst performance.

Figure 5.2. Conversion and selectivity in the oxidation of benzyl alcohol using 3% Ru_xAu_y/TiO₂ and its monometallic counterparts.

Figure 5.3. Conversion and selectivity in the oxidation of benzyl alcohol using 3% Co₂Pt₂/TiO₂ and its monometallic counterparts.

The Ru, Pt and Au catalysts gave similar selectivity for benzaldehyde; however, the overall yield of benzaldehyde is lower for Pt and Au catalysts due to lower conversion. Moreover, although the Co catalyst's selectivity for benzaldehyde are the lowest compared to the other platinum group metal catalysts, it performed better in terms on overall yield of benzaldehyde due to higher conversion compared to the Pt and Au catalysts. Nevertheless, the Ru catalyst performed the best amongst the monometallic systems (Figure 5.4).

Figure 5.4. Conversion and selectivity in the oxidation of benzyl alcohol of the monometallic catalysts.

5.3 Catalyst characterisation

Of the three bimetallic systems that were tested for benzyl alcohol oxidation, the RuPt system was the most promising in terms of the overall yield of benzaldehyde, thus the best performing catalyst, Ru₆Pt/TiO₂, was characterized in detail.

Cluster-derived catalysts are known to give well-dispersed metallic nanoparticles with narrow size distribution.^{26,27} The high-resolution transmission electron microscope (HRTEM) images of both the Ru₆Pt/TiO₂ and the Ru/TiO₂ catalysts show well-dispersed nanoparticles with a narrow particle size range of around 1.0 ± 0.3 nm (Figure 5.5).

Figure 5.5. TEM analysis and particle size distribution of (Top) Ru₆Pt/TiO₂ catalyst, (Bottom) Ru/TiO₂ catalyst.

A scanning electron microscope (SEM) image of the RuPt catalyst showed only the surface morphology of the titania nanopowder (Figure 5.6). However, an energy dispersive X-ray (EDX) analysis indicated that the weight ratio of Ru:Pt was 3:1, which equated to a 6:1 chemical composition of Ru:Pt. This showed that the bimetallic ratio was maintained during deposition. The false colour elemental composition diagrams also show that the Ru and Pt are well-dispersed (Figures 5.7 and 5.8).

Figure 5.6. SEM image of Ru₆Pt/TiO₂.

Figure 5.7. EDX spectrum of Ru₆Pt/TiO₂ catalyst.

Figure 5.8. Images of the elemental compositions of Ru, Pt, Ti and O in false colour.

X-ray photoelectron spectroscopic (XPS) studies were also carried out on both fresh and spent $\text{Ru}_6\text{Pt}/\text{TiO}_2$ catalysts, and the monometallic counterparts Ru/TiO_2 and Pt/TiO_2 ; the adventitious carbon peak at 284.5 eV was used as the reference (Table 5.2). As the binding energies of $\text{Ru}3d$ coincide with those of $\text{C}1s$, it was difficult to identify all the chemical states of Ru. Nevertheless, the peak corresponding to the $\text{Ru}3d_{5/2}$ binding energy could be resolved. Ruthenium was found to exist in Ru^{III} state for both the fresh $\text{Ru}_6\text{Pt}/\text{TiO}_2$ and Ru/TiO_2 , while the binding energy value for the spent $\text{Ru}_6\text{Pt}/\text{TiO}_2$ catalyst was found to be intermediate between Ru^{III} and RuO_2 , which suggests that some of the Ru^{III} species were oxidized after the catalytic reaction. Platinum was identified to exist as Pt^0 for all the platinum-containing catalysts. Based on the XPS analysis, it is clear that the Ru^{III} is the active species for this catalytic reaction (Figure 5.9). Although Ru^{III} species has been reported as an active species for alcohol oxidation,²⁸ it is also possible to carry out effective

catalytic alcohol oxidation using ruthenium of other oxidation states.²⁹⁻³¹ As both the Ru₆Pt/TiO₂ and Ru/TiO₂ catalyst show very similar trends for their HRTEM and XPS data, it does not provide with further information for the role of Pt in the catalytic reaction.

Table 5.2. Identified Ru and Pt chemical states from XPS studies.

Catalysts	Measured binding energies (eV)	Component	Literature binding energies (eV)	Ref.
Fresh Ru ₆ Pt/TiO ₂	281.5 ^a	Ru ^{III}	281.8	32
	71.1 ^b	Pt ⁰	70.4 -71.3	33
Spent Ru ₆ Pt/TiO ₂	281.2 ^a	Ru ^{III}	281.8	32
		RuO ₂	280.7	32
	70.9 ^b	Pt ⁰	70.6 -71.3	33
Ru/TiO ₂	281.8 ^a	Ru ^{III}	281.8	32
Pt/TiO ₂	71.1 ^b	Pt ⁰	70.6 -71.3	33

^a Ru3d_{5/2}

^b Pt4d_{7/2}

A peak at ~400 eV was observed for the Ru₆Pt/TiO₂ catalysts (Figure 5.10). This peak was not observed for the monometallic Ru/TiO₂ catalyst derived from a ruthenium carbonyl species but was observed in the monometallic Pt/TiO₂ catalyst, and could be assigned to the N1s electron's binding energy. This suggested the presence of C-N bonding.³² Moreover, it has been reported that NHC-protected Au and Pd nanoparticles gave a similar peak at ~400 eV which was assigned to N1s binding energy of the NHC.³⁴ Thus, it is possible that the NHC ligand, or some C-N decomposed species, was present in all the platinum-containing catalysts, which were derived from a Pt(NHC) precursor.

Figure 5.9. Ru3d peak for fresh Ru₆Pt/TiO₂ catalyst.

Figure 5.10. N1s peak for Pt-containing catalysts.

Based on the characterisation studies and various mechanisms reported in the literature, two plausible mechanisms - the monometallic Ru (Scheme 5.2) and the bimetallic Ru-Pt (Scheme 5.3) systems were proposed.^{35,36}

Scheme 5.2

Scheme 5.3

5.4 Effect of calcination temperature

To study the effects of changing calcination temperature on the catalyst performance, the Ru₆Pt/TiO₂ catalyst was also calcined at higher temperatures of 300 °C and 400 °C. While the selectivity for benzaldehyde remained similar with all three catalysts, the overall conversion and hence yield of benzaldehyde was slightly lowered for the catalyst calcined at 400 °C (Figure 5.11).

Figure 5.11. Effect of calcination temperature on the conversion and selectivity using 3% Ru_xPt_y/TiO₂.

5.5 Studies on the deposition process

The deposition of $\text{Ru}_6\text{Pt}(\mu_3\text{-H})_2(\text{IPr})(\text{CO})_{18}$, **11** onto titania was studied in order to gain an understanding on the process. An *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiment showed that CO stretches could be observed when the cluster was first deposited onto TiO_2 . However, upon heating under helium atmosphere, the terminal CO stretches simplified to two broad peaks at around 2050 and 1970 cm^{-1} , and a new bridging CO stretch appeared at $\sim 1750 \text{ cm}^{-1}$. However, all CO stretches were lost at around 400 $^\circ\text{C}$, indicative of a total removal of CO ligands (Figure 5.12).

Figure 5.12. DRIFTS spectra of $\text{Ru}_6\text{Pt}/\text{TiO}_2$.

Thermogravimetric analysis (TGA) showed four observable changes in mass (Figure 5.13). The initial percentage mass loss (0.60%) may be assigned to adventitious moisture. All the ligands were lost at $\sim 450 \text{ }^\circ\text{C}$; some of the ligands remained at 200 $^\circ\text{C}$ and even 300 $^\circ\text{C}$, and is consistent with the *in-situ* DRIFTS experiment. The TGA also

suggested that the IPr ligand remained intact at 200 °C, consistent with the XPS results which showed an N1s peak at ~ 400 eV.

Temperature Range / °C	Experimental mass loss / %	Calculated mass loss / %	Corresponding molecules
162 - 250	1.49	1.06	10 CO + 2H
250 - 340	1.79	1.77	IPr + 3 CO
340 - 450	0.556	0.524	5 CO

Figure 5.13. TGA spectrum of cluster **11** supported on TiO₂.

Thus, both the *in-situ* DRIFTS and TGA experiments indicated that complete loss of ligands only occurred at ~400 °C. Since it was observed that the performance of the catalyst calcined at 400 °C was actually lower than that calcined at 200 °C or 300 °C, removal of the ligand shell was not the only factor affecting catalyst activity; aggregation of the bimetallic nanoparticles may have occurred at 400 °C. Thus, calcination at 200 °C appear to be optimal; although the ligand shell was only partially removed, the TEM images showed that nanoparticles were indeed formed. This observation that partial removal of the ligand shell can give rise to better catalytic activity have been reported with Au

nanoparticles; the presence of these ligands was believed to stabilize the nanoparticles against sintering,^{37,38} and a similar situation may have occurred here.

5.6 Concluding remarks

The results obtained show that the RuPt system was a potential bimetallic combination for the selective oxidation of alcohol to aldehyde; it showed synergistic effects between the two metals, in contrast to the RuAu and CoPt systems. However, a lower Pt content appeared desirable as an increase in Pt content resulted in a decrease in performance. It is thus possible that a catalyst with a chemical composition of Ru:Pt = x:1 (where $x > 6$) could give a better performance.

Deposition from cluster precursors did indeed give nanoparticles with a narrow size distribution and controlled metal ratio, as was shown with the HRTEM and SEM-EDX studies. An XPS study on the Ru₆Pt/TiO₂ catalyst showed that the ruthenium existed as Ru^{III} while platinum existed as Pt⁰, similar to its monometallic counterparts. However, these characterizations did not provide further information with regards to the role of Pt in the catalytic system as the HRTEM and XPS data for both the Ru₆Pt/TiO₂ and Ru/TiO₂ catalysts were very similar.

A lower calcination temperature of 200 °C was found to be optimal for the preparation of cluster-derived catalysts as the partially intact ligand shell could possibly act as stabilizers and protection against sintering, which was observed when the ligand shell was completely removed at the higher temperature of 400 °C, resulting in a reduced catalyst performance.

5.7 Experimental

5.7.1 Materials

All other reagents purchased from commercial suppliers were used as received. Titanium dioxide (21 nm nanopowder), t-butyl hydroperoxide (TBHP) (70 wt. % in water) and Au(IPr)Cl were purchased from sigma Aldrich. Ru₃(CO)₁₂ was purchased from Oxkem. Co₂(CO)₈ was purchased from Alfa Aesar. Pt(C₄H₇)(IPr)Cl was synthesized according to the published method.³⁹ The bimetallic clusters were synthesized based on methodologies described in the previous chapters.

5.7.2 Preparation of catalysts

Supported catalysts of nominal 3 wt. % metal loadings were prepared as follow. 200 mg of TiO₂ was charged into a schlenk tube with vacuum was slowly applied. The sample was heated to 200 °C in an oil bath for 2 h under vacuum. Upon cooling, an appropriate amount of the precursor, given in Table 5.3, dissolved in 20 mL of DCM, was added to TiO₂, along with a magnetic stirrer bar. The solution was left to stir for 15 h. Solvent was removed under vacuum and the resulting dried sample was placed under vacuum and heated to 200 °C in an oil bath for 2 h. Vacuum calcination above 200 °C were carried out in a tube furnace.

Table 5.3. Organometallic precursors, acronyms used for the catalysts and precursor amount required for 200 mg of TiO₂ to achieve nominal 3 wt. % metal loadings.

Organometallic precursor	Catalyst acronyms	Precursor required for 200 mg of TiO ₂ / mg
Ru ₃ (CO) ₁₂	Ru/TiO ₂	12.7
Pt(IPr)(C ₄ H ₇)Cl	Pt/TiO ₂	20.7
Co ₂ (CO) ₈	Co/TiO ₂	17.4
Au(IPr)Cl	Au/TiO ₂	18.9

$\text{RuPt}_2(\text{IPr})_2(\mu\text{-CO})_3(\text{CO})_3$	$\text{RuPt}_2/\text{TiO}_2$	17.5
$\text{Ru}_3\text{Pt}_2(\text{IPr})_2(\mu\text{-CO})_4(\text{CO})_8$	$\text{Ru}_3\text{Pt}_2/\text{TiO}_2$	15.6
$\text{Ru}_6\text{Pt}(\mu_3\text{-H})_2(\text{IPr})(\text{CO})_{18}$	$\text{Ru}_6\text{Pt}/\text{TiO}_2$	12.7
$\text{Ru}_6\text{Pt}_2\text{H}_6(\text{IPr})_2(\text{CO})_{16}$	$\text{Ru}_6\text{Pt}_2/\text{TiO}_2$	13.4
$\text{Ru}_6\text{Au}(\mu_6\text{-H})(\text{IPr})(\text{CO})_{18}$	$\text{Ru}_6\text{Au}/\text{TiO}_2$	12.7
$\text{Ru}_4\text{Au}_2(\mu_3\text{-H})_2(\text{IPr})_2(\text{CO})_{12}$	$\text{Ru}_4\text{Au}_2/\text{TiO}_2$	14.4
$\text{Ru}_3\text{Au}_2(\text{IPr})_2(\mu_3\text{-CO})_3(\text{CO})_6$	$\text{Ru}_3\text{Au}_2/\text{TiO}_2$	14.9
$\text{Co}_2\text{Pt}_2(\text{IPr})_2(\mu_2\text{-CO})_4(\text{CO})_4$	$\text{Co}_2\text{Pt}_2/\text{TiO}_2$	17.8

5.7.3 Evaluation of catalysts

Benzyl alcohol (2.00 g, 18.5 mmol), diglyme (1.00 g, 7.45 mmol), catalyst (50 mg) and $t\text{BuOOH}$ in water (2.38 mL, 18.5 mmol) were added into a 25 mL rbf sequentially. The reaction mixture was heated in air under a drying tube at 95 °C for 6 h. The reaction mixture was subsequently quenched with acetone and centrifuged. The supernatant was collected and the products analysed by Gas Chromatography (GC); Agilent Technologies 6890N, employing Agilent HP-5 5% phenyl methyl siloxane capillary column (length 30 m). Helium was used as a carrier gas with a flow rate of 1.0 mL/min. The injection temperature was 220 °C. The identity and the quantification of the products were established by using diglyme as an internal standard, using the calibration method. The compounds were detected using a Flame Ionisation Detector (FID).

5.7.4 Characterization of catalysts

X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MKII spectrometer using a Mg $K\alpha$ radiation source. All XPS spectra were reference to adventitious carbon at 284.5 eV. XPS spectra were resolved and binding energies calculated using XPS Peak 4.1 software with respect to the adventitious carbon C1s peak set at 284.5 eV.⁴⁰ Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer. *In-situ* diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) experiments were performed

using a ZnSe window in a Perkin Elmer spectrometer and a mercury-cadmium-telluride (MCT-A) detector cooled with liquid nitrogen. Spectra were acquired at a resolution of 4 cm^{-1} and over 64 scans. KBr was used as the background reference. A powdered sample was put into a reaction cell and calcined under He under varying temperatures. Spectra were taken at 50 $^{\circ}\text{C}$ increments. High-resolution transmission electron microscopy (HRTEM) analysis were carried using Tecnai G2 TF20 S-twin, FEI Company operated at 200 kV. Samples were dispersed on carbon grids after sonicating the samples in ethanol for 0.5 h. Scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) studies was carried out using JEOL JSM-6700F microscope. Thermogravimetric analysis (TGA) was carried out on a TGA Q500 instrument. Catalyst was loaded on to an auto-sampler and was heated at 30 $^{\circ}\text{C}$ per minute under He atmosphere.

5.8 References

- (1) Hinde, C. S.; Gill, A. M.; Wells, P. P.; Hor, T. S. A.; Raja, R. *ChemPlusChem* **2015**, 80, 1226.
- (2) Ndolomingo, M. J.; Meijboom, R. *Appl. Surf. Sci.* **2017**, 398, 19.
- (3) Brühne, F.; Wright, E. In *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 5, 7th ed.*, Wiley-VCH, Weinheim 2011, p 223
- (4) Opgrande, J. L.; Brown, E.; Hesser, M.; Andrews, J. In *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York 2003.
- (5) Franz, G.; Sheldon, R. A. In *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 25, 7th ed.*, Wiley-VCH, Weinheim, 2000 2000, p 543
- (6) E., I. W. C.; Arends, R. A. S. In *Modern Oxidation Methods (Ed.: J.-E. Bäckvall)*, Wiley-VCH, Weinheim 2004, p 83
- (7) Sheldon, R. A. *Chem. Soc. Rev.* **2012**, 41, 1437.
- (8) Gasteiger, H. A.; Markovic, N.; Ross, P. N.; Cairns, E. J. *The Journal of Physical Chemistry* **1993**, 97, 12020.

- (9) Iwasita, T.; Hoster, H.; John-Anacker, A.; Lin, W. F.; Vielstich, W. *Langmuir* **2000**, *16*, 522.
- (10) Park, K.-W.; Sung, Y.-E.; Han, S.; Yun, Y.; Hyeon, T. *The Journal of Physical Chemistry B* **2004**, *108*, 939.
- (11) Koh, A. C. W.; Chen, L.; Leong, W. K.; Ang, T. P.; Johnson, B. F. G.; Khimyak, T.; Lin, J. *Int. J. Hydrogen Energy* **2009**, *34*, 5691.
- (12) Koh, A. C. W.; Leong, W. K.; Chen, L.; Ang, T. P.; Lin, J.; Johnson, B. F. G.; Khimyak, T. *Catal. Commun.* **2008**, *9*, 170.
- (13) Chinchilla, L. E.; Olmos, C. M.; Villa, A.; Carlsson, A.; Prati, L.; Chen, X.; Blanco, G.; Calvino, J. J.; Hungría, A. B. *Catal. Today* **2015**, *253*, 178.
- (14) Chinchilla, L. E.; Olmos, C.; Kurttepel, M.; Bals, S.; Van Tendeloo, G.; Villa, A.; Prati, L.; Blanco, G.; Calvino, J. J.; Chen, X.; Hungría, A. B. *Particle & Particle Systems Characterization* **2016**, *33*, 419.
- (15) Kirichenko, O. A.; Redina, E. A.; Davshan, N. A.; Mishin, I. V.; Kapustin, G. I.; Brueva, T. R.; Kustov, L. M.; Li, W.; Kim, C. H. *Applied Catalysis B: Environmental* **2013**, *134–135*, 123.
- (16) Nouralishahi, A.; Rashidi, A. M.; Mortazavi, Y.; Khodadadi, A. A.; Choolaei, M. *Appl. Surf. Sci.* **2015**, *335*, 55.
- (17) Kepenienė, V.; Tamašauskaitė-Tamašiūnaitė, L.; Jablonskienė, J.; Semaško, M.; Vaičiūnienė, J.; Vaitkus, R.; Norkus, E. *Mater. Chem. Phys.* **2016**, *171*, 145.
- (18) Yang, H.; Deng, J.; Liu, Y.; Xie, S.; Xu, P.; Dai, H. *Chinese Journal of Catalysis* **2016**, *37*, 934.
- (19) Yu, X.; Li, H.; Tu, S.-T.; Yan, J.; Wang, Z. *Int. J. Hydrogen Energy* **2011**, *36*, 3778.
- (20) López, A.; Navascues, N.; Mallada, R.; Irusta, S. *Appl. Catal., A* **2016**, *528*, 86.
- (21) Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 170.

- (22) Fung, S. C. *J. Catal.* **1982**, 76, 225.
- (23) Tauster, S. J. *Acc. Chem. Res.* **1987**, 20, 389.
- (24) Choudhary, V. R.; Dumbre, D. K.; Bhargava, S. K. *Industrial & Engineering Chemistry Research* **2009**, 48, 9471.
- (25) Enache, D. I.; Barker, D.; Edwards, J. K.; Taylor, S. H.; Knight, D. W.; Carley, A. F.; Hutchings, G. J. *Catal. Today* **2007**, 122, 407.
- (26) Ozkaya, D.; Zhou, W.; Thomas, J. M.; Midgley, P.; Keast, V. J.; Hermans, S. *Catal. Lett.* **1999**, 60, 113.
- (27) Zhou, W.; Thomas, J. M.; Shephard, D. S.; Johnson, B. F. G.; Ozkaya, D.; Maschmeyer, T.; Bell, R. G.; Ge, Q. *Science* **1998**, 280, 705.
- (28) Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, 122, 7144.
- (29) Guo, Z.; Liu, B.; Zhang, Q.; Deng, W.; Wang, Y.; Yang, Y. *Chem. Soc. Rev.* **2014**, 43, 3480.
- (30) Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Rao, K. V. R.; Robertson, K. N.; Cameron, T. S. *J. Am. Chem. Soc.* **2003**, 125, 2195.
- (31) Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2002**, 41, 4538.
- (32) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. *Handbook of X-ray photoelectron spectroscopy; Perkin-Elmer (Physical Electronics Division): Eden Prairie MN*, 1992.
- (33) *National Institute of Standards and Technology. NIST X-ray photoelectron spectroscopy (XPS) database, version 3.5*, <https://srdata.nist.gov/xps/Default.aspx> [Last access Dec 2016].
- (34) Hurst, E. C.; Wilson, K.; Fairlamb, I. J. S.; Chechik, V. *New J. Chem.* **2009**, 33, 1837.

- (35) Gogoi, N.; Begum, T.; Dutta, S.; Bora, U.; Gogoi, P. K. *RSC Advances* **2015**, *5*, 95344.
- (36) Zhou, C.; Chen, Y.; Guo, Z.; Wang, X.; Yang, Y. *Chem. Commun.* **2011**, *47*, 7473.
- (37) Elliott, E. W.; Glover, R. D.; Hutchison, J. E. *ACS Nano* **2015**, *9*, 3050.
- (38) Li, G.; Abroshan, H.; Liu, C.; Zhuo, S.; Li, Z.; Xie, Y.; Kim, H. J.; Rosi, N. L.; Jin, R. *ACS Nano* **2016**, *10*, 7998.
- (39) Fantasia, S.; Nolan, S. P. *Chem. Eur. J.* **2008**, *14*, 6987.
- (40) R., K. In *XPSPEAK4.1*, <http://xpspeak.software.informer.com/4.1/> [*last accessed Dec 2016*].

Chapter 6: Conclusion

In this thesis, the syntheses of NHC-containing heteronuclear clusters via the addition of the $[M(\text{NHC})]$ (where $M = \text{Pt}^0$ or Au^{I}) fragments across the metal-metal bonds of carbonyl clusters were examined. In general, the neutral $[\text{Pt}(\text{NHC})]$ synthon which was generated *in situ* could undergo addition reaction with neutral carbonyl clusters. Similarly, the cationic $[\text{Au}(\text{NHC})]^+$ synthon, generated *in situ*, could undergo ionic coupling with anionic carbonyl clusters, but condensation reaction with hydrido-carbonyl clusters using $\text{Au}(\text{NHC})\text{OH}$ could also be achieved. In some cases, multiple addition of these fragments occurred (Scheme 6.1).

Scheme 6.1

In some of these reactions, fragmentation and subsequent cluster rearrangement were also observed. Some of these products may be viewed as the stabilized forms of unobserved intermediates. For example, cluster **26a** may be viewed as the unobserved neutral cluster $\text{Co}_4(\mu_4\text{-C})(\text{CO})_{11}$ stabilized by two $[\text{Pt}(\text{IPr})]$ fragments, while **38** may be viewed as the unobserved anionic cluster $[\text{Ru}_3(\text{CO})_9]^{2-}$ stabilised by two $[\text{Au}(\text{IPr})]^+$ fragments (Scheme 6.2).

Scheme 6.2

The valence electron count for **38** was found to be unique as it was more appropriate to regard the two gold atoms as part of the cluster metal core. This implied that the individual gold atoms adopted a 16-electron configuration instead of a 14-electron configuration when the $[\text{AuL}]^+$ fragment was regarded as an isolobal analogue of H^+ . This isolobal relationship between $[\text{AuL}]^+$ and H^+ has been widely used in arriving at the valence electron count for $[\text{AuL}]$ -derived heteronuclear carbonyl clusters and, within the scope of this thesis, clusters **35a** and **37a**. It was found that NBO second-order perturbative energy (E_2) analysis may be employed satisfactorily to differentiate between these two bonding descriptions in **38** with **35a**, in terms of the Ru-Au donor-acceptor interactions.

The synthetic methodologies examined can be useful for building NHC-containing heteronuclear clusters as they offer good control over the addition of the $[\text{M}(\text{NHC})]$ fragments onto carbonyl clusters. Such precise control of the bimetallic ratio are useful in catalytic reactions in which this ratio affects the catalytic outcome. However, they are also limited by their unpredictability, as illustrated in the reactions in Scheme 6.2. Furthermore,

some of the products with the desired bimetallic ratio may be limited by their instability or because they could not be isolated. For example, a Co₂Pt species could not be obtained from the reaction of **20** even with a lower molar equivalent of [Pt(IPr)], while a tri- and tetra-gold substituted derivative of **2** could not be obtained even with a larger molar equivalent of Au(IPr)OH. In general, it appears that bimetallic catalysts where the Au or Pt content is higher than that of Ru or Co are inaccessible via these synthetic methodologies.

The clusters were found to be good precursors to RuPt, RuAu and CoPt bimetallic systems. Among them, the first showed catalytic potential for the selective oxidation of alcohol to aldehyde. Synergistic effect between the two metals was observed, although the precise role of Pt in the catalytic system was not determined. A lower Pt content was found desirable, and it may be postulated that a catalyst with a chemical composition of Ru:Pt = x:1 (where x > 6) could give a better performance. More importantly, it was observed that these cluster-derived catalysts performed better with a partially intact ligand shell compared to if the ligand shell was completely removed (Scheme 6.3). Some of the NHC ligands remained intact with calcination at lower temperatures, and the partially intact ligand shell possibly acted as stabilizers and protection against sintering, thus improving catalytic performance. Such ligand-stabilized nanoparticles may have properties intermediate between those of homogeneous and heterogeneous catalysts, and it could be worthwhile to explore the effect that changing the NHC ligands may have on nanoparticle formation, size distribution, and catalytic activity.

Scheme 6.3