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Coordination Chemistry Reviews 252 (2008) 1460–1485

COORDINATION CHEMISTRY REVIEWS

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Review

Platinum based mixed-metal clusters ($Pt_nM_m(CO)_xL_y$, M = Ru or Os; $n + m = 2$ to 10 and L_y = other ligands)—Synthesis, structure, reactivity and applications

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Received 4 July 2007; accepted 4 October 2007
Available online 11 October 2007

Contents

Abbreviations: Pt_nRu_m, platinum–ruthenium carbonyl cluster ($n + m = 2$–10); Pt_nOs_m, platinum–osmium carbonyl cluster ($n + m = 2$–10); M–M, metal–metal; Bu^t, tertiary butyl; Pr^i, isopropyl; L, ligand; nb, bicyclo[2,2,1]hept-2-ene; dba, dibenzylideneacetone; dppm, bis(diphenylphosphino)methane; dppe, 1,2-bis(diphenyphosphino)ethane; dppp, 1,3-bis(diphenyphosphino)propane; dppf, 1,1-bis(diphenylphosphino)ferrocene; dppr, 1,1-bis((diphenylphosphino)ruthenocene; COD, 1,5-cyclooctadiene; bpy, bipyridyl; py, pyridyl; Cp, cyclopentadienyl; THF, tetrahydrofuran; TLC, thin layer chromatography; EXAFS, extended X-ray absorption fine structure; NMR, nuclear magnetic resonance spectroscopy; IR, infrared spectroscopy; PSEPT, polyhedral skeletal electron pair theory; CVE, cluster valence electron count; TEM, transmission electron microscopy; TPR, temperature programmed reduction; XRD, X-ray diffraction; RT, room temperature.

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0010-8545/$ – see front matter
doi:10.1016/j.ccr.2007.10.007

Abstract

This review provides an overview of the synthetic pathways, structure, reactivity and applications of platinum based ruthenium and osmium carbonyl clusters of the types $Pt_nRu_m(CO)_xL_y$ and $Pt_nOs_m(CO)_xL_y$ (where $m+n=2$ to 10 and L_y = other ligands). Some important binuclear complexes are also included. The structural aspects of the clusters are briefly discussed. The application of these clusters in organic transformations and catalysis is reviewed and the future prospects are also highlighted.

Keywords: Platinum–ruthenium; Platinum–osmium; Carbonyl clusters; Synthetic routes; Structural aspects; Catalytic applications

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1. Introduction

Carbon monoxide is one of the most important ligands in transition metal chemistry. The synthesis and the catalytic applications of metal carbonyl clusters with hetero or homonuclear metal centres are pioneering research areas in chemistry [1]. Such cluster compounds are useful as high performance catalysts in various catalytic reactions [1].

In the last three decades, numerous carbonyl clusters with many interesting structural features have been prepared and characterized by various techniques [2]. A variety of ligand systems such as tertiary phosphine (PR_3) [2], ene-yne [3], diyne [3], ynamine [4], and bridging thietane [5] have also been used to substitute some of the labile CO ligands in order to make other interesting cluster compounds [6].

Considerable attention has also been paid towards theoretical models to rationalize the structures of clusters in the solid state as well as in solution. Studies on the relative stabilities of metal clusters and the strengths of their metal–metal and metal–ligand bonds have also been carried out [7].

A vast amount of literature on the synthesis and catalytic applications of a wide range of metal carbonyl clusters has been reviewed by various authors [1–10]. These clusters are known for their reactivity with a variety of substrates to undergo pyrolysis, photolysis, oxidation, double exchange reactions, electron redistribution, and halogen and ligand abstraction [11]. The bonding and stereochemistry of these clusters have also been discussed including edge-and-face bridging, conformational effects, back-bonding and coordination, metal–metal, and localized bonds [11].

Multi-centred metal clusters have been shown to be useful catalysts in petroleum industry and as precursors in supported nano-catalysts [12–14]. A systematic study of the catalytic behaviour of supported bimetallic clusters to determine the effects of changes in the metal frame-work on the catalytic activity has been reported [12–16].

There has been a significant increase in the interest of discovering and developing synthesis, reactivity and applications of new platinum based cluster compounds (see Fig. 1). There have been relatively few groups contributing to the synthesis and chemistry of the Pt–Ru and Pt–Os clusters in particular. Adams and his group have developed elegant synthetic routes for the preparation of a wide range of platinum based ruthenium and osmium clusters, some of which have been used as the model catalysts for hydrogenation reactions [13]. The applications of these clusters have been extended by Johnson and co-workers who have carried out a variety of synthesis of high nuclearity Pt–Ru clusters. These cluster derived bimetallic nanoparticles have been successfully deposited onto multi-wall carbon nanotubes [15]. Farrugia and co-workers also synthesized a variety of clusters involving many interesting reactivity aspects.

In particular, clusters that combine platinum with other metals have received considerable attention because they can model some of the structural and reactivity properties of the important bimetallic platinum alloy catalysts that are used in petroleum reforming [17].

The main objective of this review is to survey the synthetic procedures, structures, reactivity patterns and catalytic applications of platinum based mixed metal carbonyl cluster compounds of the type $Pt_nRu_m(CO)_xL_y$ and $Pt_nOs_m(CO)_xL_y$ (where $n+m=2$–10). This is a growing field (see Fig. 1) and to the best of our knowledge, this is the first review article devoted exclusively to these platinum based heterobimetallic metal carbonyl clusters.

In this article we will cover bimetallic and polynuclear mixed-metal carbonyl complexes from 2 up to a total of 10 metals, with at least one platinum atom while the others are osmium or ruthenium, i.e. $Pt_nRu_m(CO)_xL_y$ and $Pt_nOs_m(CO)_xL_y$.

2. Synthesis and reactivity

The development of systematic routes for the synthesis of mixed-metal cluster compounds has been one of the foremost challenges of modern inorganic chemistry [18]. Despite their

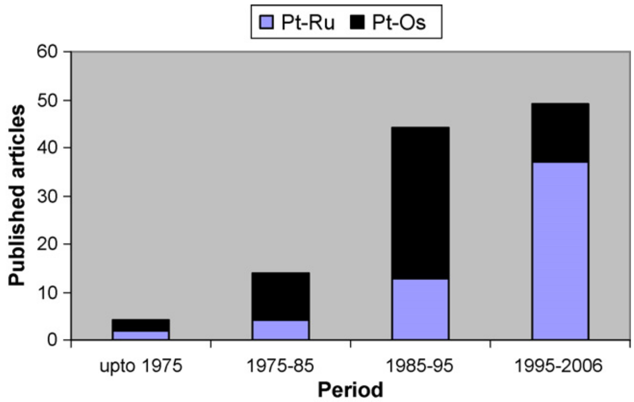


Fig. 1. Histogram of the number of papers reporting Pt–Ru and Pt–Os carbonyl clusters (data obtained from Scifinder).

significance and importance in various catalytic reactions, metal carbonyl cluster compounds have proved remarkably difficult to synthesize in good yields. Therefore there is a need to develop novel synthetic procedures for the selective preparation of a wide range of metal cluster compounds. In this section, we summarize and assess key synthetic routes that have been used to prepare various Pt–Ru and Pt–Os cluster compounds. Reactivity studies of mixed metal carbonyl clusters have led to the isolation and characterization of a variety of interesting new cluster compounds of both low and high nuclearity.

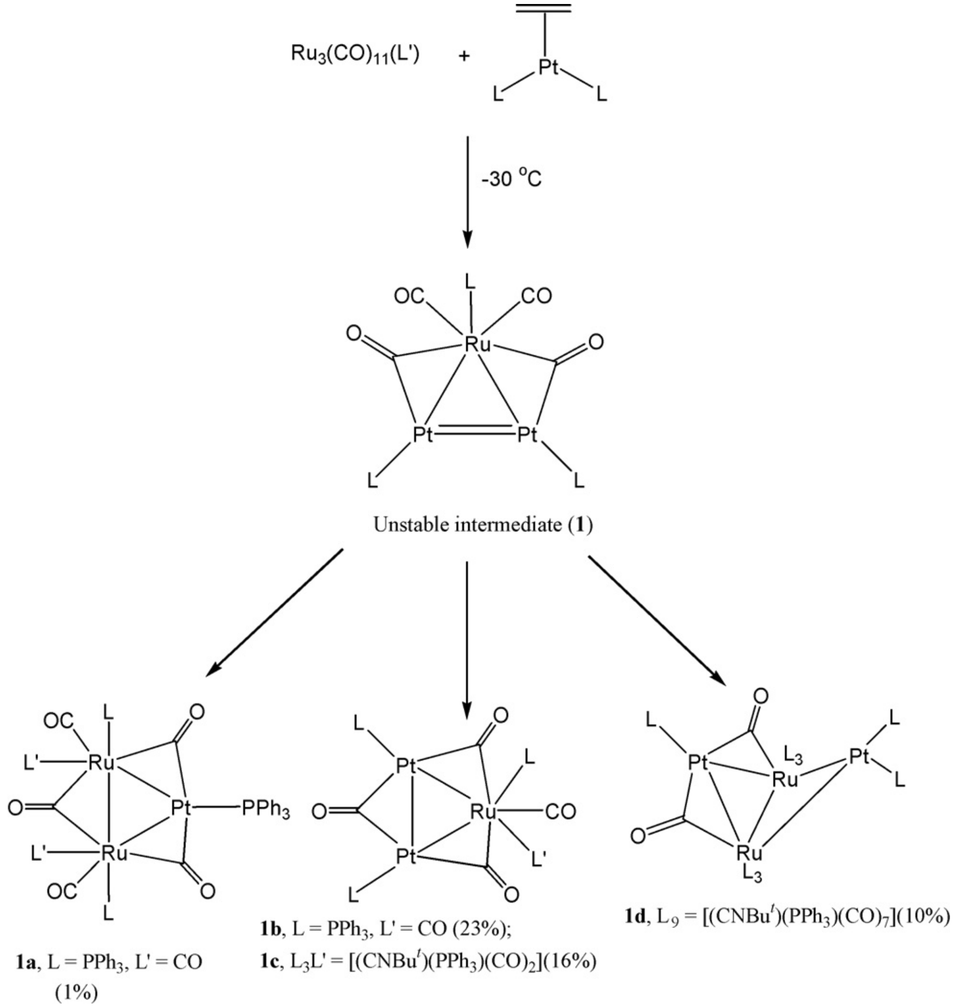
The main methods used for the synthesis of these compounds are (i) reaction of either $Pt(0)L_4$ or $L_2Pt(II)Cl_2$ ($L = PPh_3$ and other ligands), with various $M_3(CO)_{12}$ complexes or their derivatives (where M = Os or Ru), (ii) by splitting the larger clusters to smaller ones and, (iii) aggregating small clusters to give the multi nuclear heterobimetallic clusters.

Generally these cluster compounds react by: (i) the cleavage of metal–metal bonds in the larger clusters to form the smaller clusters, (ii) condensation of two mixed metal clusters thus forming higher nuclearity clusters, (iii) ligand substitution and/or addition (including: phosphine, diphosphine, thioether, carbonyl, 1,5-cyclooctadiene (COD), alkynyl and vinylidene ligands, (iv) the reaction with different substrates, and (v) intramolecular M–M rearrangement of ligands and/or dynamical fluxionality within clusters. In this review, the synthesis and reactivity sections are inseparable as a number of reactions of these clusters with various substrates yield a variety of novel cluster compounds of high nuclearity.

2.1. Pt–Ru carbonyl clusters

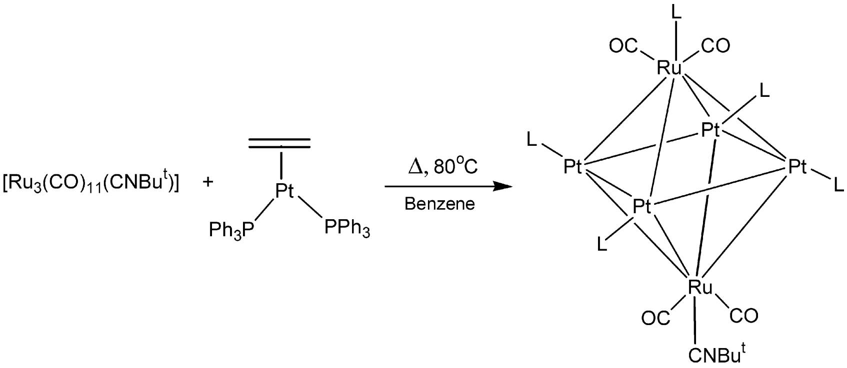
2.1.1. Reactions of platinum(0) compounds with derivatives of $Ru_3(CO)_{12}$

The reaction between $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ at −30 °C affords [19,20] a thermally unstable intermediate complex (**1**), which decomposes at room temperature affording the trinuclear clusters: $[PtRu_2(CO)_7(PPh_3)_3]$ (**1a**), $[Pt_2Ru(CO)_5(PPh_3)_3]$ (**1b**), and $[Pt_2Ru(CO)_6(CNBu^t)(PPh_3)]$ (**1c**); the tetranuclear cluster $[Pt_2Ru_2(CO)_9(CNBu^t)(PPh_3)]$ (**1d**) as well as the hexanuclear clusters, $[Pt_4Ru_2(CO)_{5-n}(CNBu^t)(PPh_3)_{4+n}$ (**2**, $n = 0$ and **3**,



Scheme 1.

$n = 1$) (see Scheme 1 and Eq. (1)).



2, L = PPh$_3$, L' = CO (21%)
3, L = L' = PPh$_3$ (10%)

(1)

The reaction of Pt[COD]$_2$ with Ru(CO)$_5$ at 25 °C produced the hexanuclear dimeric complex, Pt$_2$Ru$_4$(CO)$_{18}$ (**4a**, M = Ru), which has been used to synthesize many other known trinuclear Pt–Ru cluster derivatives with various ligand systems [21] (Eq. (2)). The reaction of Pt(COD)$_2$ with the pentacarbonyl complex of osmium also yielded a new mixed-metal carbonyl clusters of the type Pt$_2$M$_4$(CO)$_{18}$ (**4b**, M = Os).

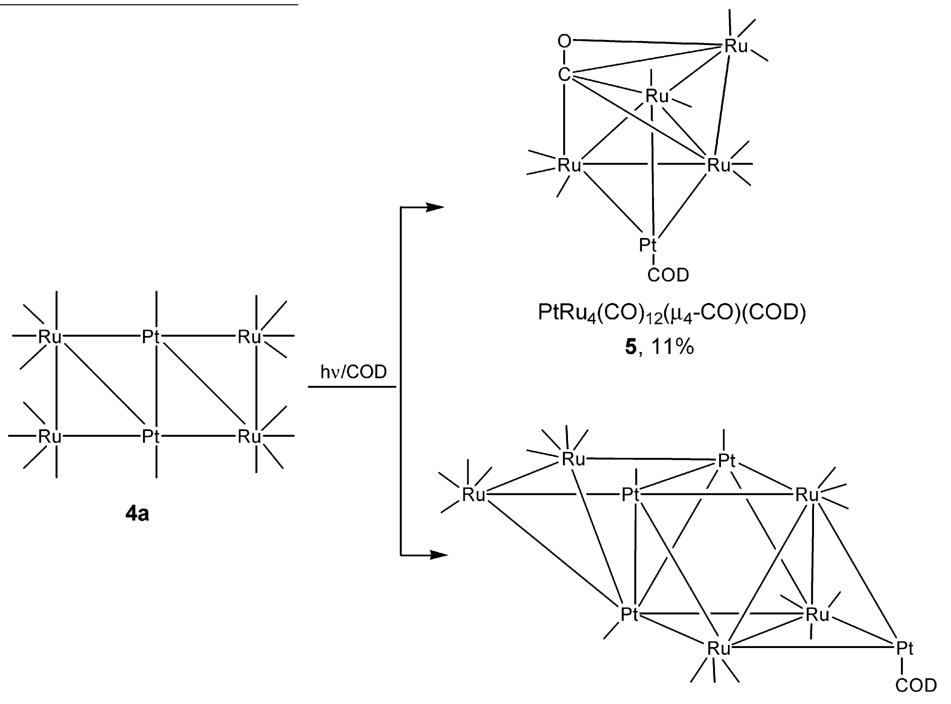
$$\mathrm{Pt[COD]_2\ +\ 2\ Ru(CO)_5 \xrightarrow{25\,^{\circ}C} [PtRu_2(CO)_9]_2}$$

4a, 31%

(2)

2.1.2. Reactions with a variety of ligands

The reaction of **4a** with cyclooctadiene under UV irradiation resulted in the formation of two new mixed metal clusters **5** and **6** (Eq. (3)) [22].

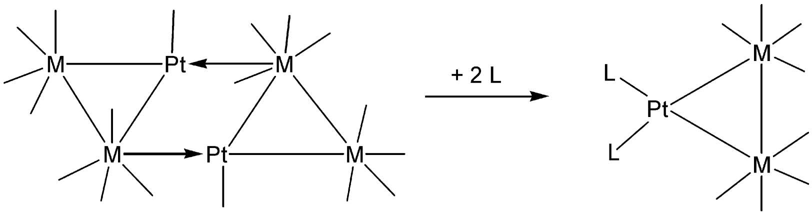


PtRu$_4$(CO)$_{12}$(μ_4-CO)(COD)
5, 11%

Pt$_4$Ru$_5$(CO)$_{20}$(COD)
6, 16%

(3)

However, reaction under similar conditions in the presence of dppe or CO resulted in the formation of PtM$_2$(CO)$_8$L$_2$ (**7**) (where L$_2$ = dppe or 2 CO). These clusters can undergo degradation on reaction with dppe and CO at 50 atm/25 °C (Eq. (4)) [21]. The reaction of **4** with $\mathrm{Pt(PBu^t_3)_2}$ allowed the isolation of $[\mathrm{Pt_3Ru_4(CO)_{17}(PBu^t_3)}]$ in good yields [23]. Also the reaction of $\mathrm{Pt(PBu^t_3)_2}$ with $\mathrm{Ru(CO)_5}$ yielded the products such as $[\mathrm{PtRu_2(CO)_9(PBu^t_3)}]$ and $[\mathrm{PtRu_2(CO)_9(PBu^t_3)_2}]$. The latter complex reacts with molecular hydrogen at 1 atm in hexane at 68 °C to afford the tetranuclear cluster $[\mathrm{Pt_2Ru_2(CO)_8(PBu^t_3)_2(\mu\text{-}H)_2}]$ [24].



4a, M = Ru

7a, L_2 = dppe,
7b, L = CO

(4)

The reaction of $[\mathrm{RuH(CO)_4}]^-$ with $[\mathrm{Pt(dppm)_2}]^{2+}$ has been reported to occur in a stepwise manner to give $[\mathrm{PtRuH(CO)_3(\mu\text{-}dppm)_2}]^+$ and then $[\mathrm{PtRu_2(CO)_6(\mu\text{-}dppm)_2}]$. These products have also been used as precursors to prepare further Pt–Ru bonded complexes such as $[\mathrm{PtRuHCl(CO)_2(\mu\text{-}dppm)_2}]$ and $[\mathrm{PtRuHCl(CO)_3(\mu\text{-}dppm)_2}]$ [25].

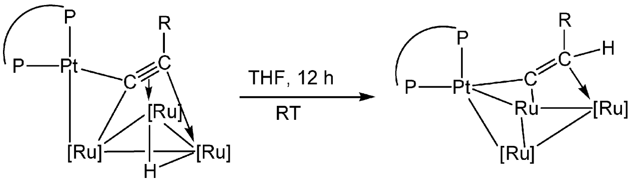
The synthesis of $[\mathrm{Pt_3(\mu\text{-}H)(\mu\text{-}dppm)_3\{Ru(CO)_4\}}]^+$ containing the PtRu(μ-H) unit is formed by reaction of $[\mathrm{Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3}]^{2+}$ with the anion $[\mathrm{RuH(CO)_4}]^-$. In solution, this complex rearranges to the cluster $[\mathrm{Pt_3Ru(\mu\text{-}H)(CO)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)_3}]^+$. It is interesting to note that these two complexes exhibit fluxionality [26].

2.1.3. *Reactions with various unsaturated hydrocarbons*

Formation of new clusters on irradiation with UV light in the presence of alkynes as ligands has been reported [27–31]. For example the reaction of **8** with diphenylacetylene has been reported to give a hexanuclear cluster **9** and the reverse reaction has been observed in the presence of carbon monoxide (Eq. (5)).

Interestingly, novel mixed–metal compounds such as $\mathrm{PtRu_3(\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^3{:}\eta^4\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_{10}(dppe)}$ with different isomers have been formed by reacting the *cis*-dialkynyl platinum(II) complex, $\mathrm{Pt(C{\equiv}CPh)_2(dppe)}$, with $\mathrm{Ru_3(CO)_{12}}$, via a C–C bond coupling of the alkynyl ligands [27]. The trinuclear cluster $[\mathrm{Pt_2Ru(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2}]$ was obtained by treating $\mathrm{Ru_3(CO)_{12}}$ with $[\mathrm{Pt(\eta^3\text{-}PhC{\equiv}CC{\equiv}CPh)(PPh_3)_2}]$ [27]. This cluster has been used for the synthesis of other Pt–Ru cluster compounds and their derivatives with PhC≡CH in good yields [28].

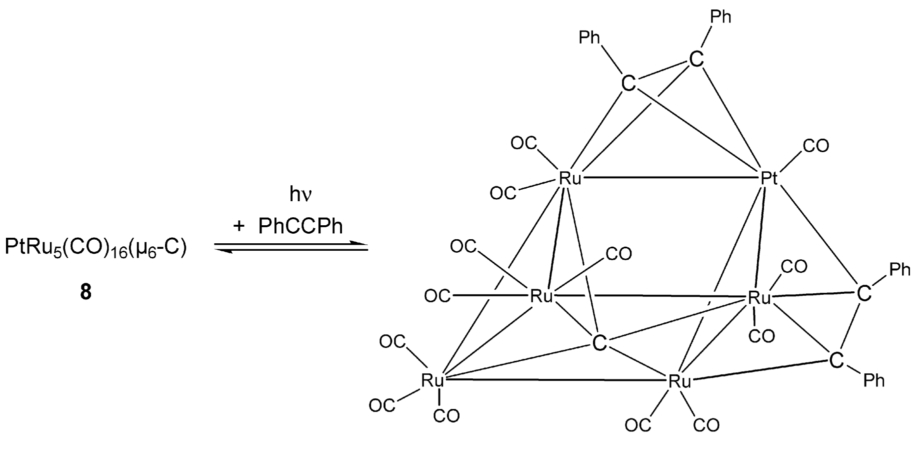
The rearrangement of the spiked triangular cluster $[\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}CCBu^t)(CO)_9(dppe)}]$ (**10**) in solution into the butterfly cluster $[\mathrm{PtRu_3(\mu_4\text{-}\eta^2\text{-}C{=}CHBu^t)(CO)_9(dppe)}]$ (**11**) has been reported using EXAFS spectra (Eq. (6)) [29]. The reaction of tetranuclear $[\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}CCBu^t)(CO)_9(dppe)}]$ complex with $\mathrm{Ph_2PC{\equiv}CPPh_2}$ affords the butterfly cluster $[\mathrm{PtRu_3((\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_7(dppe)}]$ [29].



10

11

(6)

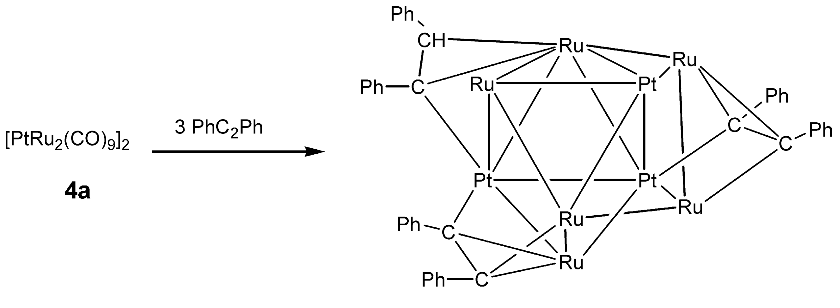


$\mathrm{PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)}$

9, 37%

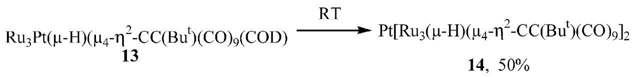
(5)

The reaction of $Pt(PPh_3)_2(PhC{\equiv}CPh)$ with $Ru_3(CO)_{12}$ yielded $Pt_2Ru(CO)_5(PPh_3)_2(PhC{\equiv}CPh)$ (24%) and $PtRu_2(CO)_7(PPh_3)_2(PhC{\equiv}CPh)$ (45%) [32]. The reaction of **4a** with various substituted alkynes yielded the corresponding alkyne coupling products in low yields as a result of fragmentation of the Pt_2Ru_4 cluster [33]. When $Pt_2Ru_4(CO)_{18}$ was treated with 3 equivalents of $PhC{\equiv}CPh$, the new complex $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ was formed [21] (Eq. (7)).



$Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$ (7)

The elimination of a Pt atom and COD was demonstrated in the reaction of the tetranuclear cluster $PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}C(Bu^t)(CO)_9(COD)$ (**13**) to give the novel hexaruthenium alkynyl cluster $Pt[Ru_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}C(Bu^t)(CO)_9]_2$ (**14**), showing that the linking of two trinuclear clusters by a Pt atom is feasible (Eq. (8)). Fluxional behaviour of this Pt bridged cluster was also observed using variable temperature NMR spectroscopy [33].



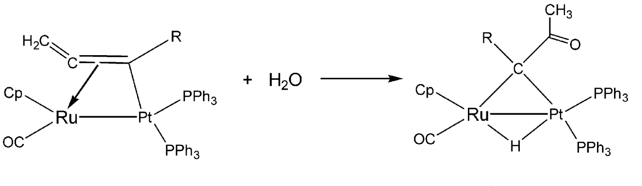
$$\underset{\mathbf{13}}{Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}CC(Bu^t)(CO)_9(COD)} \xrightarrow{RT} \underset{\mathbf{14},\ 50\%}{Pt[Ru_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}CC(Bu^t)(CO)_9]_2} \qquad (8)$$

In the reactions of $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**12**) with CO at 25 °C new compounds $Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ (**15**) and $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ (**16**) were obtained (Scheme 2), with the reaction pathway leading to **12** being reversible, yielding the starting cluster quantitatively under reflux. In contrast, reaction with dppe leads to the formation of a single product, $PtRu_4(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppe)$ (**17**) [34].

Displacement of the labile COD ligand was easily achieved by reacting dppe with the tetranuclear alkynyl cluster $PtRu_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(Bu^t)\}(CO)_9(COD)$ (**18**) to give two complexes, the alkynyl cluster $PtRu_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{\equiv}C(Bu^t)\}(CO)_9(dppe)$ (**19**) and the tautomeric vinylidene cluster $Ru_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)(Bu^t)\}(CO)_9(dppe)$ (**20**). These two products were found to interconvert in solution through an intramolecular mechanism. Kinetic studies further revealed that the vinylidene is the thermodynamically favoured isomer (Scheme 3) [35].

Protonation of both the alkynyl and vinylidene clusters was carried out using HBF_4 to give the alkyne complex $[PtRu_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}HC{\equiv}C(Bu^t)\}(CO)_9(dppe)]^+BF_4^-$ (**21**) and the cationic hydrido vinylidene cluster $[PtRu_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)(Bu^t)\}(CO)_9(dppe)]^+BF_4^-$ (**22**) respectively. Thus α-carbon protonation was seen in the latter complex (Scheme 3) [35].

The synthesis and reaction chemistry of heterobinuclear and trinuclear Pt–Ru allenyl complexes such as **23**, **24** have been reported by Wojcicki and co-workers [36]. The treatment of the complexes **23** and **24** in organic solvents with deactivated alumina or silica yielded the corresponding hydridoalkylidene complexes **25** and **26** (Eq. (9)) [37].

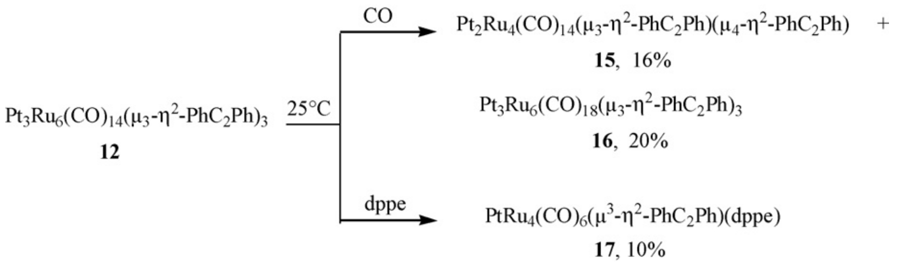


23, R = H;
24, R = Ph

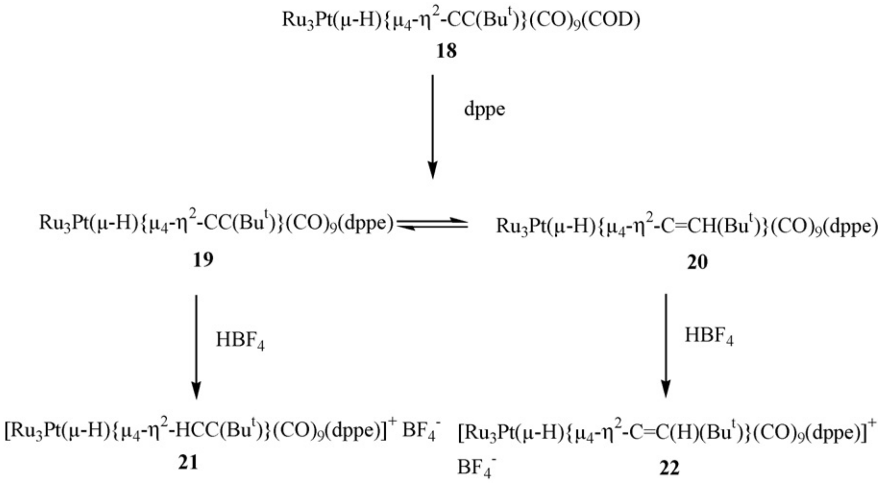
25, R = H;
26, R = Ph

(9)

The complexes $Pt(nb)_{3-n}(PPr^i_3)_n$ ($n = 1, 2$; nb = bicyclo [2.2.1]hept-2-ene) prepared *in situ* from $Pt(nb)_3$, have been used to prepare novel Pt–Ru clusters such as $PtRu_3(CO)_{11}(PPr^i_3)_2$



Scheme 2.



Scheme 3.

(61%), $PtRu_3(\mu\text{-}H)(\mu\text{-}\eta^3\text{-}MeCCHCMe)(CO)_9(PPr^i_3)$ (51%), $PtRu_3(\mu_3\text{-}\eta^2\text{-}PhCCPh)(CO)_{10}(PPr^i_3)$ (40%), $PtRu_3(\mu\text{-}H)(\mu_4\text{-}N)(CO)_{10}(PPr^i_3)$ (15%) and $PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}NO)(CO)_{10}(PPr^i_3)$ by adding $Pt(PPr^i_3)_n$ fragments to saturated triruthenium clusters [38].

2.1.4. Synthesis of novel clusters with bridging phosphorus groups

The preparation of $[PtRu_4(\mu_4\text{-}PR)(CO)_{13}(PPh_3)$ where R = NPr^i_2 (**27**), F (**29**)] was carried out by capping the Ru_3P face of the *nido* clusters $[Ru_4(CO)_{13}(\mu_3\text{-}PR)]$ with the labile $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$. Complex **27** undergoes acid hydrolysis to yield the corresponding phosphorus monoxide complex, $[Ru_4(CO)_{12}Pt(CO)PPh_3(\mu_4\text{-}PO)][H_2NPr^i_2]$ (**28**) and complex **29** reacts with ethanol to form the alkoxyphosphinidene complex **30**, $[Ru_4(CO)_{12}Pt(CO)PPh_3(\mu_4\text{-}POEt)]$ (see Scheme 4) [39].

2.1.5. Clusters with hydride and carbide bridging ligands

Heterobimetallic clusters with bridging hydride ligands have also been synthesized by the reaction of $Ru_4(CO)_{13}(\mu\text{-}H)_2$ with $Pt(COD)_2$. From this reaction, $PtRu_4(CO)_{13}(COD)(\mu\text{-}H)_2$ (37%) was obtained as a major product, while other minor products such as $PtRu_3(CO)_9(COD)$ $(\mu\text{-}CO)(\mu\text{-}H)_2$ (10%), $Pt_2Ru_4(CO)_{11}(COD)_2(\mu_3\text{-}H)_2$ (2.5%) and $Pt_5Ru_5(CO)_{18}(COD)_2(\mu_3\text{-}H)_2$ (1%) were also obtained [40].

Recently, the synthesis and reactivity of Pt–Ru mixed-metal imido clusters without CO ligands have been reported from a diruthenium imido-methylene scaffold $[(Cp^*Ru)_2(\mu_2\text{-}NPh)(\mu_2\text{-}CH_2)]$ [41].

Multi-site bound unsaturated hydrocarbyl ligands have been given considerable attention in cluster chemistry [42]. A number of studies with C_1 fragments such as CH_2, CH, and C as ligands have also been reported in transition metal cluster chemistry [43]. The platinum–ruthenium containing clusters such as $PtRu_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(PR_3)(\eta\text{-}C_5H_5)_2]$, $Pt_2Ru_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$ and $Pt_2Ru_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$ were prepared by reacting $Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(L)(\eta\text{-}C_5H_5)_2]$ (where L = CO, NCMe) with $Pt(C_2H_4)_2(PR_3)$ (where R = C_6H_{11}, Pr^i). These μ_4-methylidine and μ_4-carbido ligands may provide an insight into certain catalytic processes that occur on surfaces [44].

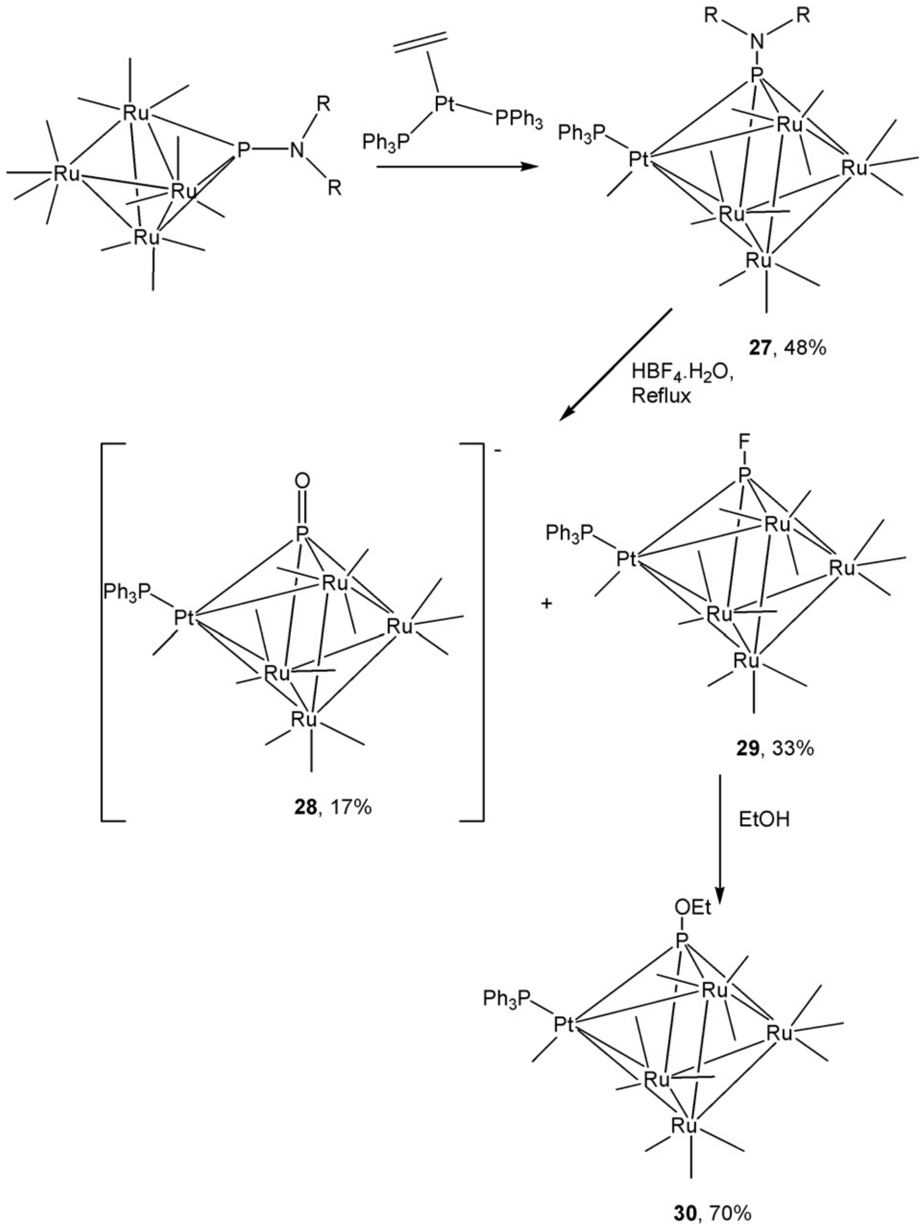
The hydride and carbide bridging cluster compound $PtRu_5(CO)_{14}(PBu_3{}^t)(\mu\text{-}H)_2(\mu_6\text{-}C)$ (**32**) was formed by the reaction of $PtRu_5(CO)_{15}(PBu^t_3)_2(C)$ (**31**) with H_2 at 97 °C. The resulting product was observed to undergo addition of $Pt(Bu^t_3)_2$ to give the complex $Pt_2Ru_5(CO)_{14}(PBu_3{}^t)_2(\mu\text{-}H)_2(\mu_6\text{-}C)$ (**33**) (Scheme 5) [45]. Also, the reaction of $PtRu_5(CO)_{16}((\mu_6\text{-}C)$ with $Pt(PBu^t_3)_2$ and $Pd(PBu^t_3)_2$ produced the mixed metal clusters, $PtRu_5(CO)_{16}(\mu_6\text{-}C)[Pt(PBu^t_3)]$, $PtRu_5(CO)_{16}(\mu_6\text{-}C)[Pt(PBu^t_3)]_2$, $PtRu_2(CO)_{16}(\mu_6\text{-}C)[Pd(PBu^t_3)]$ and $PtRu_5(CO)_{16}(\mu_6\text{-}C)[Pd(PBu^t_3)]_2$ [45].

The synthesis of new Sn and Ge containing $PtRu_5$ clusters (**34–37**) was achieved by the reaction of $PtRu_5(CO)_{14}(PBu_3{}^t)(\mu\text{-}H)_2(\mu_6\text{-}C)$ with $HGePh_3$ and $HSnPh_3$ under reflux (Scheme 6) [45].

Observations of intramolecular exchange of phosphine and thioether ligands between the Ru and Pt atoms in $PtRu_5(CO)_{15}(L)(\mu_6\text{-}C)$ (L = PMe_2Ph, PMe_3, PBu^t_3 and SMe_2) have also been reported [46].

$PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)$ (**39**) has been shown to exhibit facile intramolecular exchange of the phosphine ligand between a platinum and ruthenium atom (Eq. (10)) to give **40** [46].

$$\underset{\textbf{38}}{PtRu_5(CO)_{16}(\mu_6\text{-}C)} + PMe_2Ph \xrightarrow{25^\circ C} \underset{\textbf{39},\ 36\%}{PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)} + \underset{\textbf{40},\ 45\%}{PtRu_5(CO)_{14}(PMe_2Ph)_2(\mu_6\text{-}C)} \qquad (10)$$



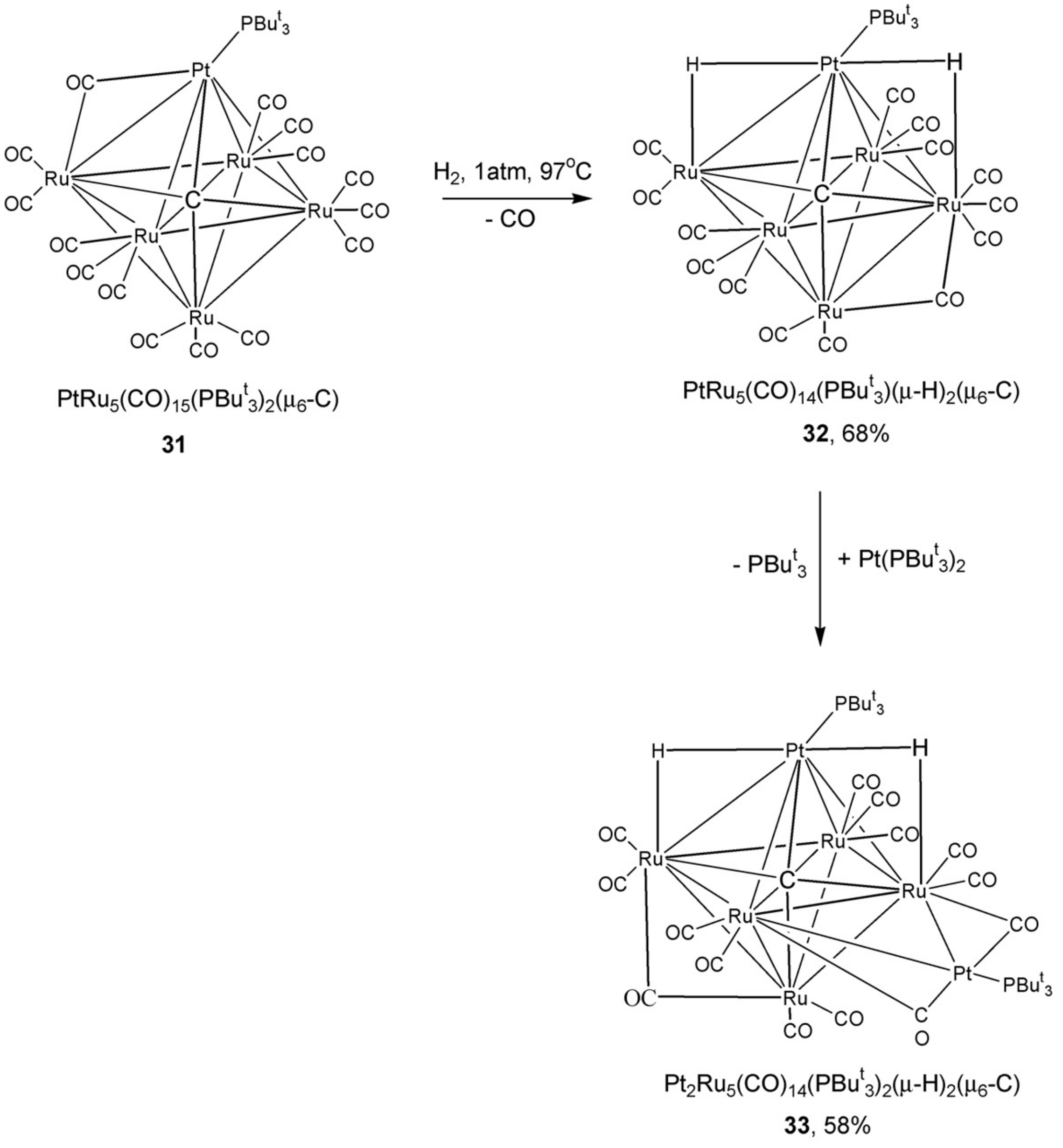
Scheme 4.

A fluxional process involving CO exchange in solution was observed for $PtRu_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PPr^i_3)$ using variable-temperature NMR spectroscopy. The lowest energy process resulted in complete equilibration of all Ru-bound CO ligands while the higher energy process resulted in complete CO scrambling [47].

The reaction of $Pt_2Ru_4(CO)_{18}$ (**4**) with $Ru_4(CO)_{13}(\mu\text{-}H)_2$ at 97 °C yielded the new decanuclear bimetallic cluster $Pt_2Ru_8(CO)_{23}(\mu\text{-}H)_2$. This complex reacted with 1,2-bis(diphenylphosphino)ethane (dppe) to form the corresponding dppe derivative, $Pt_2Ru_8(CO)_{21}(\mu\text{-}CO)_2(\mu\text{-}H)(dppe)$. In a similar manner, the reaction of **4** with $PtRu_3(CO)_{10}(\mu\text{-}H)_2(COD)$ to yield $Pt_3Ru_7(CO)_{21}(\mu\text{-}CO)(\mu_3\text{-}H)_2$ was seen. The reaction of $Pt_2Ru_8(CO)_{23}(\mu_3\text{-}H)_2$ with $Pt_3Ru_7(CO)_{21}(\mu\text{-}CO)(\mu_3\text{-}H)_2$ yielded $Pt_3Ru_6(CO)_{21}(\mu\text{-}CO)(\mu_3\text{-}H)_2$ in 55% yield [47].

2.1.6. Ionic clusters

The cluster $[Pt_3(\mu\text{-}H)(\mu\text{-}dppm)_3\{Ru(CO)_4\}]^+$ (**41**) was observed to rearrange to the isomeric cluster $[Pt_3Ru(\mu\text{-}H)(CO)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)_3]^+$ (**42**) quantitatively at room temperature in solution (Eq. (11)) [26]. The cluster salt $[Ru_6C(CO)_{16}]^{2-}[Pt_2(CO)_2(dppm)_2]^{2+}$ was obtained from the reaction of $[Ru_6C(CO)_{17}]$ with $[Pt_2(CO)_3(dppm)_2]$. Heating of this ion pair in an autoclave at 145 °C resulted in the fusion of the metal frame works to give a nanonuclear mixed metal cluster $[Pt_3Ru_6C(CO)_{16}(dppm)_2]$. Also the coupling of two neutral clusters $[Ru_5C(CO)_{15}]$, and $[Pt_2Rh_2(CO)_6(dppm)_2]$ yielded the



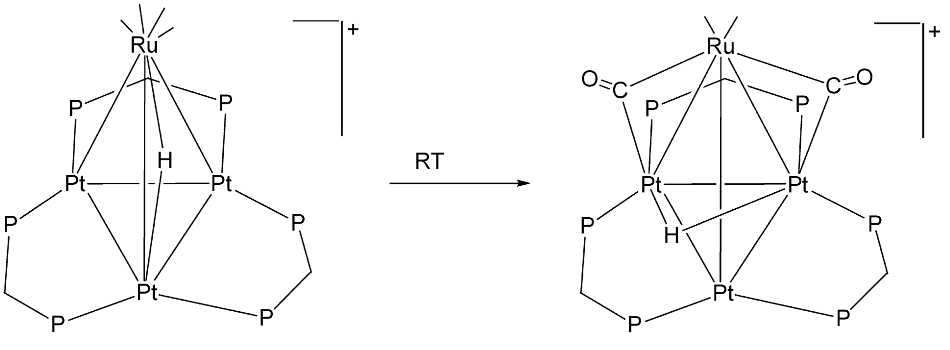
$PtRu_5(CO)_{15}(PBu^t_3)_2(\mu_6\text{-}C)$
31

$PtRu_5(CO)_{14}(PBu^t_3)(\mu\text{-}H)_2(\mu_6\text{-}C)$
32, 68%

$Pt_2Ru_5(CO)_{14}(PBu^t_3)_2(\mu\text{-}H)_2(\mu_6\text{-}C)$
33, 58%

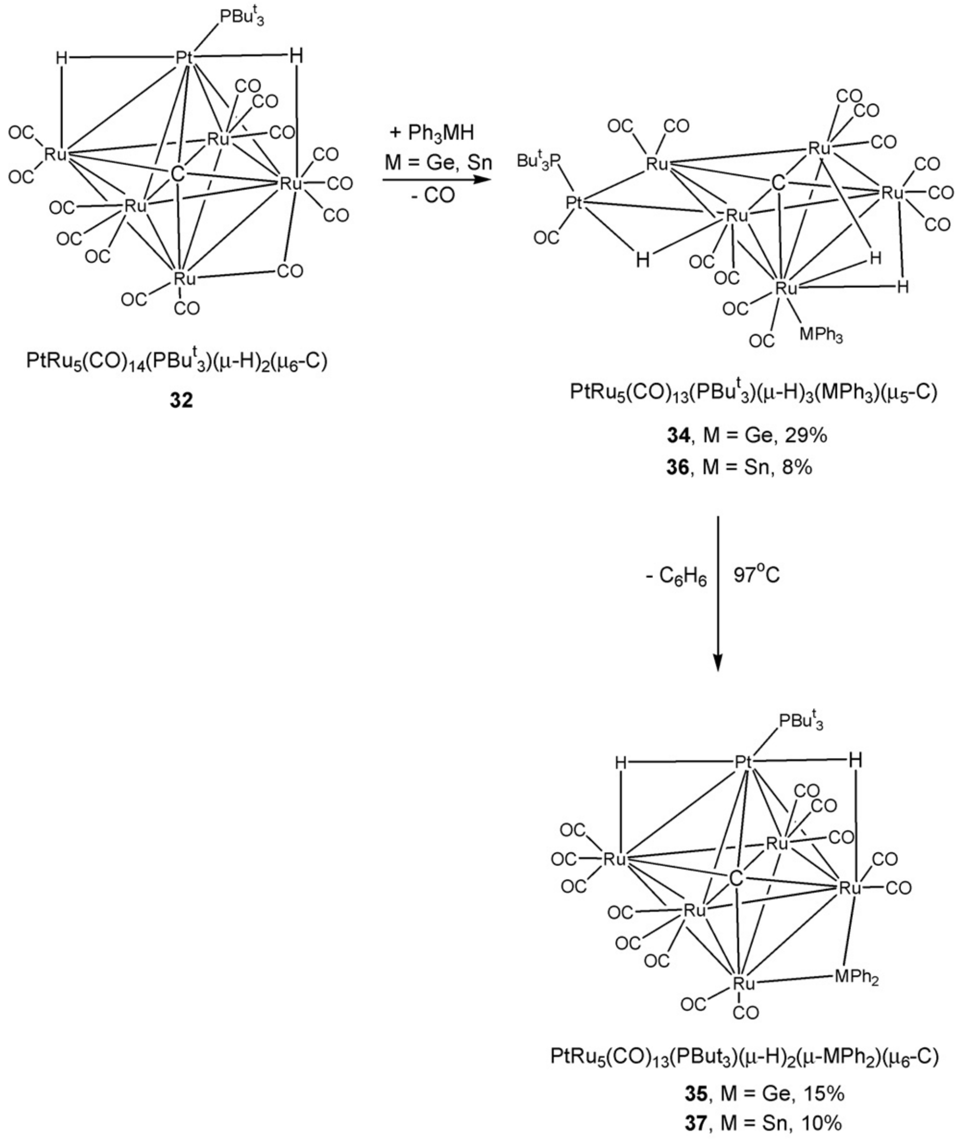
Scheme 5.

trimetallic $[Pt_2Ru_5CRh_2(CO)_{16}(dppm)_2]$ [48].



41 **42** (11)

The chemically activated nucleation and growth of nanoscale materials of Pt–Ru cluster compounds such as $PtRu_5C(CO)_{16}$ (**43**) is of fundamental importance in heterogeneous catalysis, microelectronics and advanced materials synthesis [49,50].



Scheme 6.

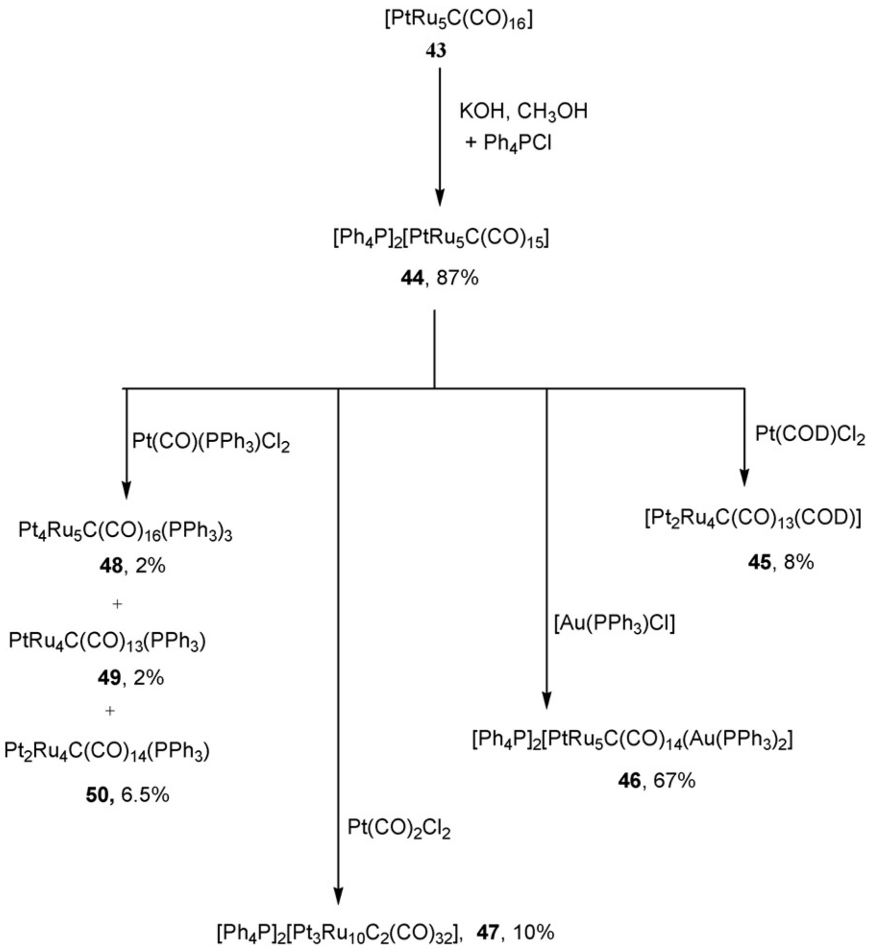
These applications have been extended to the preparation of carbon-supported molecular mixed-metal cluster compounds [51].

The synthesis of novel Pt–Ru mixed metal cluster compounds has been reported starting from the neutral carbide cluster [$PtRu_5C(CO)_{16}$], which undergoes almost quantitative reduction to the dianionic [$PtRu_5C(CO)_{15}$]$^{2-}$ (**44**) on reaction with KOH in methanol (Scheme 7). The reactivity of **44** with metal halides yielded a variety of products **45–50** containing platinum and gold metals as additives.

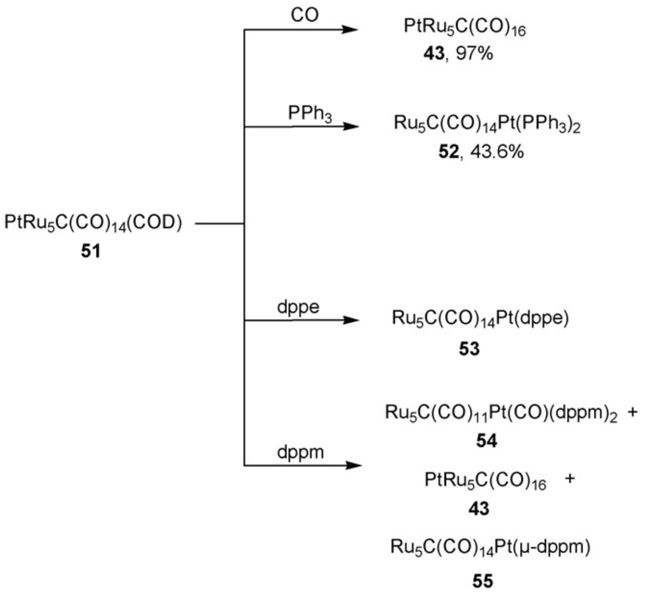
Interesting ligand exchange reactions involving Pt–Ru clusters have been reported in the literature [52]. Treatment of $PtRu_5C(CO)_{14}(COD)$ (**51**) with CO gave the compound $PtRu_5C(CO)_{16}$ (**43**) cleanly, while reaction with PPh_3 displaced COD to afford $Ru_5C(CO)_{14}Pt(PPh_3)_2$ (**52**). Intramolecular exchange of one phosphine between the Pt atom and an adjacent Ru atom was observed. Similarly the reaction with dppe resulted in the direct substitution of the COD ligand to give $PtRu_5C(CO)_{14}(dppe)$ (**53**). In contrast, reaction with dppm gave three products $PtRu_5C(CO)_{12}(dppm)_2$ (**54**), $PtRu_5C(CO)_{16}$ (**43**) and $PtRu_5C(CO)_{14}(\mu\text{-dppm})$ (**55**) (Scheme 8) [52].

The dianionic ruthenium cluster [$Ru_6C(CO)_{16}$]$^{2-}$ has been used as precursor in the preparation of novel heterobimetallic clusters (**56**, **57**) (see Scheme 9) [53]. The cluster **57** can react with various ligands such as PPh_3, CO and dppm to yield the corresponding clusters (**58**, **59**).

Johnson and co-workers reported a new method, based on chloride abstraction by silica from PtL_2Cl_2 complexes, followed by reaction with anionic ruthenium clusters, to produce Pt–Ru clusters (**60–63**) with a chosen nuclearity in high yields (Scheme 10) [54,53].



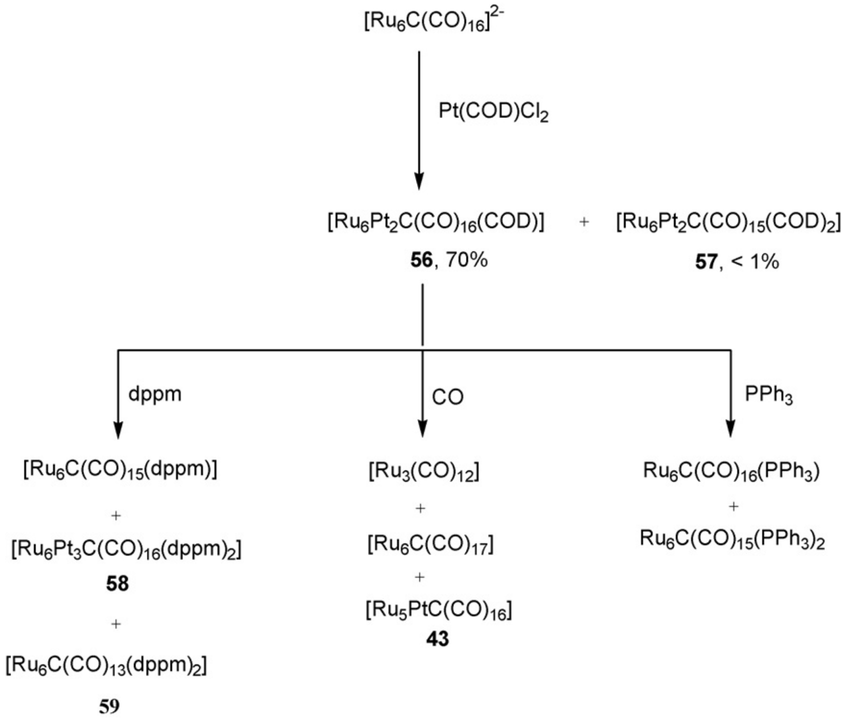
Scheme 7.



Scheme 8.

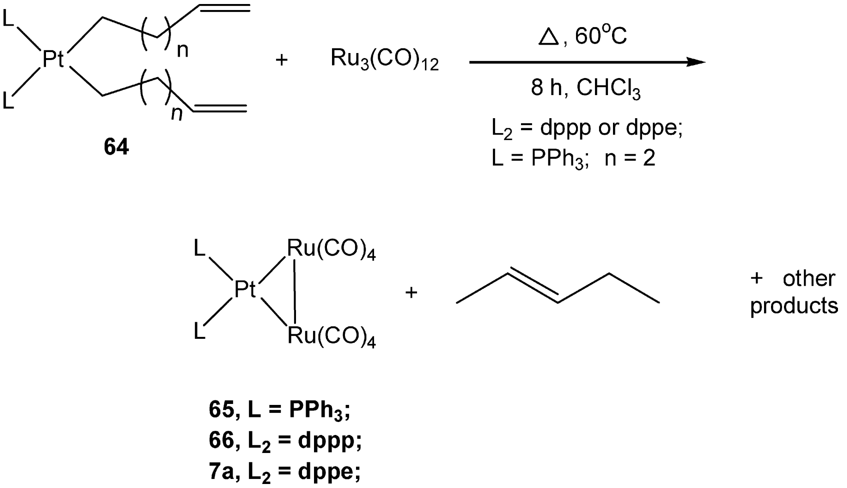
A useful synthetic approach has been reported for the construction of Pt_2Ru_4 clusters such as $[\{Pt_2(\mu\text{-dppm})_2(C{\equiv}Cbpy)_4\}\{Ru(bpy)_2\}_4](PF_6)_8$ using $Ru(bpy)_2Cl_2$ and the diplatinum complex $Pt_2(\mu\text{-dppm})_2(C{\equiv}Cbpy)_4$ [55]. The synthesis of iodide bridging heterobimetallic complexes (for e.g. $PtRuCp(CO)(\mu\text{-I})(\mu\text{-dppm})I_2$) have also been prepared with $Cp(CO)Ru(\kappa^1\text{-dppm})I$ and $Pt(COD)I_2$ [56].

Recently, we have also found a novel route to prepare a variety of known $PtRu_2$ and Pt_2Ru type carbonyl clusters by the reaction of the platinum-alkenyl complexes of the type $L_2Pt(1\text{-alkenyl})_2$ (**64**) [where L = PPh_3 (**65**) or L_2 = dppe (**7a**) or dppp (**66**)] with $Ru_3(CO)_{12}$ (Eq. (12)). In solution, the PPh_3 containing $PtRu_2$ cluster undergoes an irreversible reorganization to the Pt_2Ru cluster $[RuPt_2(CO)_5(PPh_3)_3]$ (**1b**) where the PPh_3 ligand migrates from platinum to ruthenium while some of the terminal CO ligands become bridging between the platinum and ruthenium centres. The reactivity of these clusters with several substituted alkynes and elemental sulfur to give the respective



Scheme 9.

bridging carbonyl clusters have been studied [57].



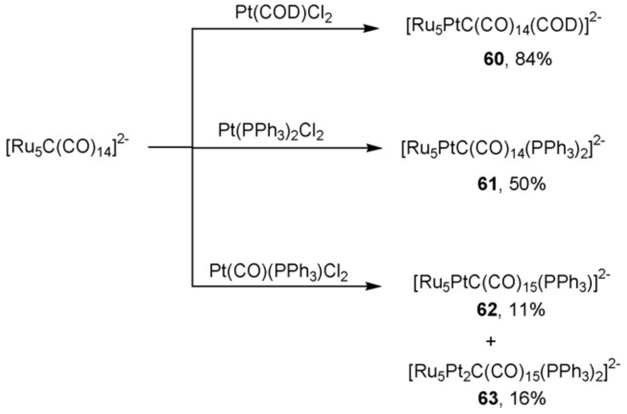
(12)

2.2. *Pt–Os carbonyl clusters*

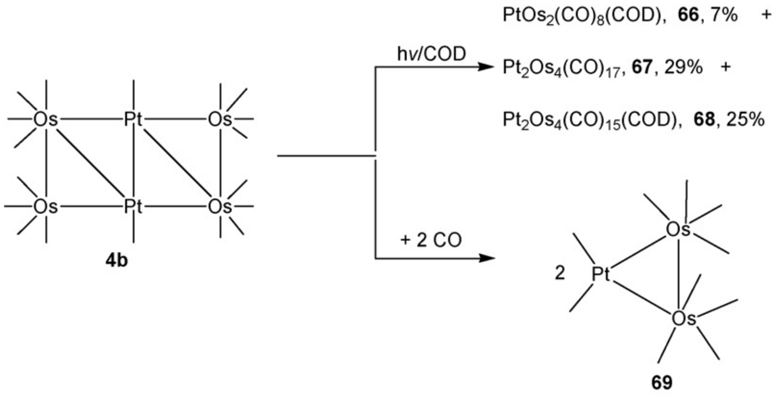
2.2.1. *Reactions of $Pt_2Os_4(CO)_{18}$*

The reaction of Pt[COD]$_2$ with $Os_3(CO)_{12}$ produced $Pt_2Os_4(CO)_{18}$ (**4b**) [21,22]. The reaction of **4b** with COD in the presence of light has been carried out to produce the COD derivatives of Pt–Os clusters (**66–68**). The synthesis of Pt–Os cluster **69** was reported from the carbonylation of $Pt_2Os_4(CO)_{18}$ as shown in Scheme 11 [21,23].

The hydrogenation of **4b** yielded several hydrogen-rich platinum osmium clusters at room temperature such as $PtOs_5(CO)_{16}(\mu\text{-}H)_6$, $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$, $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$ and $PtOs_6(CO)_{18}((\mu\text{-}H)_8$ [58].



Scheme 10.



Scheme 11.

Recently, Adams et al. have reported [59] the synthesis of new Pt–Os cluster compounds by the sequential addition of $\mathrm{Pt(PBu^t_3)}$ groups to the three Os–Os bonds of the metal cluster of $\mathrm{Os_3(CO)_{12}}$, which yielded $\mathrm{PtOs_3(CO)_{12}(PBu^t_3)}$, $\mathrm{Pt_2Os_3(CO)_{12}(PBu^t_3)_2}$, $\mathrm{Pt_3Os_3(CO)_{12}(PBu^t_3)_3}$ as the products. When $\mathrm{Pt_2Os_3(CO)_{12}(PBu^t_3)_2}$ is treated with $\mathrm{PPh_3}$, the elimination of the $\mathrm{Pt(PBu^t_3)}$ groups together with either one or two CO ligands was observed by forming the $\mathrm{PPh_3}$ derivatives of $\mathrm{Os_3(CO)_{12}}$ such as $\mathrm{Os_3(CO)_{11}(PPh_3)}$ and $\mathrm{Os_3(CO)_{10}(PPh_3)_2}$.

Two new clusters $\mathrm{Pt_2Os_4(CO)_{11}(COD)_2}$ (**70**) and $\mathrm{Pt_2Os_4(CO)_{12}(COD)_2}$ (**71**) were obtained from the reaction of **4b** with COD at 97 °C (Eq. (13)). It was also shown that the cluster **70** reacted reversibly with CO thus proving its unsaturation (Eq. (14)) [60].

$$\underset{\textbf{4b}}{\mathrm{Pt_2Os_4(CO)_{18}}} \xrightarrow[97^{\circ}\mathrm{C}]{\mathrm{COD}} \underset{\textbf{70}}{\mathrm{Pt_2Os_4(CO)_{11}(COD)_2}} + \underset{\textbf{71}}{\mathrm{Pt_2Os_4(CO)_{12}(COD)_2}} \tag{13}$$

$$\underset{\textbf{70}}{\mathrm{Pt_2Os_4(CO)_{11}(COD)_2}} \underset{\substack{25^{\circ}\mathrm{C,\ 1atm} \\ \mathrm{-CO}}}{\overset{\mathrm{+CO}}{\rightleftharpoons}} \underset{\textbf{71}}{\mathrm{Pt_2Os_4(CO)_{12}(COD)_2}} \tag{14}$$

Aggregation of the cluster $\mathrm{Pt_2Os_3(CO)_{10}(COD)_2}$ (**72**) in refluxing hexane was described by Adams et al. to give $\mathrm{Pt_4Os_6(CO)_{22}(COD)}$ (**73**) and $\mathrm{Pt_4Os_6(CO)_{21}(COD)_2}$ (**74**) (Eq. (15)) [22].

$$\underset{\textbf{72}}{\mathrm{Pt_2Os_3(CO)_{10}(COD)_2}} \xrightarrow[\mathrm{Reflux}]{\mathrm{Hexane}} \underset{\textbf{73}}{\mathrm{Pt_4Os_6(CO)_{22}(COD)}} + \underset{\textbf{74}}{\mathrm{Pt_4Os_6(CO)_{21}(COD)_2}} \tag{15}$$

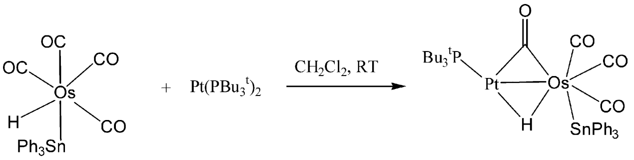
Conversely, symmetric splitting of the cluster **4** in the presence of COD and promoted by UV has been reported to afford the complex $\mathrm{PtOs_2(CO)_8(COD)}$ (**75**) together with three hexanuclear complexes $\mathrm{Pt_2Os_4(CO)_{15}(COD)}$ (**76**), $\mathrm{Pt_2Os_4(CO)_{12}(COD)_2}$ (**77**) and $\mathrm{Pt_2Os_4(CO)_{17}}$ (**78**) (Eq. (16)) [61].

$$\underset{\textbf{4b}}{\mathrm{Pt_2Os_4(CO)_{18}}} \xrightarrow[\mathrm{UV,\ 25^{\circ}\ C}]{\mathrm{COD}} \begin{array}{l} \underset{\textbf{75},\ 7\%}{\mathrm{PtOs_2(CO)_8(COD)}} + \underset{\textbf{76},\ 25\%}{\mathrm{Pt_2Os_4(CO)_{15}(COD)}} + \\ \underset{\textbf{77},\ 6\%}{\mathrm{Pt_2Os_4(CO)_{12}(COD)_2}} + \underset{\textbf{78},\ 29\%}{\mathrm{Pt_2Os_4(CO)_{17}}} \end{array} \tag{16}$$

2.2.2. Clusters with main-group metals

The mono(triphenylstannylane)triosmiumhydrido carbonyl cluster $\mathrm{Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)}$ and tris(diphenylstannylene)triosmium carbonyl complex, $\mathrm{Os_3(CO)_9(\mu\text{-}SnPh_2)_3}$ have been shown to react with $\mathrm{Pt(PBu^t_3)_2}$ by adding a $\mathrm{Pt(PBu^t_3)}$ group across one of the Os–Sn bonds to give a bridging μ_3 $\mathrm{SnPh_2}$ ligand in **79** (as shown in Scheme 12). However, a similar reaction of $\mathrm{Pt(PPh_3)_4}$ with **80** leads instead to insertion of a $\mathrm{Pt(PPh_3)_2}$ group into Sn–C bonds of one of the phenyl rings of one of the bridging $\mathrm{SnPh_2}$ groups and interestingly, this insertion is reversible [62].

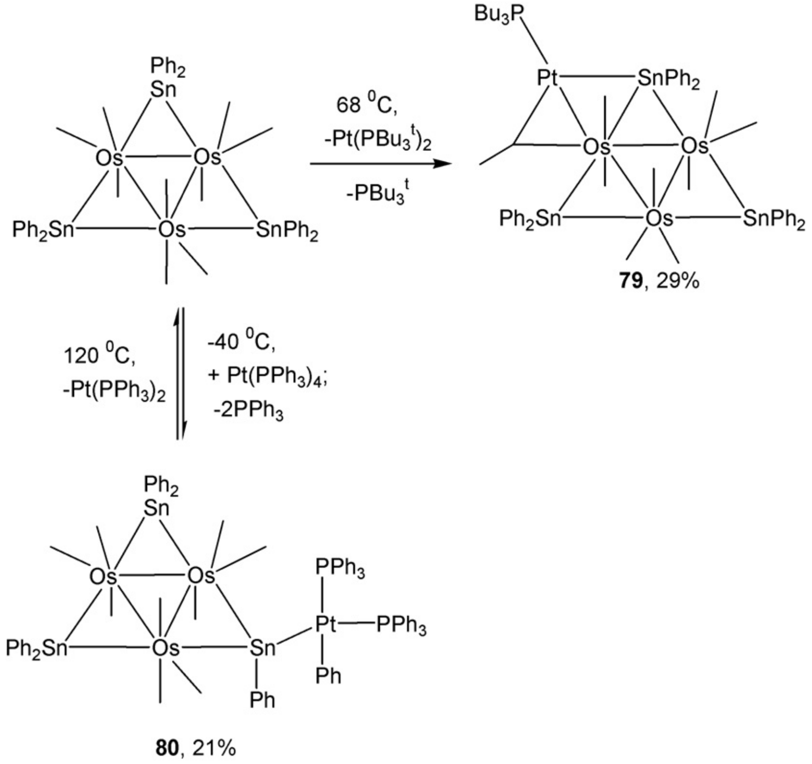
The preparation of the Pt–Os complex (**81**) has been reported by reaction of $\mathrm{[OsH(CO)_4(SnPh_3)]}$ with $\mathrm{Pt(PBu^t_3)_2}$ in dichloromethane at room temperature for 30 min in 45% yield (Eq. (17)) [63].



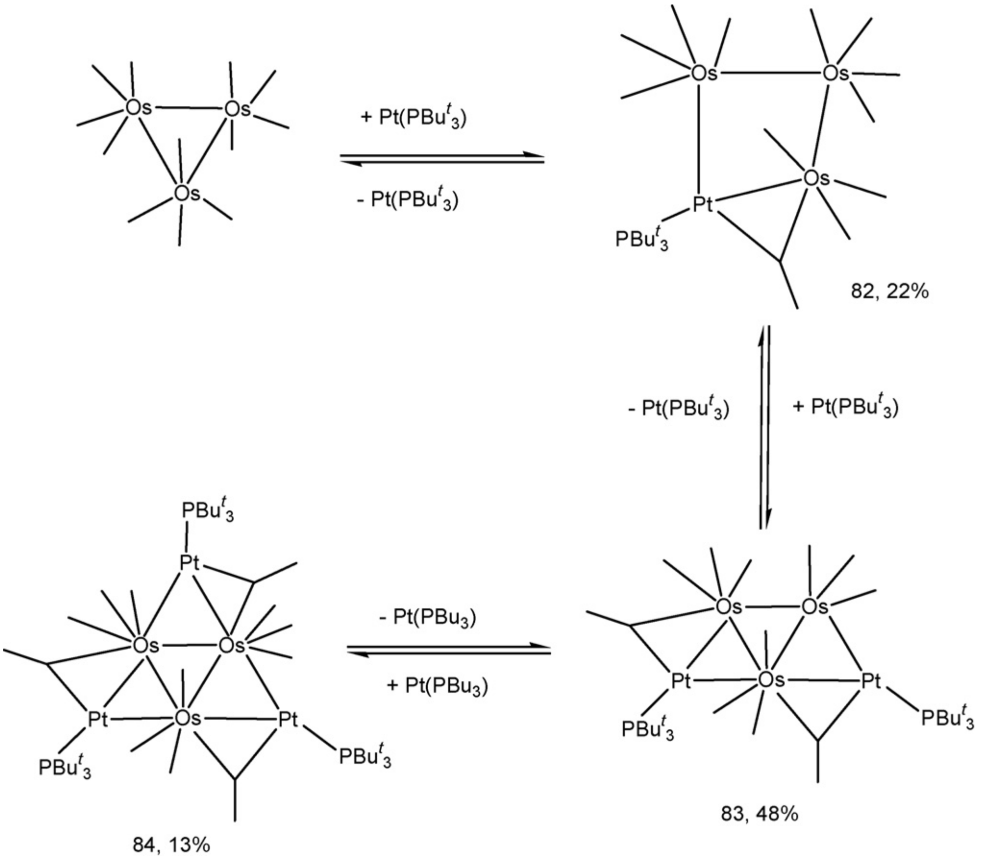
81, 45%

(17)

Three new compounds, $\mathrm{PtOs_3(CO)_{12}(PBu^t_3)}$ (**82**), $\mathrm{Pt_2Os_3(CO)_{12}(PBu^t_3)_2}$ (**83**) and $\mathrm{Pt_3Os_3(CO)_{12}(PBu^t_3)_3}$ (**84**) have been obtained from the reaction of $\mathrm{Pt(PBu^t_3)_2}$ with $\mathrm{Os_3(CO)_{12}}$ by the sequential addition of $\mathrm{Pt(PBu^t_3)}$ groups to the $\mathrm{Os_3(CO)_{12}}$ precursor. In solution, these compounds interconvert among themselves by intermolecular exchange of the $\mathrm{Pt(PBu^t_3)}$



Scheme 12.



Scheme 13.

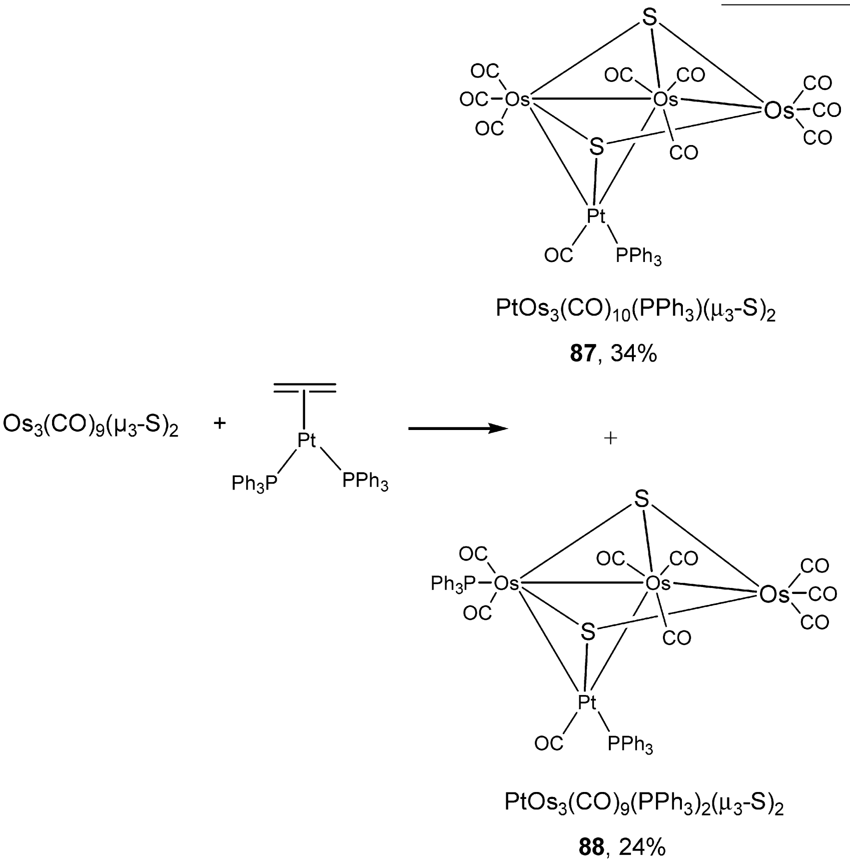
groups (Scheme 13). Also compound **85** was transformed into a new product $\mathrm{Pt_2Os_3(CO)_{10}(PBu^t_3)(PBu^t_2(Me_2CH_2)(\mu\text{-}H)}$ on heating [63].

The synthesis of high nuclearity clusters (**85, 86**) was reported [64] from the precursor, $\mathrm{Pt_2Os_3(CO)_{10}(COD)_2}$ (**72**) (Eq. (18)).

$$\underset{\mathbf{72}}{\mathrm{Pt_2Os_3(CO)_{10}(COD)_2}} \xrightarrow{\text{Hexane, Reflux, 30 min.}} \underset{\mathbf{85}}{\mathrm{Pt_5Os_6(CO)_{21}(COD)_2}} + \underset{\mathbf{86}}{\mathrm{Pt_4Os_6(CO)_{22}(COD)}} \quad (18)$$

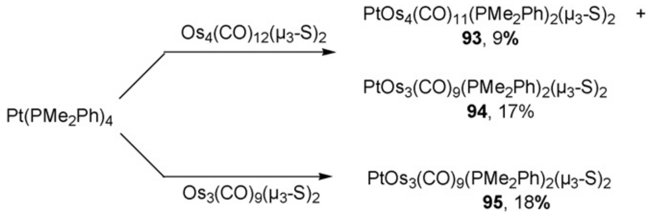
2.2.3. Sulfido bridging clusters

The reaction of $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)_2}$ with $\mathrm{Pt(PPh_3)_2(C_2H_4)}$ under N_2 atm gave the products **87**, **88** as shown in Eq. (19) [65].



(19)

Four platinum–osmium sulfide carbonyl cluster compounds (**89–92**) have also been isolated from the same reaction (Eq. (20)). The relative yields of the four products vary with the reaction temperature and the reaction time [66]. Thermal decarbonylation reactions of the Pt–Os sulfido carbonyl cluster compounds $\mathrm{PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)}$ (**89**) and $\mathrm{PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)}$ (**90**) have been also shown to give new clusters by the loss of some carbonyl ligands (Eq. (21)) [67].



Scheme 14.

$$\mathrm{Os_3(CO)_{10}(\mu_3\text{-}S)} + \mathrm{Pt(PMe_2Ph)_4} \longrightarrow \underset{\mathbf{89},\ 15\%}{\mathrm{PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)}} + \underset{\mathbf{90},\ 20\%}{\mathrm{PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)}} + \underset{\mathbf{91},\ 26\%}{\mathrm{PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)}} + \underset{\mathbf{92},\ 10\%}{\mathrm{PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)}} \quad (20)$$

$$\underset{n\,=\,9,\ (\mathbf{89});\ n\,=\,10,\ (\mathbf{90})}{\mathrm{PtOs_3(CO)_n(PMe_2Ph)_m(\mu_3\text{-}S)}} \xrightarrow{-\mathrm{CO}} \underset{\mathbf{91}}{\mathrm{PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)}} + \underset{\mathbf{92}}{\mathrm{PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)}} \quad (21)$$

Other sulfide ligand containing Pt–Os clusters (**93–95**) have been also reported according to the following Scheme 14 [67]. The sulfido-bridged cluster $\mathrm{PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2}$ (**96**) is formed upon the treatment of the complex $\mathrm{PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2}$ (**93**) in the presence of CO at 25 °C (Eq. (22)), while a similar reaction with the complex $\mathrm{PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)}$ (**97**) gave two clusters $\mathrm{PtOs_4(CO)_{13}(PPh_3)_2(\mu_4\text{-}S)}$ (**98**) and $\mathrm{Os_5(CO)_{14}(PPh_3)_2(\mu_4\text{-}S)}$ (**99**) as products (Eq. (23)) [68].

$$\underset{\mathbf{93}}{\mathrm{PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2}} \xrightarrow[25^{o}C]{CO} \underset{\mathbf{96},\ 24\%}{\mathrm{PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2}} \tag{22}$$

$$\mathrm{PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)} \xrightarrow[25^{o}C]{CO} \begin{array}{c}\mathrm{PtOs_4(CO)_{13}(PPh_3)_2(\mu_4\text{-}S)}\ +\\ \mathbf{98}\\ \mathrm{Os_5(CO)_{14}(PPh_3)_2(\mu_4\text{-}S)}\\ \mathbf{99}\end{array} \tag{23}$$

2.2.4. *Reactions with hydride, carbide and iodide bridging clusters*

The hydrido complex $\mathrm{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6}$ (**100**) has been used as a precursor for the synthesis of sulfido bridging cluster $\mathrm{PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6}$ (**101**) which was obtained in a good yield (Eq. (24)) [68].

$$\underset{\mathbf{100}}{\mathrm{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6}} \xrightarrow{H_2S} \underset{\mathbf{101},\ 83\%}{\mathrm{PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6}} \tag{24}$$

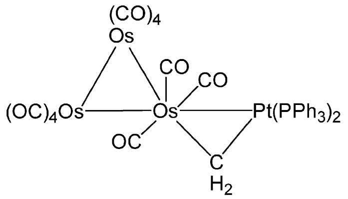
This compound was found to undergo a dynamic process involving intramolecular rotation of the $\mathrm{Os_3}$ group relative to the $\mathrm{Os_2S}$ group at the Pt atom (Scheme 15) [68].

Reaction of the cluster $\mathrm{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6}$ (**102**) with $\mathrm{Os(CO)_5}$ at 25 °C afforded the two products $\mathrm{PtOs_5(CO)_{18}(\mu\text{-}H)_4}$ (**103**) and $\mathrm{PtOs_4(CO)_{15}(\mu\text{-}H)_2}$ (**104**). The former complex reacted sequentially with CO, yielding the homonuclear osmium cluster $\mathrm{H_2Os_2(CO)_8}$ together with an unknown compound first, then $\mathrm{PtOs_2(CO)_{10}}$ (**105**) and $\mathrm{H_2Os(CO)_4}$ over time (Scheme 16) [68].

In addition to this, Pt–Os mixed metal clusters containing bridging sulphide ligands including $\mathrm{PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)}$ (26%) have been prepared [69] by the reaction of $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)}$ with $\mathrm{Pt(PMe_2Ph)_4}$ under mild conditions in THF.

The methylene- bridged cluster, $\mathrm{Os_3(CO)_{11}(\mu\text{-}CH_2)}$ has been used as a precursor in the preparation of $\mathrm{PtOs_3(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2}$ (**106**), where the methylene ligand bridges an Os–Pt bond as shown in Eq. (25) [70].

$$\mathrm{Os_3(CO)_{11}(\mu\text{-}CH_2)}\ +\ \mathrm{Pt(PPh_3)_2(CH_2{=}CH_2)} \xrightarrow{THF}$$



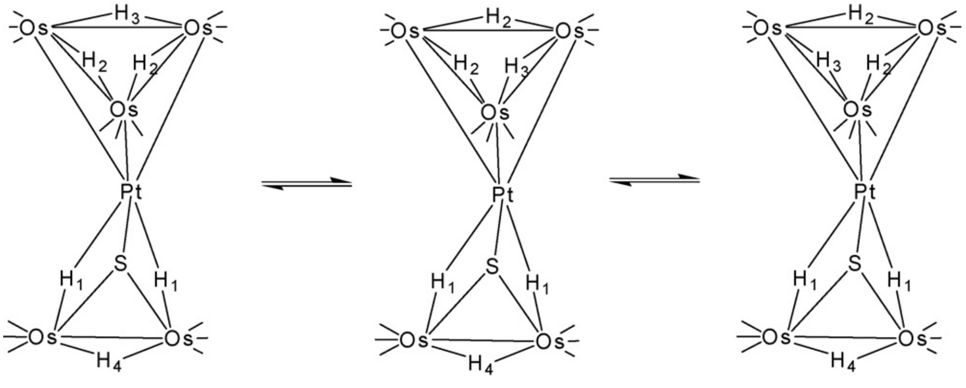
(**106**, 68%)

(25)

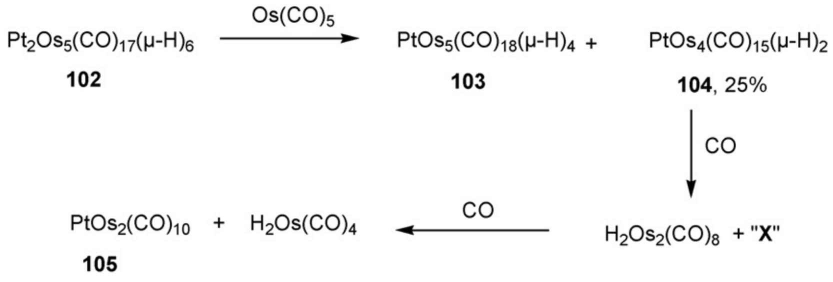
A novel hydride bridging cluster $\mathrm{Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2}$ (**107**) has been obtained from the reaction of $\mathrm{Os_3(CO)_{10}(\mu\text{-}H)_2}$ with two equivalents of $\mathrm{Pt(COD)_2}$ at 25 °C [71]. This complex has been transformed into the new decanuclear complex, $\mathrm{Pt_4Os_6(CO)_{21}(COD)(\mu\text{-}H)_2}$ (**109**) by the aggregation of two molecules of the intermediate product (**108**) (Scheme 17).

The decacarbonyldi- μ-hydrido-triosmium complex reacts with $\mathrm{[Pt(C_2H_4)(PR_3)]}$ to yield $\mathrm{PtOs_3(CO)_{10}(PR_3)(\mu\text{-}H)_2}$ where $\mathrm{R = C_6H_{11}}$ (25%) or Ph (61%) [72].

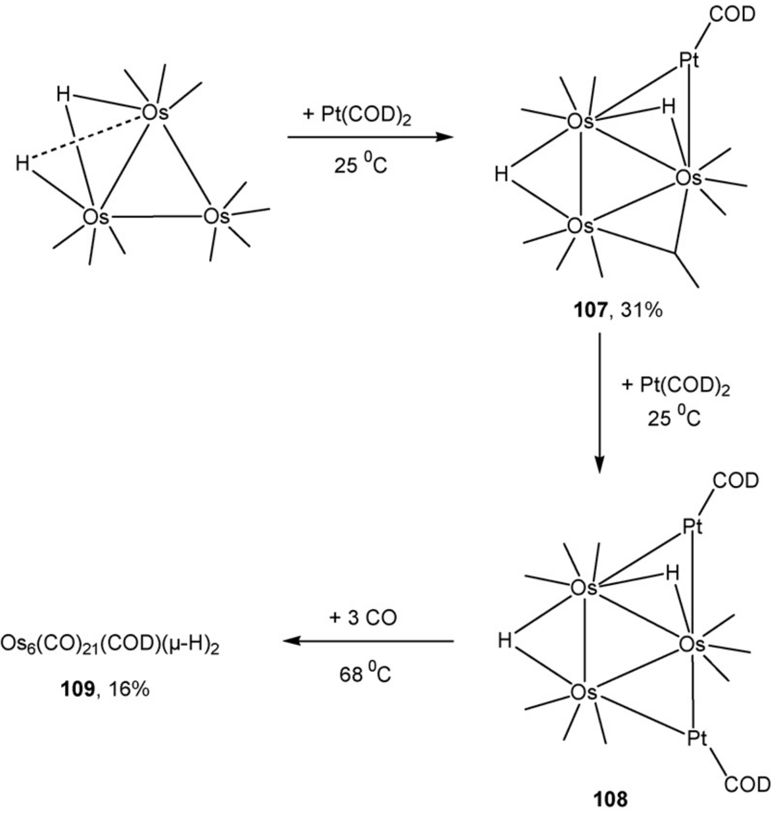
Hydrogen-rich $\mathrm{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6}$ can be prepared from either the reaction of $\mathrm{Pt_2Os_4(CO)_{18}}$ with hydrogen [73] or the reaction of dihydrido complex $\mathrm{[H_2Os_3(CO)_{10}]}$ with $\mathrm{Pt(C_2H_4)_2(R_3P)}$ (where $\mathrm{R = C_6H_{11}}$ or Ph) [73]. Other hydrogen-rich clusters $\mathrm{PtOs_5(CO)_{16}(\mu\text{-}H)_6}$ (**110**) and $\mathrm{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6}$ (**111**) were obtained from the reaction of the complex **4** and



Scheme 15.



Scheme 16.



Scheme 17.

H_2 at 25 °C (Eq. (26)) [74].

$$\underset{\textbf{4b}}{Pt_2Os_4(CO)_{18}} \xrightarrow{H_2} \underset{\textbf{110}\text{, 11\%}}{PtOs_5(CO)_{16}(\mu\text{-}H)_6} + \underset{\textbf{111}\text{, 32\%}}{Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6} \qquad (26)$$

The $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ complex can afford a new cluster with the formation of a sulfido bridging complex, $PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6$ (83%) after the reaction with H_2S at room temperature [68]. Also, the reaction of $Os(CO)_5$ with $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ yielded new complexes such as $PtOs_5(CO)_{18}(\mu\text{-}H)_4$ (38%) and $PtOs_4(CO)_{15}(\mu\text{-}H)_2$ (25%) [63]. Treatment of $[PtOs_3(\mu\text{-}H)_2(CO)_{10}(PCy_3)]$ with either H_2 or CO resulted in 1:1 adduct formation producing $[PtOs_3(\mu\text{-}H)_4(CO)_{10}(PCy_3)]$ and $[PtOs_3(\mu\text{-}H)_2(CO)_{11}(PCy_3)]$. A variety of hydride bridging Pt–Os clusters have been synthesized by the reactions of the unsaturated cluster compound $[PtOs_3(\mu\text{-}H)_2(CO)_{10}(PCy_3)]$ with hydrogen and with diazomethane [75]. This group also reported the synthesis of various Pt–Os carbide clusters (**112**, **113**) from non-carbido precursors as shown in Eq. (27) [76]. These types of complexes can react with various donor molecules such as CO, PPh_3 or $AsPh_3$ to afford their corresponding adducts [77].

$$[Pt(C_2H_4)_2(PCy_3)] + Os_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}CH) \xrightarrow[\text{Toluene}]{80\ ^0C} \underset{\textbf{112}}{Os_3Pt(CO)_{10}(\mu\text{-}H)_2(\mu_4\text{-}C)(PCy_3)\}} + \underset{\textbf{113}}{Os_3Pt_2(CO)_9(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)_2(PCy_3)\}} \qquad (27)$$

The boron containing hydride bridging Pt-Os heterobimetallic cluster (**114**) was prepared as shown in the Eq. (28) [78].

$$\mathrm{Na[(PPh_3)_2(CO)OsB_5H_8]} + \mathrm{[PtCl_2(PMe_2Ph)_2]} \longrightarrow \mathrm{PMe_2Ph} + \mathrm{NaCl} + \underset{\textbf{114}}{\mathrm{[(PPh_3)_2(CO)Os(PMe_2Ph)ClHB_5H_7]}} \qquad (28)$$

The complex $\mathrm{PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-}H)}$ was obtained in 50% yield from the reaction of the substituted osmium carbonyl cluster with $\mathrm{Pt(COD)_2}$ at 68 °C through a novel photoinduced reorganization of the metastable isomer [79].

Two saturated platinum triosmium clusters $\mathrm{[PtOs_3H_2(COD)(CH_2)(CO)_9]}$ and $\mathrm{[PtOs_3H_2(CH_2)(CO)_{11}]}$ were isolated in 10-20% yields after refluxing the $\mathrm{Os_3H_2(CO)_{10}}$ complex with $\mathrm{PtMe_2(COD)}$ in toluene [80].

Reaction of the Pt–Os clusters $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_{10}(PR_3)}$ (**115a**, R = Cy and **115b**, R = Ph) with $\mathrm{SO_2}$ was reported by Farrugia and co-workers. In this study the $\mathrm{SO_2}$ adducts of the type $\mathrm{PtOs_3(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PR_3)}$ (**116a**, R = Cy and **116b**, R = Ph) were isolated (Eq. (29)). NMR data collected for the cluster $\mathrm{PtOs_3(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PCy_3)}$ suggested the existence of two interconverting isomers in solution, with the major isomer containing inequivalent hydrides bridging an Os–Pt and an Os–Os edge, while the minor isomer contained equivalent hydrides bridging Os–Os edges [81]. The clusters $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_9(Pt\text{-}PCy_3)(Os\text{-}PR_3)}$ ($\mathrm{R_3 = Me_2Ph, Me_3, Ph_3}$, Pr^i_3, $\mathrm{Cy_2Pr}^i$) have been synthesized from the reaction of $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_9(PR_3)}$ with $\mathrm{Pt(C_2H_4)_2(PCy_3)}$. The structure of the cluster was found to be dependent on the steric bulk of the phosphine ligand, $\mathrm{PR_3}$ [81].

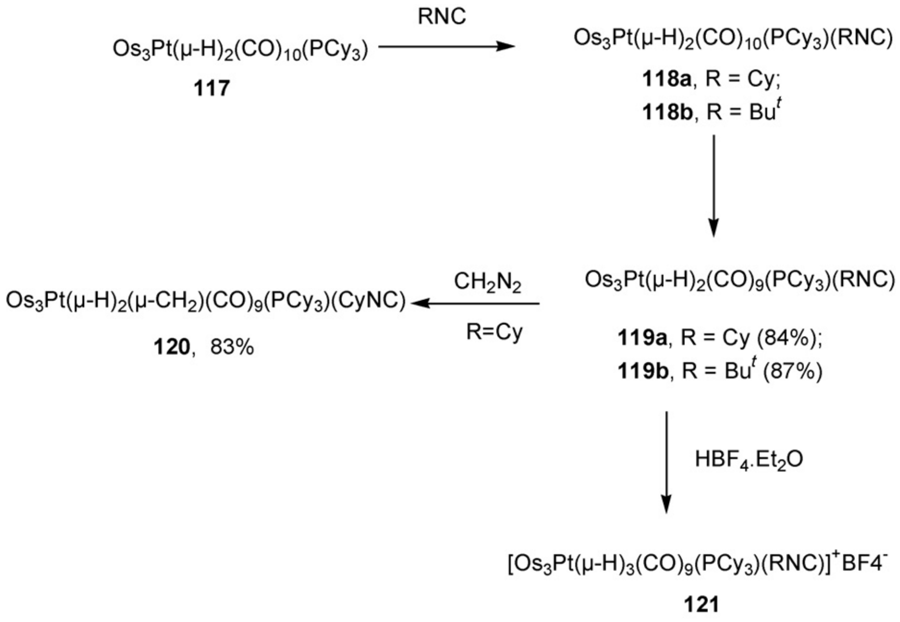
$$\underset{\textbf{115}}{\mathrm{Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)}} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{SO_2}} \mathrm{Os_3Pt(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PR_3)} \qquad (29)$$

116a, R = Cy (53%);
116b, R = Ph (75%)

Similar addition reactions were observed for the cluster $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_{10}(PCy_3)}$ (**117**) with RNC (R = Cy and Bu^t) to give the clusters $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_{10}(PCy_3)(RNC)}$ (**118a**, R = Cy and **118b**, R = Bu^t). Thermal decarbonylation was also observed allowing isolation of coordinatively unsaturated clusters $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_9(PCy_3)(RNC)}$ (**119a**, R = Cy and **119b**, R = Bu^t) in high yields (Scheme 18) [82a].

Further treatment of the cluster $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_9(PCy_3)(RNC)}$ where R = Cy with $\mathrm{CH_2N_2}$ and $\mathrm{HBF_4{\cdot}Et_2O}$ resulted in the methylene adduct $\mathrm{PtOs_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)}$ (**120**) and the cationic $\mathrm{[PtOs_3(\mu\text{-}H)_3(CO)_9(PCy_3)(RNC)]^+BF_4^-}$ (**121**) [82b]. Studies on the fluxional behaviour of the hydride ligands in $\mathrm{PtOs_3}$ clusters of the type $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)}$ and $\mathrm{PtOs_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)}$ have been reported [82c]. In a similar way, $\mathrm{PtOs_3(\mu\text{-}H)_2(CO)_{10}(PCy_3)}$ showed three distinct carbonyl exchange processes in variable-temperature NMR studies. Protonation of this product with $\mathrm{HBF_4}$ afforded the trihydrido salt $\mathrm{[PtOs_3(\mu\text{-}H)_3(CO)_{10}(PCy_3)]^+BF_4^-}$ in high yield [82c].

The reaction of $\mathrm{Os_2(CO)_6(\mu\text{-}I)_2}$ with $\mathrm{Pt(dba)(PPh_3)_2}$ or $\mathrm{Pt(PhCCPh)(PPh_3)_2}$ produced the novel iodo bridging $\mathrm{Pt_2Os(CO)_2(\mu\text{-}I)_2(\mu\text{-}CO)(PPh_3)_3}$ [83].



Scheme 18.

Table 1
Geometries of $\mathrm{Pt}_n\mathrm{Ru}_m(\mathrm{CO})_x\mathrm{L}_y$ clusters as determined by X-ray crystallography

N	CVE	Geometry	Cluster	Reference
2	34	Linear	$[\mathrm{PtRuH(CO)_3(\mu\text{-}dppm)_2}]^+$	[25]
3	42	Linear	$\mathrm{PtRu_2(CO)_6(\mu\text{-}\eta^2\text{-}C_{10}H_6C_4Ph_2)_2}$	[33b]
	44	Triangular	$\mathrm{Pt_2Ru(CO)_5(PPh_3)_3}$	[19]
	44	Triangular	$\mathrm{Pt_2Ru(CO)_6(CNBu^{\mathit{t}})(PPh_3)}$	[20]
	46	Triangular	$\mathrm{PtRu_2(CO)_7(PPh_3)_3}$	[20]
	46	Triangular	$\mathrm{PtRu_2(CO)_9(PBu^{\mathit{t}}_3)}$	[24]
	46	Triangular	$\mathrm{PtRu_2(CO)_5(\mu\text{-}CO)(\mu\text{-}dppm)_2}$	[25]
	46	Triangular	$\mathrm{Pt_2Ru(CO)_5(PPh_3)_2(PhC{\equiv}CPh)}$	[32]
	46	Triangular	$\mathrm{PtRu_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(PPr^{\mathit{i}}_3)(\eta\text{-}C_5H_5)_2}$	[44]
	48	Triangular	$\mathrm{PtRu_2(CO)_7(PPh_3)_2(PhC{\equiv}CPh)}$	[32]
	46	Triangular	$\mathrm{PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)(dppe)}$	[34]
4	54	Butterfly	$[\mathrm{Pt_3Ru(\mu\text{-}H)(CO)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)_3}]^+$	[26]
	58	Butterfly	$\mathrm{Pt_2Ru_2(CO)_9(PBu^{\mathit{t}}_3)_2}$	[24]
	58	Butterfly	$\mathrm{PtRu_3(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_7(dppe)}$	[29a]
	58	Butterfly	$[\mathrm{Pt_3Ru(\mu\text{-}H)(CO)_2(\mu\text{-}CO)_2(\mu\text{-}dppm)_3}]^+$	[26a]
	60	Butterfly	$\mathrm{PtRu_3(\mu_3 - \eta^2 - PhC \equiv CPh)(CO)_{10}(PPr^{\mathit{i}}_3)}$	[38]
	62	Butterfly	$\mathrm{PtRu_3(\mu\text{-}H)\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)(Bu^t)\}(CO)_9(dppe)}$	[35]
	58	Tetrahedron	$\mathrm{Pt_2Ru_2(CO)_8(PBu^{\mathit{t}}_3)_2(\mu\text{-}H)_2}$	[24]
	58	Tetrahedron	$\mathrm{Pt_2Ru_2(CO)_8(PPh_3)_2(\mu\text{-}H)_2}$	[32]
	60	Tetrahedron	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PCy_3)}$	[47a]
	60	Tetrahedron	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}MeCCHCMe)(CO)_9(PPr^{\mathit{i}}_3)}$	[38]
	60	Tetrahedron	$\mathrm{PtRu_3(CO)_{10}(PPh_3)(\mu_3\text{-}PNPr^{\mathit{i}}_2)}$	[39]
	60	Tetrahedron	$\mathrm{PtRu_3(CO)_9(COD)(\mu\text{-}CO)(\mu\text{-}H)_2}$	[40]
	62	Spiked triangular	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9(dppe)}$	[35]
	62	Spiked triangular	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9(COD)}$	[35]
	62	Spiked triangular	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}N)(CO)_{10}(PPr^{\mathit{i}}_3)}$	[38]
	62	Spiked triangular	$\mathrm{PtRu_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}NO)(CO)10(PPr^{\mathit{i}}_3)}$	[38]
	60	Square	$\mathrm{Pt_2Ru_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PPr^{\mathit{i}}_3)_2(\eta\text{-}C_5H_5)_2}$	[44]
	60	Square	$\mathrm{Pt_2Ru_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PPr^{\mathit{i}}_3)_2(\eta\text{-}C_5H_5)_2}$	[44]
5	74	Face-capped butterfly	$\mathrm{PtRu_4(CO)_{13}(COD)(\mu\text{-}H)_2}$	[40]
	74	Face-capped butterfly	$\mathrm{PtRu_4(CO)_{12}(\mu_4\text{-}CO)(COD)}$	[23]
	72	Square pyramid	$\mathrm{Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_2(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)}$	[34]
	74	Square pyramid	$\mathrm{PtRu_4(CO)_{12}(CO)PPh_3(\mu_4\text{-}PNPr^i2)}$	[39]
	74	Square pyramid	$\mathrm{PtRu_4(CO)_{12}(CO)PPh_3(\mu_4\text{-}PF)}$	[39]
	74	Square pyramid	$\mathrm{PtRu_4(CO)_{12}(CO)PPh_3(\mu_4\text{-}POEt)}$	[39]
6	86	Octahedron	$\mathrm{PtRu_5(CO)_{16}(\mu_6\text{-}C)}$	[45a]
	86	Octahedron	$\mathrm{PtRu_5(CO)_{14}(PBu^{\mathit{t}}_3)(\mu\text{-}H)_2(\mu_6\text{-}C)}$	[45a]
	86	Octahedron	$\mathrm{PtRu_5(CO)_{15}(PMe_2Ph)(\mu_6\text{-}C)}$	[46b]
	86	Octahedron	$\mathrm{PtRu_5(CO)_{15}(PMe_3)(\mu_6\text{-}C)}$	[46b]
	86	Octahedron	$\mathrm{PtRu_5(CO)_{15}(SMe_2)(\mu_6\text{-}C)}$	[46b]
	86	Octahedron	$\mathrm{PtRu_5(CO)_{15}(PBu^{\mathit{t}}_3)(\mu_6\text{-}C)}$	[46c]
	86	Octahedron	$\mathrm{PtRu_5C(CO)_{14}(dppm)}$	[51]
	86	Octahedron	$\mathrm{PtRu_5C(CO)_{12}(dppm)_2}$	[51]
	86	Octahedron	$\mathrm{PtRu_5C(CO)_{14}(PPh_3)_2}$	[54]
	86	Octahedron	$\mathrm{PtRu_5C(CO)_{15}(PPh_3)}$	[54]
	86	Octahedron	$\mathrm{PtRu_5C(CO)_{14}(COD)}$	[54]
	88	Raft	$\mathrm{Pt_2Ru_4(CO)_{18}}$	[21,69]
	84	Bi face-capped tetrahedron	$\mathrm{Pt_2Ru_4(CO)_{11}(COD)_2(\mu_3\text{-}H)_2}$	[40]
	86	Face-capped square pyramid	$\mathrm{PtRu_5(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}PhC_2H)(PBu^{\mathit{t}}_3)(\mu_5\text{-}C)}$	[29b]
	86	Edge-bridged square pyramid	$\mathrm{PtRu_5(CO)_{15}(PBu^{\mathit{t}}_3)(\mu_5\text{-}C)}$	[46c]
	88	Edge-bridged square pyramid	$\mathrm{Pt_2Ru_4(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)}$	[34]
7	98	Face-capped octahedron	$\mathrm{Pt_2Ru_5C(CO)_{15}(PPh_3)_2}$	[54]
	98	Face-capped octahedron	$\mathrm{PtRu_6C(CO)_{16}(COD)}$	[54]
	106	Two combined spiked triangular units	$\mathrm{Pt[Ru_3(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9]_2}$	[33c]
9	118	Face-capped octahedron	$\mathrm{Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3}$	[21,34]
	122	Octahedron faced-capped by a triangular $\mathrm{Pt_3}$ unit	$\mathrm{Pt_3Ru_6C(CO)_{16}(dppm)_2}$	[51]
	124	Square pyramid fused to face-capped octahedron	$\mathrm{Pt_4Ru_5(CO)_{20}(COD)}$	[23]
	124	Face-shared bioctahedron	$\mathrm{Pt_3Ru_6(CO)_{21}(\mu\text{-}CO)(\mu_3\text{-}H)_2}$	[47b]
	124	Face-shared bioctahedron	$\mathrm{Pt_3Ru_6(CO)_{21}(\mu\text{-}CO)(\mu\text{-}H)_2}$	[47b]
	126	Triangular $\mathrm{Pt_3}$ centre with $\mathrm{Ru_2}$ units bridging each edge	$\mathrm{Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3}$	[34]
10	132	Edge-fused bioctahedron	$\mathrm{Pt_2Ru_8(CO)_{23}(\mu_3\text{-}H)_2}$	[47b]
	132	Edge-fused bioctahedron	$\mathrm{Pt_3Ru_7(CO)_{21}(\mu\text{-}CO)(\mu_3\text{-}H)_2}$	[47b]
	136	Face-shared bioctahedron	$\mathrm{Pt_2Ru_8(CO)_{21}(\mu\text{-}CO)_2(\mu_3\text{-}H)_2(dppe)}$	[47b]
	136	Face-shared bioctahedron	$\mathrm{Pt_5Ru_5(CO)_{18}(COD)_2(\mu_3\text{-}H)_2}$	[40]

N = nuclearity, CVE = cluster valance electrons.

3. Structure

The geometry of the metal framework of clusters can be predicted using the polyhedral skeletal electron pair theory (PSEPT) formulated by Wade [84] and further developed by Mingos [85,86]. This theory effectively accounts for the structures of most transition metal carbonyl clusters however, heterobimetallic platinum clusters do not obey these rules. This is due to the ability of the Pt atom to have either a formal 18-electron count, giving a trigonal bipyramidal centre or the Pt atom may have a 16 electron count giving a square planar centre. In addition, for clusters of the type $Pt_xM_y(CO)_nL_m$ that have the same electron count, various metal core geometries may be possible depending on the ligands L. Using these theories to predict the skeletal geometry of a Pt containing cluster from the cluster valence electron count (CVE) would thus be exceedingly difficult, as there is no direct correlation between the CVE count and the cluster geometry as can be seen in Tables 1 and 2. However some ratio-

Table 2
Geometries of $Pt_nOs_m(CO)_xL_y$ clusters as determined by X-ray crystallography

N	CVE	Geometry	Cluster	Reference
2	28	Linear	$PtOs(CO)(PPh_3)_2(PMe_2Ph_3)ClB_5H_7$	[78]
3	46	Triangular	$PtOs_2(CO)_{10}$	[68]
	46	Triangular	$PtOs_2(CO)_8(COD)$	[21,68]
	46	Triangular	$Pt_2Os(CO)_2(\mu\text{-}I)_2(\mu\text{-}CO)(PPh_3)_3$	[83]
4	60	Butterfly	$PtOs_3(CO)_{12}(PBu^t_3)$	[59]
	60	Butterfly	$PtOs_3(CO)_{11}(PCy_3)(\mu\text{-}H)_2$	[75]
	60	Butterfly	$PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}dppm)[Si(OMe)_3](\mu\text{-}H)$	[80]
	60	Butterfly	$PtOs_3(CO)_{10})(PCy_3)(\mu\text{-}H)_2(CyNC)$	[82]
	60	Butterfly	$PtOs_3(CO)_{10})(PCy_3)(\mu\text{-}H)_2(Bu^tNC)$	[82]
	62	Butterfly	$PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$	[66]
	62	Butterfly	$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_2(\mu_4\text{-}C)$	[76]
	64	Spiked triangular	$PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$	[65]
	64	Spiked triangular	$PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$	[67]
	64	Spiked triangular	$PtOs_3(CO)_{11}(PPh_3)_2(\mu\text{-}CH_2)_2$	[70]
	64	Spiked triangular	$PtOs_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)_2$	[65]
	62	Tetrahedron	$PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$	[66]
	60	Tetrahedron	$PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$	[66,69]
	58	Tetrahedron	$PtOs_3(CO)_{10}(PPh_3)(\mu\text{-}H)_2$	[72]
	58	Tetrahedron	$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_2$	[72]
	60	Tetrahedron	$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_4$	[75]
	60	Tetrahedron	$PtOs_3(CO)_9(COD)(\mu\text{-}H)_2(\mu_2\text{-}CH_2)$	[80]
	60	Tetrahedron	$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_2(\mu\text{-}SO_2)$	[81]
	58	Tetrahedron	$PtOs_3(CO)_9(PCy_3)(\mu\text{-}H)_2(CyNC)$	[82]
	60	Tetrahedron	$PtOs_3(CO)_9(PCy_3)(\mu\text{-}H)_2(\mu\text{-}CH_2)(CyNC)$	[82]
5	70	Edge-bridged tetrahedron	$Pt_2Os_3(CO)_{10}(PBu^t_3)(PBu^t_2CMe_2CH_2)(\mu\text{-}H)$	[59]
	72	Edge-bridged tetrahedron	$Pt_2Os_3(CO)_9(COD)_2(\mu\text{-}H)_2$	[71]
	72	Truncated raft	$Pt_2Os_3(CO)_{12}(PBu^t_3)_2$	[59,63]
	74	Edge-bridged tetrahedron	$PtOs_4(CO)_{15}(\mu\text{-}H)_2$	[68]
	74	Edge-bridged tetrahedron	$PtOs_4(CO)_{11}(COD)(\mu\text{-}H)_2(\mu_3\text{-}S)$	[61]
	76	Edge-bridged butterfly	$PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$	[67]
	74	Square pyramid	$PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$	[67b]
	74	Square pyramid	$Pt_2Os_3(CO)_9(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(PCy_3)_2$	[76]
6	84	Raft	$Pt_3Os_3(CO)_{12}(PBu^t_3)_3$	[59,63]
	86	Raft	$Pt_2Os_4(CO)_{15}(COD)$	[21,22]
	82	Bicapped tetrahedron	$Pt_2Os_4(CO)_{11}(COD)_2$	[60,61]
	84	Bicapped tetrahedron	$Pt_2Os_4(CO)_{12}(COD)_2$	[60,61]
	88	Face-capped square pyramid	$PtOs_5(CO)_{15}\ (PPh_3)_2(\mu_4\text{-}S)$	[67b]
	88	Vertex-fused tetrahedron and triangle	$PtOs_5(CO)_{16}(\mu\text{-}H)_6$	[58,61]
	90	Vertex-fused tetrahedron and triangle	$PtOs_5(CO)_{15}(\mu\text{-}H)_6(\mu_3\text{-}S)$	[68]
	90	Vertex-fused tetrahedron and triangle	$PtOs_5(CO)_{18}(\mu\text{-}H)_4$	[68]
7	96	Bi-capped tetrahedron	$Pt_3Os_4(CO)_{11}(COD)_3$	[60,61]
	100	Vertex-shared bitetrahedron	$Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$	[58]
	102	Vertex-shared bitetrahedron	$PtOs_6(CO)_{18}(\mu\text{-}H)_8$	[58]
9	130	Vertex-shared bitetrahedron and triangle	$Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$	[58]
10	136	Triangular Pt_3 unit sandwiched by two triangular Os_3 units	$Pt_4Os_6(CO)_{22}(COD)$	[64]
	136	Triangular Pt_3 unit sandwiched by two triangular Os_3 units	$Pt_4Os_6(CO)_{21}(\mu\text{-}H)_2\ (COD)$	[71]

N = nuclearity, CVE = cluster valance electrons.

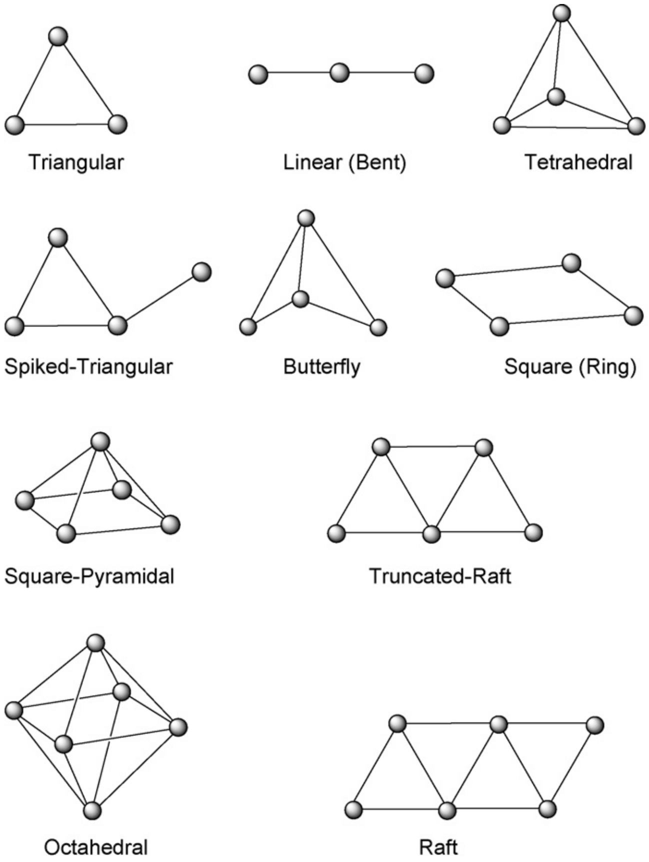


Chart 1. Common skeletal geometries for Pt containing metal clusters.

nalization of the geometry of the cluster as determined by X-ray diffraction studies can be made.

In this section we will discuss the geometry described by the metal framework of the cluster. Generally, the cluster complexes have metal atoms situated at the vertices of a polyhedron, and some common skeletal arrangements are shown in Chart 1. In the discussion, we will start with binuclear complexes and then discuss complexes with increasing nuclearity.

3.1. Binuclear complexes

Binuclear mixed metal complexes where there is a direct connectivity between the metals are restricted to a linear framework. A review of the Cambridge Structural Database reveals that the Pt–Ru bond ranges from 2.664 to 2.823 Å while the Pt–Os bond ranges from 2.688 to 2.959 Å in complexes of this type.

3.2. Trinuclear clusters

Trinuclear mixed metal clusters may adopt either a two-dimensional linear (or bent) structure with two metal–metal bonds or a planar triangular structure containing three metal–metal bonds.

It is well known that clusters in solution can undergo structural change. The change in structure may involve ligand rearrangement or metal–metal bond cleavage and formation. The cluster $PtOs_2(CO)_8(PPh_3)_2$, which has a triangular geometry, has been shown to exist as three interconverting isomers. One of the proposed pathways for rearrangement of the metal skeleton involves cleavage of the Pt–Os bonds and rotation of the diosmium fragment about an axis extending from the platinum centre as shown in Fig. 2 [8].

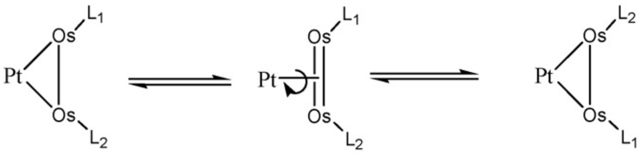


Fig. 2. Rearrangement in triangular clusters.

3.3. Tetranuclear clusters

Metal clusters containing four metal atoms may adopt a tetrahedral, butterfly, spiked-triangular or square arrangement. The most common core geometries for tetranuclear clusters are the spiked-triangular and butterfly arrangements as these are formed from the readily available triangular clusters by coordination of a metal fragment to a vertex or edge of the trinuclear cluster. The butterfly structure resembles the tetrahedron, however there are only five metal–metal bonds in this arrangement compared to the six metal–metal bonds in the tetrahedral structure. Opening of the metal framework from tetrahedral to butterfly structure generates a vacant coordination site. The butterfly arrangement consists of two equilateral triangles sharing an edge and may be either folded or planar.

Both butterfly to tetrahedral and spiked-triangular to butterfly skeletal transformations have been observed in platinum-containing tetranuclear clusters [87]. These structural interconversions, which involve metal–metal bond cleavage and bond formation, are usually reversible providing evidence for the flexibility of the metal skeleton in platinum-containing clusters.

A square arrangement is adopted by the metal core in $PtRu_3(CO)_6(\mu\text{-}CO)_2(\eta^2\text{-}P\text{-}P)(\mu_4\text{-}S)_2$ (P–P = dppf or dppr) with four metal–metal bonds [88]. This structure is stabilized by two bridging μ_4-S ligands giving a compressed octahedral structure. A square arrangement where the metal ring is supported by a central carbido carbon atom is also common for tetranuclear clusters, as found in the di-platinum di-ruthenium cluster $Pt_2Ru_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PPr^i_3)_2Cp_2$ reported by Davies et al. [44].

3.4. Pentanuclear clusters

Clusters containing five metal atoms typically adopt a square-pyramidal structure. In this arrangement the four basal metal atoms are generally not coplanar, giving the cluster a distorted square-pyramidal structure. An alternative skeletal arrangement is formed when a metal fragment combines with a tetrahedral cluster to give a tetrahedron with either one edge or one triangular face of the tetrahedron capped. A less common configuration is the truncated or incomplete raft structure, a planar triangulated arrangement of metal atoms, which has been reported for $Pt_2Os_3(CO)_{14}$ [89].

3.5. Hexanuclear and larger clusters

Hexanuclear clusters typically adopt either an octahedral structure with 12 metal–metal bonds or an open puckered raft (ladder like) structure with nine metal–metal bonds. Other common geometries for six metal clusters are based on a tetrahedral unit that is edge or face capped by two additional metal fragments, or a trigonal pyramidal unit that is mono-capped by an additional metal fragment.

In general clusters containing seven to ten metal atoms are based on a six metal octahedral arrangement that is edge or face capped by additional metal fragments. However, unusual geometries are also possible such as that displayed by the nine-membered $Pt_3Ru_6(CO)_{18}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$ cluster which has a central triplatinum cluster with diruthenium groupings bridging each Pt–Pt edge [90].

4. Applications

Multi-centred metal clusters can act as molecular catalysts which have advantages of supported metal catalysts. It is well-known that supported bimetallic catalysts of platinum mixed with other metals are widely used in the petroleum reforming industry, where they have played a key role in the development and production of unleaded gasoline [12]. These platinum clusters also exhibit interesting catalytic properties in many other reactions. In addition, the synergistic property of bimetallic clusters is an important function of most heterogeneous catalysts. This synergistic property of bimetallic clusters could be due to the presence of two or more metal atoms, where substrate activation can occur at more than one metal site. Certain carbonyl clusters may be expected to have coordinative unsaturation due to either the easy loss of ligands, or because of their intrinsic electronic characteristics [13].

Mixed-metal clusters, particularly Pt–Ru systems have been studied for their fascinating metal core geometries, and recently have been found to be potential precursors for supported nano-catalysts [14]. The performance of these bimetallic catalysts can be tuned by varying the nature and ratio of two metals. Catalysis by surface-bound metal carbonyl clusters and by structurally simple, supported metals derived by decarbonylation of surface-bound clusters has been achieved [15].

The interesting catalytic properties of bimetallic clusters may be due to several reasons: (i) their ability to undergo multi-centred binding and activation of a single reactant for substrate, (ii) their ability to bind and activate reactants on adjacent or neighbouring metal atoms, (iii) they can facilitate the formation of a transition state stabilized at multiple points and in three dimensions, (iv) they can induce cooperative influences among the metals involved, thereby assisting catalysis, and (v) facilitate in the migration of activated reactants from one metal atom to another as is seen in some heterogeneous as well as enzymatic catalysts [16].

However, a significant problem with metal clusters in catalysis is identifying the active species during the process and thereby establishing the mechanism of the reaction [16]. Polynuclear clusters can readily undergo cluster fragmentation or degradation into new and unidentified catalytically active species, which are very difficult to generate by other routes. This phenomenon complicates the understanding of these interesting mechanistic pathways as does the fact that these clusters are sensitive to the experimental conditions.

Bimetallic clusters have attracted considerable attention in the field of catalysis. These catalysts have seen applications in both homogeneous and heterogeneous conditions, due to the fact that their catalytic properties are often superior to that of their components [32,91]. Molecular heterobimetallic clusters have the additional advantages of control over the size, structure and metal:metal ratio in the preparation of cluster/support catalysts, which in turn lead to more reactive or selective heterogeneous catalysts than similar catalysts prepared from mononuclear precursors [1a,32,92].

A variety of established characterization techniques together with newly developed methods have been employed in characterizing supported bimetallic cluster catalysts, leading to several interesting and well-defined catalysts. Particularly useful characterization techniques include transmission electron microscopy (TEM), temperature programmed reduction (TPR), cyclic voltametry the O_2-CO titration technique, X-ray diffraction (XRD), extended X-ray absorption fine structure (EXFAS), infrared (IR) and mass spectrometry [32,91,92].

The bonding modes in molecular cluster complexes as determined by techniques such as single XRD and IR spectroscopy can be used to model the bonding modes of surface bound fragments such as CO, alkenes, alkynes, vinylidenes and ethylidenes which are involved in many heterogeneous catalysis processes [1a].

4.1. Mechanistic aspects of heterobimetallic clusters in catalysis

In general organometallic catalysts have shown useful applications in homogeneous catalytic processes. Their catalytic activity depends on the influence of structural properties, that impact on size, selectivity, branched or linear products and chiral catalysis. However homogeneous cluster catalysis opens the doors to both the advantages of, cooperative effects between several metal atoms as well as maintaining the ability to control reactivity and selectivity by appropriate ligand design [1a].

Generally Pt–Ru cluster catalysts have been used more than the Pt–Os analogues. Two important questions to ask when it comes to homogeneous cluster catalysts are: (1) Is the reaction catalyzed by molecular species in solution or by metallic pyrolysis product? (2) If homogeneously catalyzed is the catalyst a multinuclear cluster or a mononuclear fragment [93]?

For example it was found that Pt–Ru clusters catalyzed CO hydrogenation. The observed activity was the result of thermal decomposition of the dissolved clusters to catalytically active species [94,95]. On the other hand under quite severe conditions of temperature and pressure, solutions containing bimetallic carbonyl clusters were observed to homogeneously catalyze the synthesis of ethylene glycol and methanol from synthesis gas. Here the clusters were detected by *in situ* high pressure IR spectroscopy, though it was not clear whether or not the catalytically active species was polynuclear or mononuclear complexes formed by fragmentation [93]. Adams and co-workers also gathered information strongly suggesting that catalytic activity in clusters was a result of fragmentation products [29].

4.2. Methods for distinguishing between homogeneous and heterogeneous catalytic contributions

Several ways aimed at determining catalytic homogeneity or heterogeneity of systems have been devised and are briefly discussed here. These techniques do however have their pitfalls. Detection of metal particles has been approached by (i) direct inspection for larger metal particles, (ii) light scattering, and (iii) filtration. An alternate way of eliminating heterogeneous contributions to catalysis is by, inhibition using metallic mercury which forms inactive amalgams with transition metal particles. By so doing metal particles can be eliminated [13].

Other tests for homogeneous catalysts can involve the addition of rigid tub-shaped dienes which bind irreversibly to homogeneous catalysts, hence inhibiting catalysis and kinetic or product selectivity studies [1a,13]. Homogeneous and heterogeneous catalysts can be distinguished by the use of alkene functionalized cross-linked polymers, which are hydrogenated by homogeneous catalysts while heterogeneous catalysts are inactive [13].

The problems associated with distinguishing between homogeneous or heterogeneous catalysis can be avoided by the use of specifically designed anchoring or bridging ligands which prevent cluster fragmentation, association or decomposition (leading to heterogeneous catalysis) [1a].

4.3. Homogeneous catalysis with heterobimetallic clusters

Cooperative effects between the different metals in clusters can give rise to enhanced stability, reactivity or selectivity. For example, the clusters $Pt_3Ru_6(CO)_{20}(\mu\text{-}H)_2(PhC_2Ph)$, $Pt_3Ru_6(CO)_{20}(\mu\text{-}H)_2(\mu\text{-}PhC_2Ph)$, $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}H)(\mu\text{-}H)(\mu_3\text{-}PhC_2Ph)$ and $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu_3\text{-}H)$ are good catalysts for the hydrogenation and hydrosilylation of PhC_2Ph, with the last three exhibiting 100% selective hydrogenation of PhC_2Ph to *cis*-stilbene [1a,1e,13,96]. Interestingly an intermediate, $Pt_3Ru_6(CO)_{21}(\mu\text{-}H)(\mu\text{-}PhC_2(H)Ph)$, was isolated from hydrogenation with the cluster $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu_3\text{-}H)$. The above reactions are one of the few reported heterobimetallic cluster-catalyzed reactions. The major problem of course lies in proving cluster catalysis as opposed to catalysis by mononuclear fragmented products [1a,13]. The proposed catalytic cycle of the cluster $Pt_3Ru_6(CO)_{20}(\mu\text{-}H)_2(PhC_2Ph)$ on hydrogenation of PhCCPh is shown in Scheme 19.

The alkyne-bridged mixed-metal clusters $RuPt_2(CO)_5(PPh_3)_2(PhC_2Ph)$, $Pt_2Os(CO)_5(PPh_3)_2(PhC_2Ph)$, $PtRu_2(CO)_7(PPh_3)(PhC_2Ph)$ and $Pt_2Ru_2(CO)_8(PPh_3)_2(PhC_2Ph)H_2$ have been shown to be active for the catalytic hydrosilylation of alkynes, such as diphenyacetalyne and 1,4-bis(trimethysilyl)butadiyne. Evidence gathered during these studies suggests that the catalytic activity exhibited by these heterobimetallic cluster complexes was produced principally by fragmentation products, which were almost certainly mononuclear platinum complexes [32].

In addition $[PtRu_5(CO)_{13}(PBu^t_3)(\mu_3\text{-}PhC_2H)(\mu_5\text{-}C)]$ has also been shown to be a catalyst precursor for the hydrogenation of PhC_2H to styrene and ethyl benzene. Other new organometallic clusters were found in the catalyst solution as intermediates for example $[PtRu_5(CO)_{12}(PBu^t_3)(\mu_3\text{-}PhC_2H)(\mu_5\text{-}C)(\mu\text{-}H)_2]$ [29].

4.4. Heterobimetallic clusters in heterogeneous catalysis

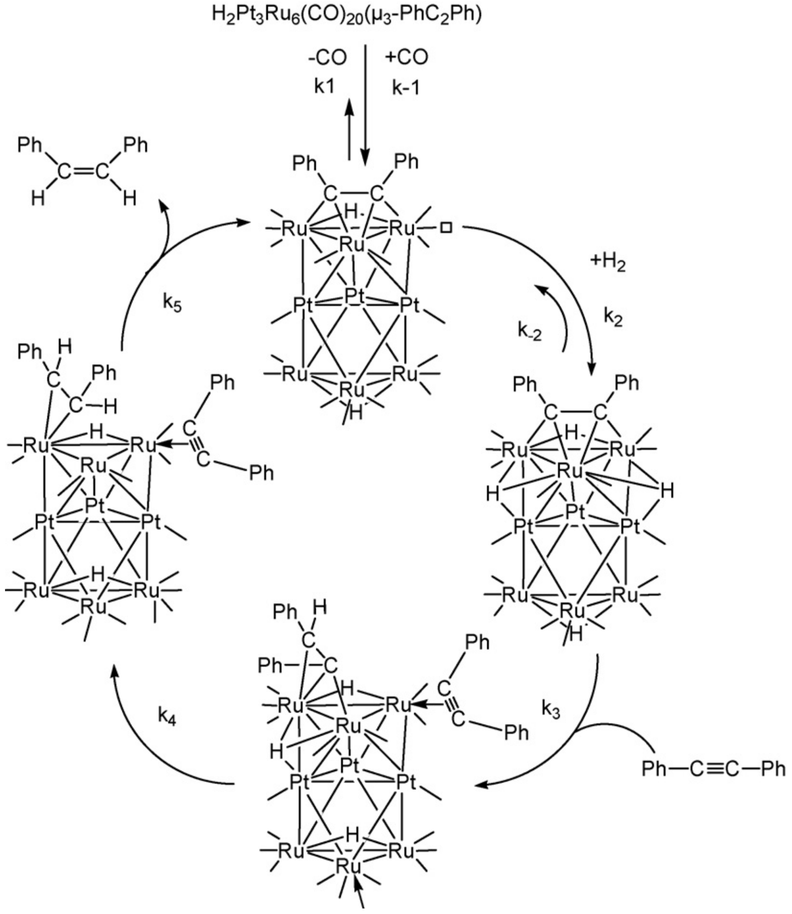
Another aspect of heterobimetallic clusters involves the preparation of small or nanostructured metal particles on supports, such as silica or alumina [1a]. The use of clusters with different metal ratios allows for comparison of the different catalysts, as well as the formation of well-defined metal particles, which can effectively influence the selectivity and activity of the catalysts [92,97,98]. For example exceptionally narrow sizes and distributions of nanoparticles on a carbon support can be obtained from the precursor cluster $PtRu_5C(CO)_{16}$ with H_2 [50]. Also in a series of silica-supported Pt–Ru bimetallic clusters for Fischer–Tropsch synthesis, increasing the surface concentration of Pt had a marked effect on methane selectivity. The methane selectivity dropped in the case of Ru-rich catalysts. Fischer–Tropsch products (hydrocarbons) were observed in significant yields only for the catalysts which had a surface concentration of less than 50% Pt and only Pt–Ru bimetallic cluster catalysts having a surface concentration in excess of 50% Ru were active in the formation of Fischer–Tropsch products [97].

Similarly, the cluster complex $Pt_2Ru_4(CO)_{18}$ was used as a precursor for the preparation of 44 wt% 1:2 Pt:Ru nanoparticles on carbon for use as an electrocatalyst in methanol oxidation. It was established that the use of bimetallic cluster precursors simplifies the synthetic procedures by eliminating the need for high temperature reduction and produces smaller more uniform bimetallic nanoparticles. These bimetallic nanoparticles in turn exhibited a higher electrocatalytic activity when compared to a 52 wt% 1:1 Pt:Ru commercial catalyst [92].

The supported cluster $Pt\text{–}Ru/\gamma\text{-}Al_2O_3$ obtained from $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_3$ selectively catalyzed the hydrogenation of ethylene while reactions with *n*-butane and H_2 produced methane, ethane and propane, consistent with bifunctional effects which may be governed by the high hydrogenation activity of Pt and high hydrogenolysis activity of Ru [91].

A complex formulated as $PtRu_3(CO)_{12}(py)_3$ impregnated on an inorganic oxide or carbon support showed similar hydrogenolysis activity and selectivity [1a]. A phosphine-functionalized poly(styrene-divinylbenzene) supported cluster $Pt_2Ru(CO)_5(Ph_2P{\sim}P^I)_3$ (P^I = phosphine-functionalized poly (styrene-divinylbenzene)) was also able to catalyze ethylene hydrogenation, with catalytic activities much higher than the mononuclear counterparts [1a,99].

Other examples of bimetallic Pt-Ru catalysts are the “alloy” catalysts or electrocatalysts which are commonly used in petroleum reforming and electrolyte fuel cells, respectively. These can be prepared by impregnating solutions of simple neu-



Scheme 19.

tral or charged coordination complexes like $PtCl_4^{2-}$ or H_2PtCl_4 and $RuCl_3$ on supports followed by reduction [1a,91,97,100].

The supported Pt–Ru 0.5%Pt–0.5%Ru/2% Ce/(θ + α)-Al_2O_3 catalyst was prepared using a similar method (i.e impregnation of dispersed (θ + α)-Al_2O_3 with separate solutions of the metal salts). Tests in the reaction of catalytic partial oxidation (CPO) of methane into synthesis-gas resulted in high CH_4 conversions ranging from 84.3% to 57.1% as well as CO and H_2 selectivities ranging from 95.8% to 87.5% and 98.7% to 100% respectively [98].

Accordingly, the Pt–Ru electrocatalyst, prepared from an oxidized sulfitic platinum complex and $RuCl_3$ on carbon powder, showed better hydrogen-oxidation in the presence of CO after thermal treatment or reduction [100].

Pt–Ru alloys can also be prepared by electrodeposition techniques, which result in anodes that display high catalytic activities towards direct methanol fuel cells (DMFCs) [101,102].

It was also shown that Pt–Ru nanoparticles can be electrodeposited onto graphite felt and the resulting material functions as a (DMFC) anode, which replace the conventional gas diffusion electrode [101].

Nanometer scale Pt–Ru alloys (nm-Pt–Ru) can also be prepared by electrochemical co-deposition under cyclic voltammetric conditions or galvanostatic pulse techniques. Higher catalytic activities for DMFC can be observed in the resulting anodes [102,103].

The existence of more than one metal centres in these type of catalysts also allows synergistic interplay of the metal particles, as was shown in a study of the oxidation of methanol on ruthenium and osmium, for the application to DMFCs, where dehydrogenation of water occurred at Ru sites, while the Pt sites in this catalyst were found to be responsible for methanol dehydrogenation [104].

5. Concluding remarks and future prospects

From this review, it is clear that a large number of bimetallic compounds of Pt and Ru, as well as Pt and Os are known. These clusters range from binuclear up to decanuclear compounds and beyond. Although many complexes have carbonyl ligands, there are also known compounds with S, H, P, I and alkynes as bridging ligands. It is also clear from the review that there are a large number of possible synthetic routes which give a range of different products, some of which are only isolated in low yields after separation. Reactions of some of these clusters yield other clusters by cluster expansion, contraction or rearrangements, many of which are unexpected and occur via mechanisms which at this point are not clearly understood.

Applications have been described for some of the mixed metal compounds including both as homogeneous and heterogeneous catalysts. With new possibilities of using bimetallic catalysts in fuel cells and as models for processes occurring on bimetallic surfaces, the future may indeed be bright for these compounds.

One area that still needs to be addressed in the future is that selective and high yield synthetic routes have to be developed in order to obtain reasonable quantities of the mixed metal compounds so that their chemistry can be fully explored and their applications investigated.

Acknowledgements

We thank Anglo Platinum Corporation, Johnson Matthey, University of Cape Town and NRF (South Africa) for financial assistance.

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