DALTON
PERSPECTIVE

Cluster chemistry of ruthenium and osmium *

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This review highlights some recent studies on the synthesis, structural properties and chemical reactivities of triosmium alkylidyne clusters, ruthenium clusters containing a μ_4-nitrene ligand and mixed-metal clusters of osmium and palladium.

1 Introduction

The chemistry of transition-metal carbonyl clusters is an important area of organometallic research. In particular ruthenium and osmium clusters have been extensively studied because of their good balance of reactivities and stabilities. This review highlights some of our recent developments and related work from others in this area. The cluster and surface analogy[1] has been a very popular term used by both cluster chemists and surface scientists to bridge the two areas of work of fundamental importance in catalysis. The chemisorption of simple hydrocarbons or other small molecules and the subsequent surface reactions on well characterized transition-metal surfaces are topics of considerable interest in surface science.[2] Such studies are aimed at providing fundamental information on the initial stages of hydrocarbon catalysis and to establish a framework for the interpretation of results on more complex catalysts. Hydrocarbon ligands in clusters range from molecular species like olefins, dienes, alkynes and arenes to radicals such as simple alkyl groups, alkylidenes and benzynes. This large and diverse family of hydrocarbyl ligands is useful in the assessment of the cluster–surface analogy in that these hydrocarbyl ligand-containing clusters are potential models for hydrocarbon interactions with metal surfaces. In particular, the alkylidyne ligand is interesting as it has an extensive chemistry associated with mononuclear complexes and is implicated in acetylene metathesis.[3] The comparison between the chemical reactivity of hydrocarbyl ligands bridging two or more metals and the reactivity of these ligands when bound to a single metal centre is also of great interest.

Metal clusters containing alkylidynes have been known for many years and they typically bridge the triangular faces in these compounds.[4] An impressive example lies in the formation of the μ_3-ethylidyne ligand in $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)]$ from the reaction of ethylene and $[Os_3(CO)_{12}]$ *via* $[Os_3(\mu\text{-}H)_2(CO)_9(C{=}CH_2)]$,[5a,b] which parallels the formation of CCH_3 on the Pt(111) or Rh(111) crystal face as a result of ethylene chemisorption.[2b] More recently, the compound $[(\eta\text{-}C_5H_5)(CO)_2Ru(\mu_4\text{-}C)Co_3(CO)_6\{CH(PPh_3)\}]$ containing a tetrahedral sp^3 carbide has been prepared from the tricobalt alkylidyne precursor.[5c]

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Wing-Tak Wong was born in Hong Kong in 1963. He obtained his B.Sc. (1986) and M.Phil. (1988) from the University of Hong Kong. He did his Ph.D. (1991) with Lord Lewis on high-nuclearity metal clusters at the University of Cambridge, UK. In 1991, he joined the University of Hong Kong as a faculty member. Currently he is an associate professor of inorganic chemistry. His research interests include transition-metal clusters, organolanthanide complexes, structural chemistry of inorganic materials and X-ray crystallography.

2 Triosmium Alkylidyne Clusters

The chemical reactivities of triosmium alkylidyne clusters of general formulae $[Os_3(\mu\text{-}H)_n(CO)_9(\mu_3\text{-}CX)]$ **1** (X = O-donor, $n = 3$; N-donor, $n = 2$ or P-donor, $n = 2$)[6] have been extensively investigated in several aspects. Alkylidyne–alkyne coupling is an important reaction for monometallic alkylidyne complexes since it is the key step in the alkyne metathesis reactions.[7] Alkylidyne–alkyne coupling has also been noted in polymetallic systems.[8] In these reactions, the organometallic clusters promote alkyne oligomerization and exert a template effect on the resulting organic moieties. These ideas have produced enormous excitement in the field of alkyne cluster chemistry offering an alternative route for accessing large alkyne polymers.[9] However, reactions of transition-metal alkylidyne clusters with alkynes usually proceed non-selectively under more forcing conditions affording a wide range of products frequently in low yields. These involve those arising from C–H activation,[10] C–C coupling,[11] C–C bond cleavage,[12,13] CO activation,[14] hydrogen migration,[15,16] as well as isomerization.[17] Our investigations have showed that reaction of the triosmium alkylidyne cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}CH_2\text{-}2)]$ **2** with phenylacetylene proceeds under refluxing conditions to give five products and results in a new reaction sequence of alkylidyne–alkyne coupling (Scheme 1).[18,19] A proposed mechanism which involves the cleavage of the N–C (alkylidyne) bond in **2**, resulting in the formation of a μ_3-carbido species '$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)]$' or a μ-alkylidene fragment '$[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}CH)]$' as the intermediate has been put forward to explain the unusual coupling reaction sequence. These intermediate species possibly represent a particularly attractive analogue of a μ_3-carbide or μ-alkylidene CH fragment observed on a metal surface and are convenient models for examining their roles in the Fischer–Tropsch reaction mechanism.

The cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}CH_2\text{-}4)]$ **8** and other related compounds containing a heterocyclic nitrogen-donor at the apical carbon show some interesting spectroscopic features. They are all intensely coloured both in solution and in the solid state. Molecular orbital calculations by the Fenske–Hall technique showed that the HOMO of these compounds is largely metal based (*ca.* 70%), whilst the LUMO is mostly dominated by the organic moiety.[20] The intense colour of these compounds undoubtedly arises from a strong absorption due to a MLCT transition. The UV/VIS spectroscopic studies of these compounds in a variety of organic solvents demonstrated

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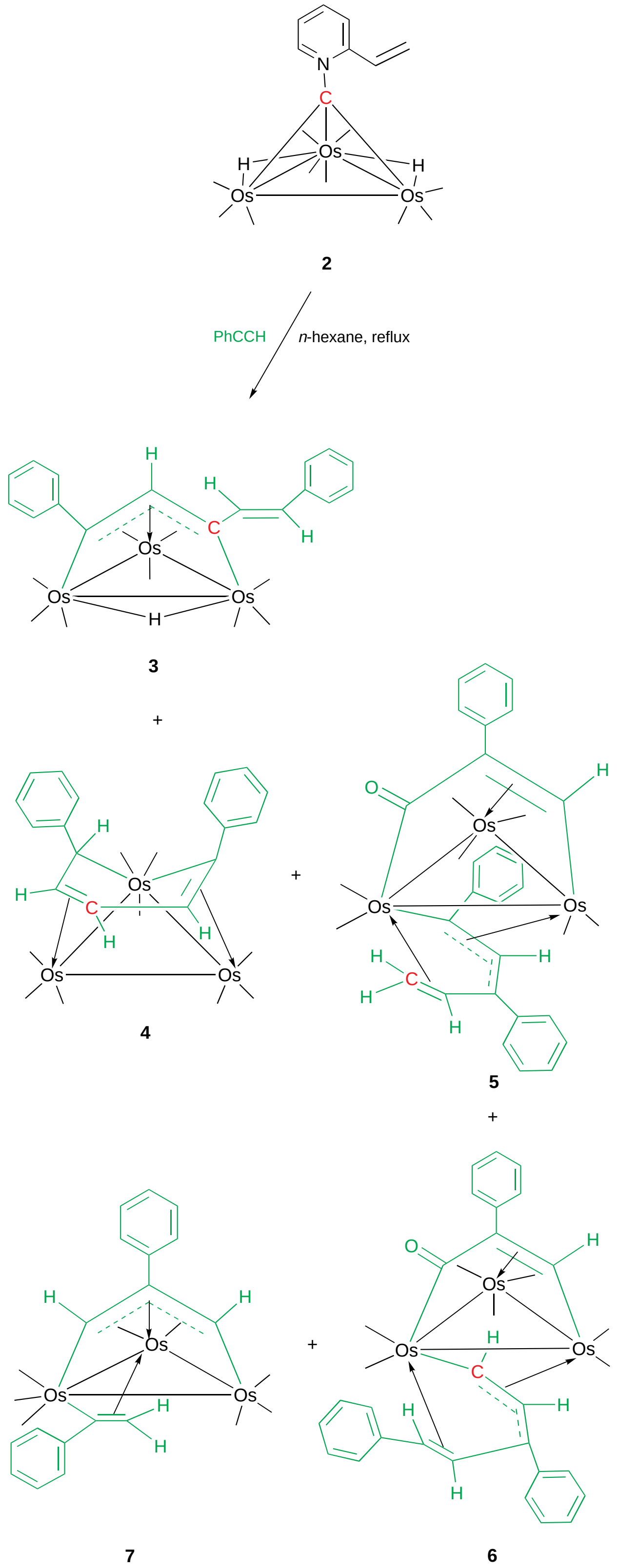
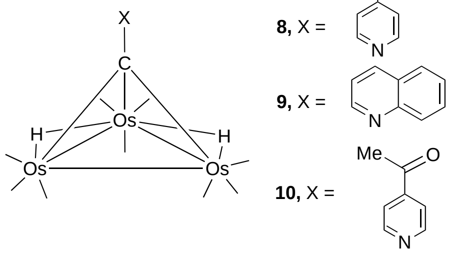
* Dedicated to Professor The Lord Lewis on the occasion of his 70th birthday.



Scheme 1

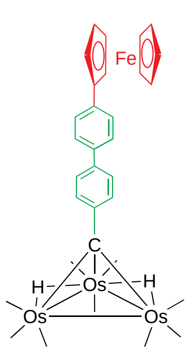
that the MLCT transition band displays negative solvatochromism.[6,21] Some optical spectral parameters of **8**–**10** are summarized in Table 1. Solvatochromism is only seen if the solvent–solute interaction in the ground state shows a significant difference from that in the excited state of the molecule. This type of molecule has a ligand–metal framework in which the bonding is polarized in the ground state, probably due to a dominating σ contribution from the nitrogen heterocycle. However, on MLCT excitation, this polarization will be either reduced, compensated, or even overcompensated for, by transfer of an electron from the metal-based orbital (HOMO) to the empty π* orbital of the organic ligand (LUMO). This results in a less polar excited state. The stronger stabilization of the ground state by solvents of increased polarity is apparent from the increased transition energies observed. This is consistent with a zwitterionic formulation with a formal negative charge residing on the Os_3 core so that the cluster valence electron count for this class of compounds is still 48.

Table 1 Optical spectral parameters for compounds **8**–**10**



	Solvent	Colour	λ_{max}/nm	10^{-3} ε/dm^3 mol^{-1} cm^{-1}
8	Hexane	Violet	570	4.8
	Carbon tetrachloride	Purple	561	4.1
	Dichloromethane	Red	520	4.3
	Acetone	Orange	492	4.3
9	Hexane	Green	620	4.0
	Carbon tetrachloride	Green	611	3.7
	Dichloromethane	Purple	566	4.4
	Acetone	Red	536	4.0
10	Hexane	Green	637	6.2
	Carbon tetrachloride	Green	627	6.2
	Dichloromethane	Blue	590	5.1
	Acetone	Red	537	4.0

Linking transition-metal centres together with ligands possessing a delocalized π system allows electronic communication between them, leading to novel physical properties. Classically, ligands such as pyrazine, 4,4′-bipyridine, 1,2-di-4-pyridylethane and *trans*-1,2-bis(4-pyridyl)ethylene have been extensively used in this context as exemplified by the archetypal Creutz–Taube system.[22] Extensive work on optical electron transfer (intervalence transfer) spectra of these systems has been done. We have shown that the $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)]$ core behaves as a good electron sink and is readily trapped by strong nucleophiles. In addition, the electronic properties of these systems can be conveniently probed by both IR and ^1H NMR spectroscopies. To build up a new system possessing 'donor–acceptor' heterometallic characteristics, we have introduced some pyridine ligands containing the ferrocenyl group as a redox spectator to the apical carbon of the $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)]$ core. Both clusters **11** and **12** show strong negative solvatochromic shifts for their low-energy bands.[23] The redox properties of **11**,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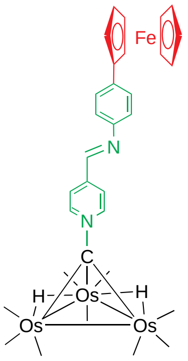
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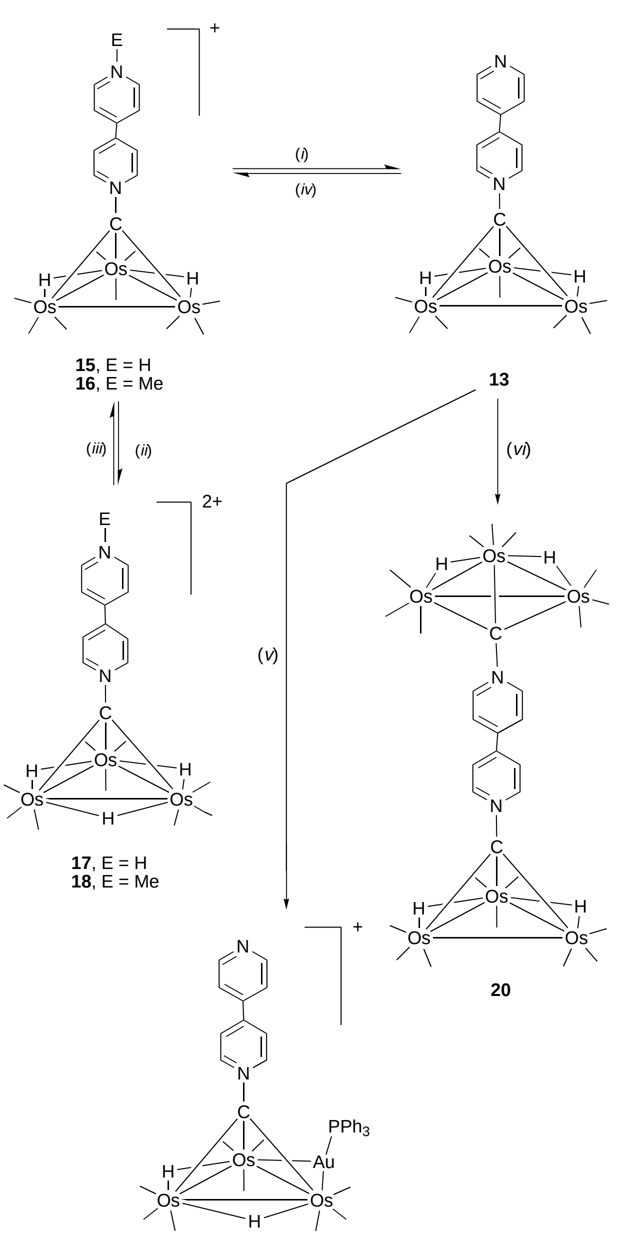
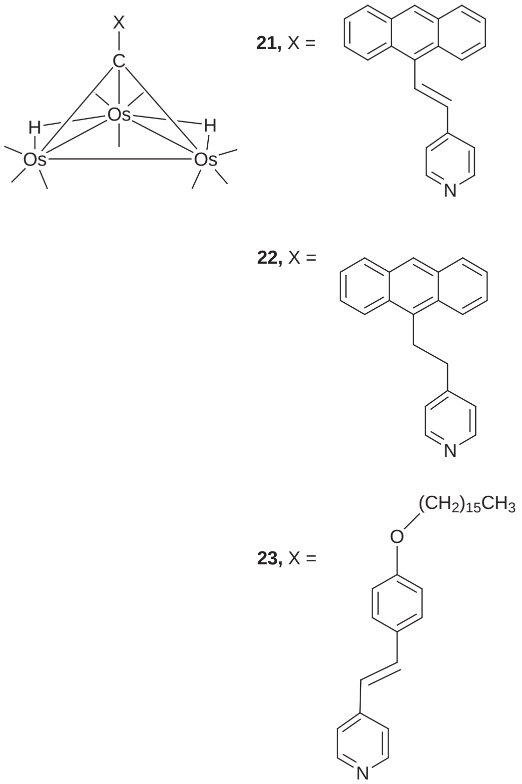


Scheme 2 (*i*) E = H, excess KOH–MeOH; (*ii*) E = H or Me, excess $HBF_4 \cdot Et_2O$; (*iii*) E = H or Me, 1 equivalent KOH–MeOH or 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu); (*iv*) E = H, 1 equivalent $HBF_4 \cdot Et_2O$; E = Me, 1 equivalent $Me_3O^+BF_4^-$; (v) 1 equivalent $AuPPh_3Cl$, $TlPF_6$; (*v*) $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$, 1 equivalent dbu

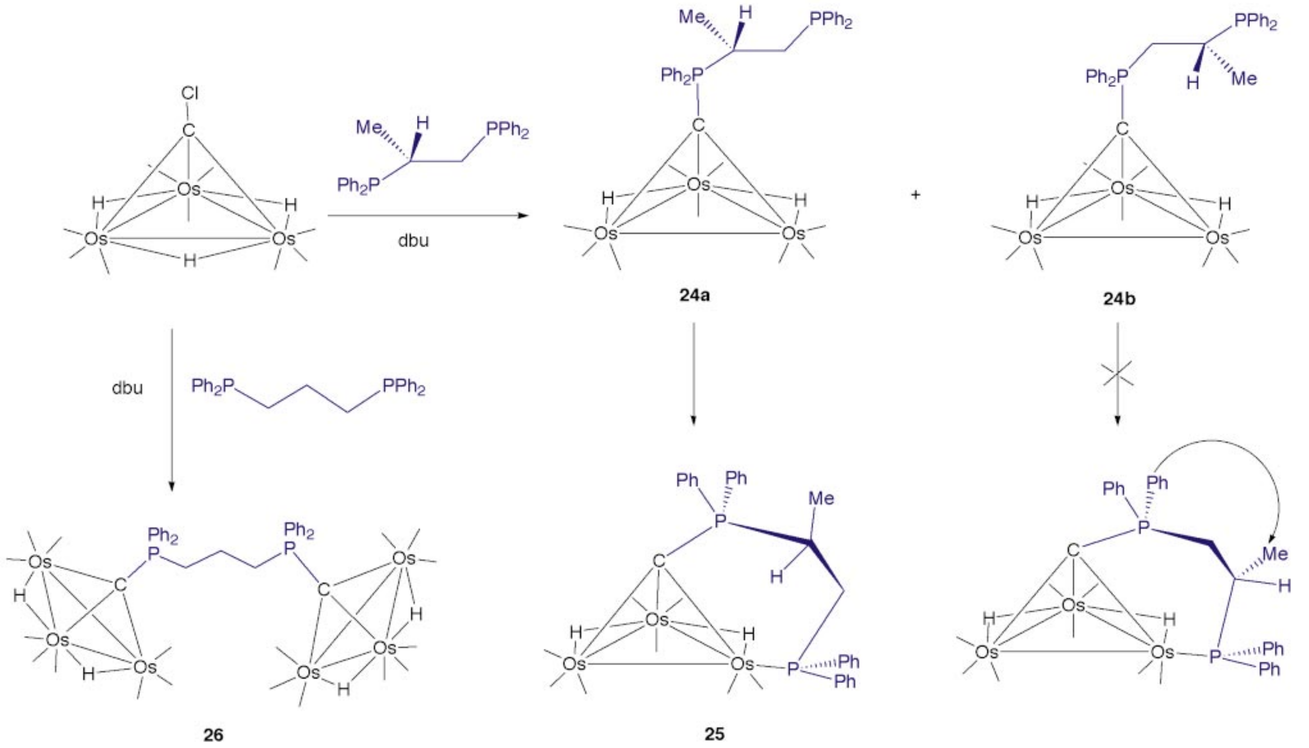
12 and the free ferrocenyl ligands have been investigated using cyclic voltammetry. The strongly electron-withdrawing Os_3C core in **11** and **12** significantly depletes the electron density at the iron centre giving rise to an anodic shift of 90 and 110 mV for **11** and **12** respectively.[24]

The cluster complexes $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}C(4,4'\text{-bipy})\}]$ **13** and $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}C(2,4'\text{-bipy})\}]$ **14**, bearing pendant pyridyl groups at the periphery were synthesized as building blocks for the stepwise synthesis of 'donor–acceptor' complexes either by direct co-ordination through the nitrogen atom or cyclometallation.[25] The electronic properties of the pyridyl ring are significantly modified due to extensive delocalization of electrons into the Os_3C core. The nucleophilicity of the pyridyl nitrogen is unusually low which makes the construction of a donor–acceptor complex non-trivial. To address this problem, chemical reactivities of **13** with various electrophiles: H^+, Me^+, $AuPPh_3^+$ and '$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C)]$' itself were examined (Scheme 2).[26,27] Initial protonation or methylation of **13** with 1 equivalent of $HBF_4 \cdot Et_2O$ or $Me_3O^+BF_4^-$ in dichloromethane occurs at the pendant nitrogen atom of the 4,4′-bipyridine ligand to give, quantitatively, the monocationic dihydrido species **15** and **16** respectively. A second protonation of **13** takes place at room temperature along the unbridged Os–Os edge of the alkylidyne metal core to give the water-soluble dicationic trihydrido cluster **17**. In contrast, no further methylation of **13** is observed on addition of more $Me_3O^+BF_4^-$. Nonetheless, cation **16** undergoes protonation along the non-bridged Os–Os edge in the presence of $HBF_4 \cdot Et_2O$. The difference in chemical reactivities between the isolobal fragments H^+ and Me^+ towards the cationic cluster species **16** can be attributed to the steric requirement along the non-bridged Os–Os bond. This edge is a less hindered site for protonation but steric congestion is much more pronounced for the methyl carbocation. In spite of this a bridging methyl group along an Os–Os edge in $[Os_3H(CO)_{10}\text{-}Me]$ has previously been reported by Calvert and Shapley.[28] Reaction of **13** with the $AuPPh_3^+$ cation produced the cluster cation **19** which was expected as interaction between Au and pyridine is relatively weak. Presumably the formal negative charge on the Os_3 core also aids the addition of the $AuPPh_3^+$ group to it. The hexanuclear species **20** which consists of two alkylidyne cluster units, which are linked together *via* a bridging 4,4′-bipyridine ligand, can also be prepared.

Other functionalized pyridine derivatives of **1** (*i.e.* complexes **21**–**23**) were also synthesized for photochemical[29] and optical microscopic studies.[24,30] The UV/VIS spectroscopic studies indicated a significant metal–anthracene interaction in the ground state *via* the conjugated ligand group in **21** when compared to **22**. Transition-metal complexes containing ligands such as 4′-alkoxystyrylpyridines $[NC_5H_4\{CH{=}CHC_6H_4\text{-}(OR\text{-}4)\}\text{-}4]$ have been the subject of considerable interest in the studies of liquid–crystalline materials.[31] However, structurally characterized examples are rare.[32] Compound **23** is an example of carbonyl clusters of the iron triad containing this kind of ligand. A crystal structure analysis of **23** revealed that it exhibited an interesting rod-like molecular geometry, see Fig. 1.



Vinylpyridine clusters **2** and **8** have also been used to generate larger clusters by either linking two cluster units *via* olefinic



Scheme 3

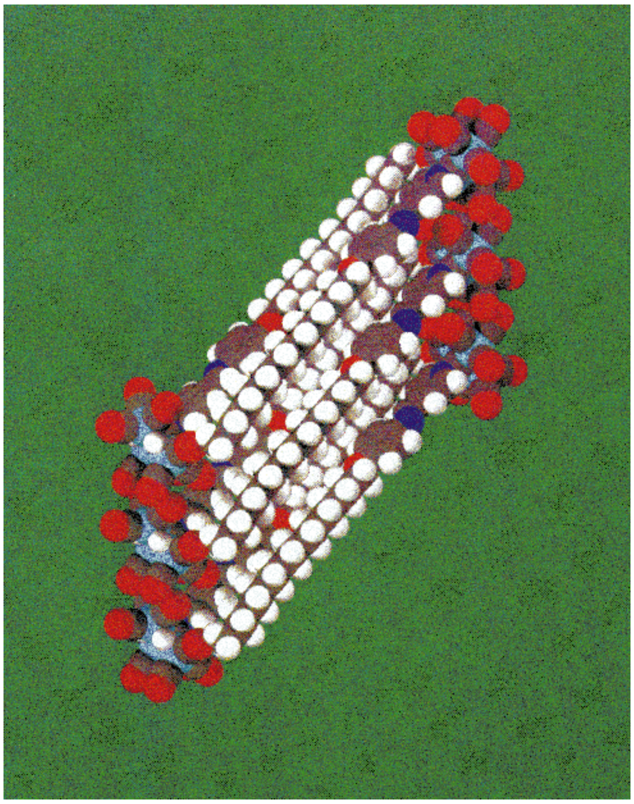
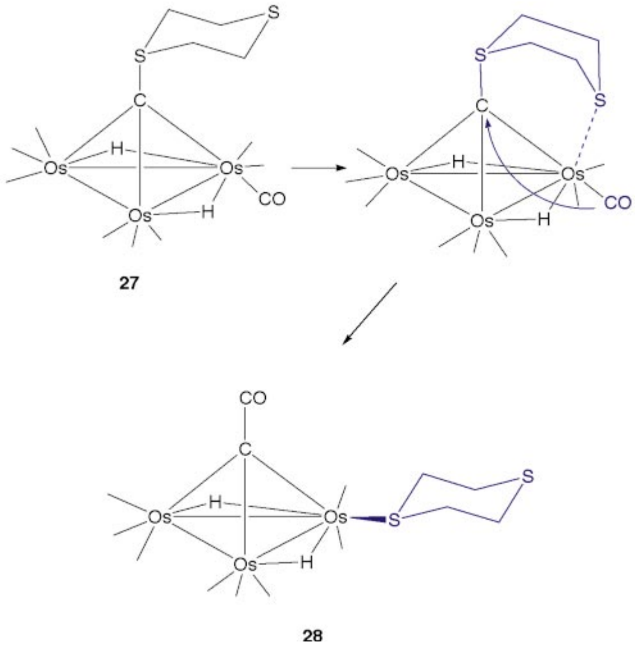


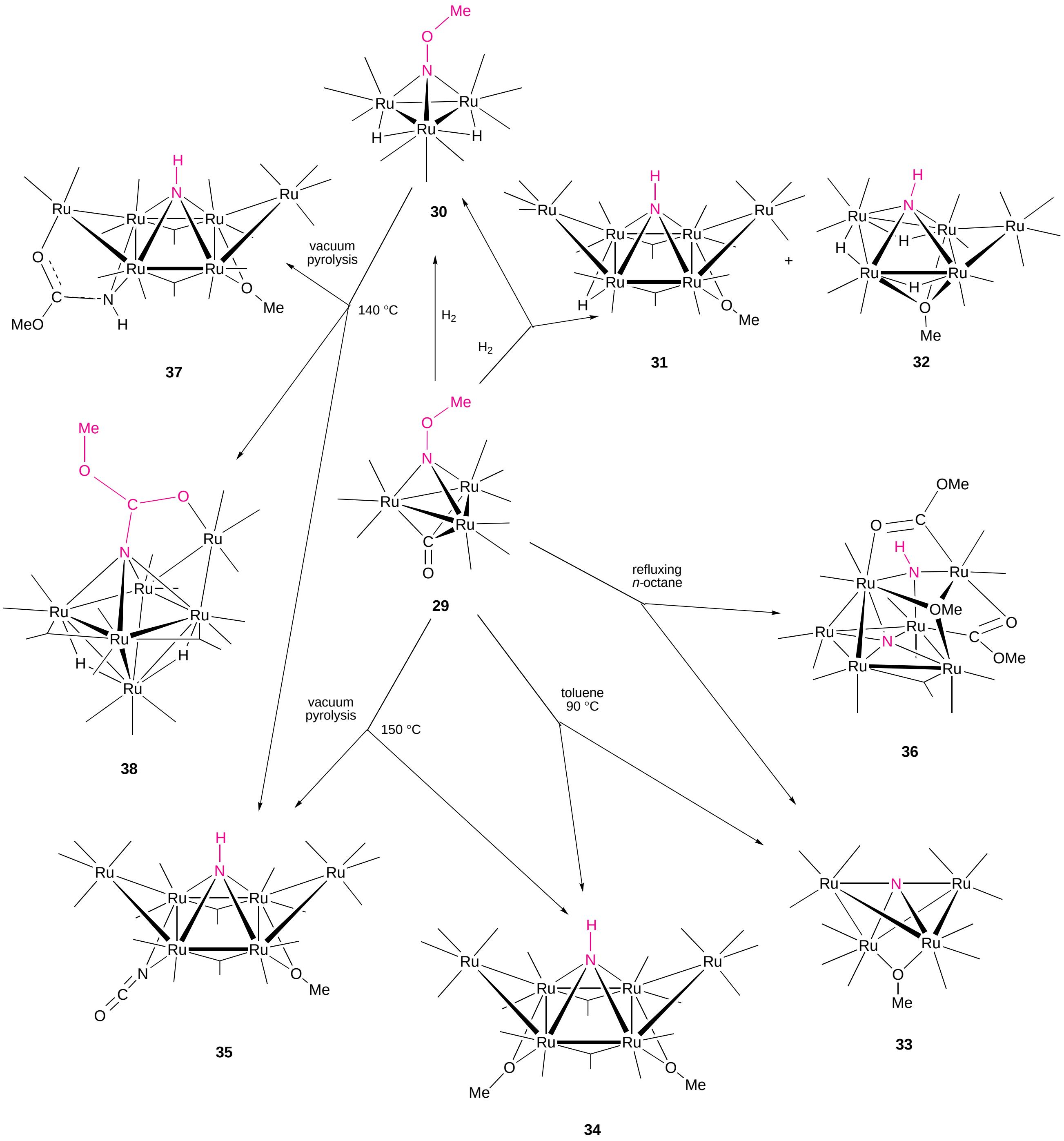
Fig. 1 Molecular packing diagram of the space-filling model of complex **23** (projection down the crystallographic *b* axis)

functionality[26] or direct metal–metal bonds.[33] Cluster **8** was copolymerized with styrene in the presence of 2,2′-azobis(2-methylpropanenitrile) to give a polymer-immobilized alkylidyne cluster of osmium.[34]



Scheme 4

The reactions between [$Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)$] and butyldiphenylphosphine or the chiral chelating diphosphine (*R*)-$Ph_2PCH(Me)CH_2PPh_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) to give the phosphine containing derivatives of **1** were investigated.[35] This particular system was chosen because it was hoped that the resulting zwitterionic cluster complexes containing phosphonium centres and negative charges formally on the triosmium core should provide an organometallic analogue of the well known phosphorus ylide. Besides, the generation of a chiral cluster *via* incorporation of a suitable chiral moiety for asymmetric catalysis is an important goal in organometallic chemistry.[36] It has been shown that the chiral triosmium alkylidyne clusters (*R*)-[$Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}$] **24a** and (*R*)-[$Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH_2CH(Me)PPh_2\}$] **24b** can be prepared and separated in good yields. Complex **24a** readily undergoes decarbonylation, followed by the formation of an Os–P bond, to afford an



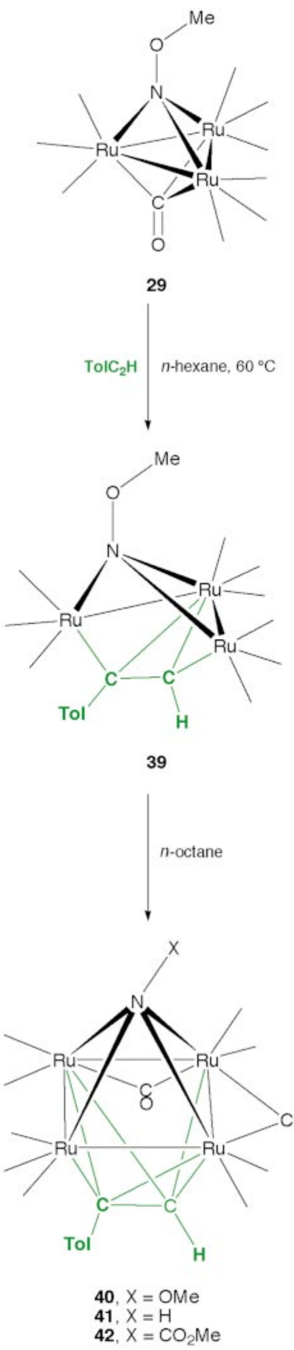
Scheme 5

octacarbonyl cluster complex **25** containing a six-membered ring structure. However, no nucleophilic substitution of CO by the non-co-ordinated P-donor atom is observed in **24b**. This is probably due to the unfavourable steric interaction caused by the axial Me group and PPh_2 group in the corresponding six-membered ring of the chair conformation (Scheme 3). This kind of ring formation involving an Os–P bond seen in **25** is also observed in bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) derivatives. However, in the case of 1,3-bis(diphenylphosphino)propane (dppp) the only isolable product is the linking cluster **26**.[37]

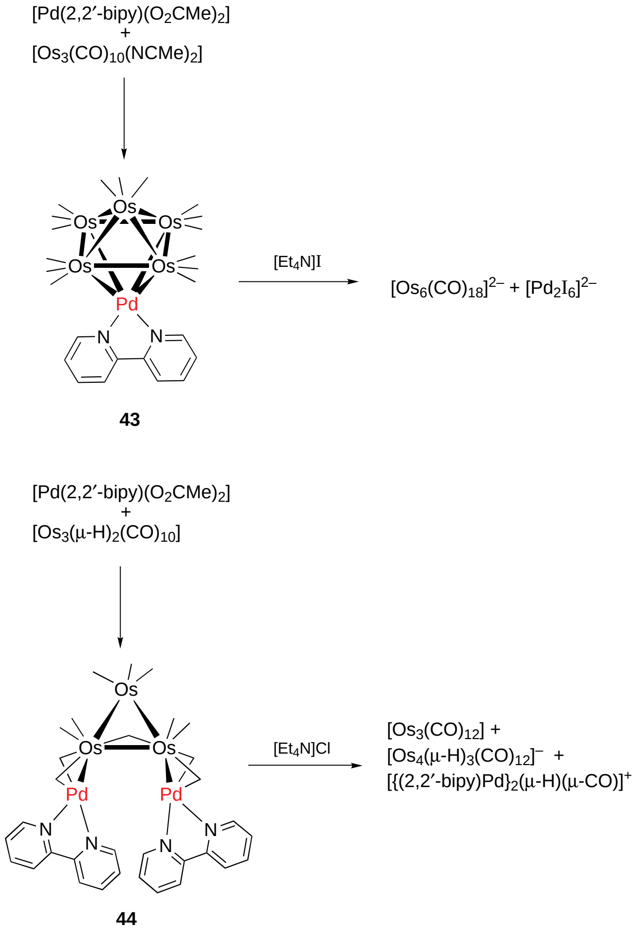
Another interesting reaction involving rearrangement of the ligand on the apical carbon is found in the neutral cluster $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}C\overline{S(CH_2)_2SCH_2C}H_2\}]$ **27**. Under ambient conditions, in solution **27** slowly rearranges to a novel μ_3-C–C≡O-bridged cluster $[Os_3(\mu\text{-}H)_2(CO)_8\{\overline{S(CH_2)_2SCH_2C}H_2\}(\mu_3\text{-}CCO)]$ **28**, which is formed by exchange of 1,4-dithiane, $\overline{S(CH_2)_2SCH_2C}H_2$, and CO at the apical carbon (Scheme 4). To explain this rearrangement, it was proposed that the more stable chair conformation of the cyclic thioether ligand slowly equilibrates to its less stable boat form in solution so that the pendant S atom of the 1,4-dithiane is sufficiently close to the Os atom and displaces a CO ligand. This proposed mechanism is favoured as no similar rearrangements are observed for the thiane or 1,3-dithiane derivatives.[38]

3 Ruthenium μ_4-Nitrene Clusters

Metal-surface-bound nitrido and nitrene species are believed to be the key intermediates in a number of chemical processes such as nitrogen oxide reduction and the Haber process.[39] Metal clusters containing either nitrido[40] or nitrene[41] ligands have



Scheme 6



Scheme 7

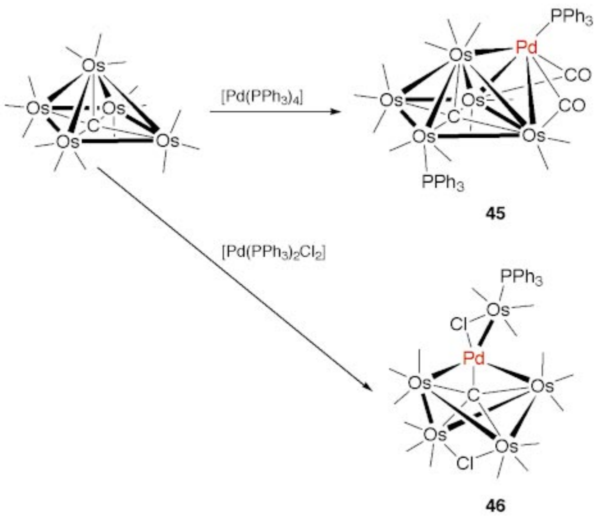
been known for a long time. In particular, trinuclear metal carbonyl clusters containing a μ_3-phenylimido ligand $[M_3(CO)_{10}(\mu_3\text{-NPh})]$ (M = Fe,[42] Ru[43] or Os[44]) have been extensively investigated over the past decades. Cluster complexes with a μ_3-NH group are also known, for example $[Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-CO})(\mu_3\text{-NH})]$,[45] $[Fe_3(CO)_8(NO)(\mu_3\text{-NH})]$[46] and $[FeCo_2(CO)_9(\mu_3\text{-NH})]$.[47] However, μ_4-nitrene species are very rare. An obvious attempt to synthesize a μ_4-nitrene cluster is by protonation of μ_4-nitrido clusters with a 'semi-open' environment. However, this reaction usually leads to the formation of a hydrido cluster rather than a nitrene species, as in the protonation of the $[Fe_4(CO)_{12}N]^-$ anion.[48]

Recently, we reported the N–O bond cleavage of $[Ru_3(CO)_{10}(\mu_3\text{-NOMe})]$ **29** to give a series of polynuclear carbonyl clusters containing either quadruply bridging nitrene or nitrido ligands (Scheme 5).[49,50] In addition, the compound containing both nitrene and nitrido moieties was also isolated in this system with a minor change of experimental conditions.[51] Another example of this kind is $[(\eta^5\text{-}C_5Me_5)_3Mo_3Co_2(CO)_8(\mu_3\text{-NH})(\mu_4\text{-N})]$ reported by Gibson and Dahl[52] from photolysis of a mixture of $[Co(CO)_3NO]$ and $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$.

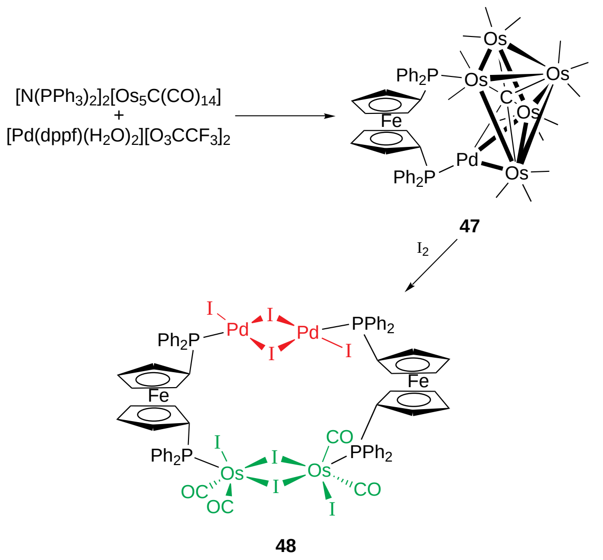
Blohm and Gladfelter have shown that protonation of the tetraruthenium nitrido cluster anion $[Ru_4N(CO)_{12}]^-$ in the presence of diphenylacetylene results in $[Ru_4(CO)_{11}(\mu_4\text{-NH})(PhCCPh)]$.[53] Reaction of triruthenium nitrene clusters $[Ru_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-NPh})]$ with diphenylacetylene were found to produce the μ_4-nitrene cluster $[Ru_4(CO)_{11}(\mu_4\text{-NPh})(PhCCPh)]$.[54] It appears that the alkynes are important auxiliary ligands that favour the formation and isolation of μ_4-nitrene species. It is interesting to note that the μ_4-nitrene species $[Ru_4(CO)_{11}(\mu_4\text{-NPh})(\mu_4\text{-}\eta^2\text{-SNPh})]$ can be isolated from the interaction of $[Ru_3(CO)_{12}]$ and *N*-sulfinylaniline (PhN=S=O).[55] These observations prompted us to examine the reactivity of cluster **29** towards alkynes at elevated temperature. Heating **29** with excess tolylacetylene [TolCCH, $MeC_6H_4(CCH)$-4] in refluxing *n*-hexane afforded $[Ru_3(CO)_9(\mu_3\text{-NOMe})(TolCCH)]$ **39** in good yield. Further heating in *n*-octane gave a mixture of μ_4-nitrene clusters **40**–**42** in moderate yields (Scheme 6).[56] Clearly the chemical reactivities of μ_4-nitrene species are of interest and will be extensively investigated as improved synthetic methods afford these species in more accessible yields.

4 Mixed-Metal Clusters of Osmium and Palladium

The chemistry of bimetallic clusters has received much attention because of their potential for cooperative reactivity in the activation of small molecules and in catalysis.[57] In the past, studies have shown that mixed-metal cluster complexes are capable of catalysing a variety of organic transformations.[58,59] Molecular mixed-metal clusters have been used to prepare bimetallic-supported nanoparticles that are active catalysts.[60] The use of heterometallic cluster precursors offers the advantages of narrow size distribution of nanoparticles,[61] and better



Scheme 8



Scheme 9

control over the specific bimetallic composition of the catalysis.[62] It is believed that bimetallic clusters of palladium and osmium are of interest as the palladium ion can attain either a 16- or an 18-electron configuration which is an important feature for catalytic processes. On the other hand, osmium clusters display a very rich chemistry and are kinetically stable, thus allowing for easy isolation and characterization. Furthermore, polar osmium–palladium bonds make it possible selectively to observe ligands binding to different metal centres. Although the chemistry of osmium–nickel and –platinum clusters is well documented,[63–67] heteronuclear clusters containing osmium–palladium bonds were not developed until recently. Here is a summary of some chemistry in this area. The reaction of $[\mathrm{Pd}(2,2'\text{-bipy})(\mathrm{O_2CMe})_2]$ (bipy = 2,2′-bipyridine) with the activated triosmium cluster $[\mathrm{Os_3(CO)_{10}(NCMe)_2}]$ yielded $[\mathrm{Os_5Pd(CO)_{15}}(2,2'\text{-bipy})]$ **43** which is the first structurally characterized mixed-metal cluster with direct Os–Pd bonds.[68] The dihydrido cluster $[\mathrm{Os_3}(\mu\text{-H})_2\mathrm{(CO)_{10}}]$ reacted with the same palladium reagent to give $[\{(2,2'\text{-bipy})\mathrm{Pd}\}_2\mathrm{Os_3(CO)_{12}}]$ **44** in which supported Os–Pd bonds are observed.[69] However, both **43** and **44** are not very stable in solution. In the presence of a nucleophile such as iodide, cluster fragmentation results (Scheme 7).

Interaction of the unsaturated cluster $[\mathrm{Os_3}(\mu\text{-H})_2\mathrm{(CO)_{10}}]$ with *trans*-$[\mathrm{Pd(py)_2Cl_2}]$ (py = pyridine) and *trans*-$[\mathrm{Pd(NH_3)_2I_2}]$ was found to yield a series of hydrido heterometallic complexes with a common $\{\mathrm{Os_3Pd}\}$ tetrahedron unit.[70,71] Palladium reagents containing phosphorus donor ligands have also been used to construct mixed-metal clusters of Os–Pd. Reactions of the pentaosmium carbide cluster $[\mathrm{Os_5C(CO)_{15}}]$ with $[\mathrm{Pd(PPh_3)_4}]$ and $[\mathrm{Pd(PPh_3)_2Cl_2}]$ gave $[\mathrm{Os_5PdC(CO)_{12}}(\mu\text{-CO})_2\mathrm{(PPh_3)_2}]$ **45** and $[\mathrm{Os_5PdC(CO)_{15}}(\mu\text{-Cl})_2\mathrm{(PPh_3)}]$ **46** (Scheme 8).[72] It is interesting to note that one osmium atom is detached from the $\mathrm{Os_5C}$ metal core and results in the formation of Pd–C (carbide) bond in **46** as it was previously believed that the $\mathrm{Os_5C}$ core is extremely stable.[73] Structurally characterized examples containing Pd–C (carbide) bonds are rare and it is believed that the carbide may have a stabilizing effect on the overall geometry of the cluster. Another example of this kind is $[\mathrm{Os_5PdC(CO)_{14}}(\mu\text{-dppf})]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] **47**. Electrochemical studies revealed that complex **47** underwent a reversible one-electron oxidation at the ferrocene centre followed by a quasi-reversible oxidation of the metal cluster core. When treated with iodine, **47** underwent cluster degradation to give the macrocyclic complex $[\mathrm{OsPd(CO)_2}(\mu\text{-dppf})(\mu\text{-I})_2\mathrm{I_2}]_2$ **48** (Scheme 9).[74]

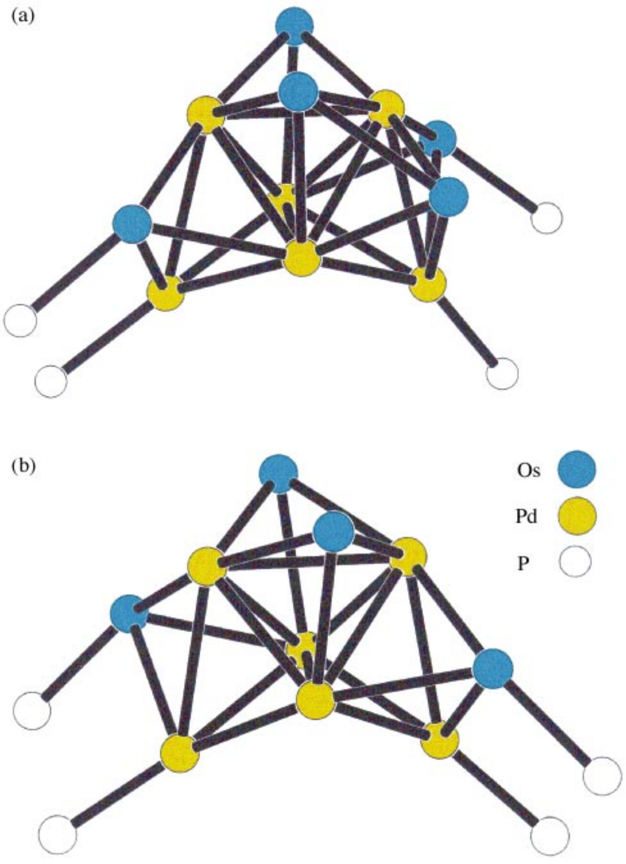


Fig. 2 (a) The metal core of complexes **49** and **50**; (b) the metal core of complex **51**

Palladium rich mixed-metal clusters are also available. The reaction of $[\mathrm{Os_3}(\mu\text{-H})_2\mathrm{(CO)_{10}}]$ with $[\mathrm{Pd_2}(\mu\text{-dppm})_2\mathrm{Cl_2}]$ gave a mixture of high nuclearity Pd–Os mixed-metal clusters $[\mathrm{Os_5Pd_6}(\mu\text{-H})_2\mathrm{(CO)_{13}}(\mu\text{-CO})_5(\mu\text{-dppm})_2]$ **49**, $[\mathrm{Os_5Pd_6(CO)_{13}}(\mu\text{-CO})_6(\mu\text{-dppm})_2]$ **50** and $[\mathrm{Os_4Pd_6(CO)_{10}}(\mu\text{-CO})_6(\mu\text{-dppm})_2]$ **51**.[75] All of them contain an 'inner' $\mathrm{Pd_6}$ bicapped tetrahedron, see Fig. 2. Obviously for the preparation of supporting bimetallic particles one would like to have metal cluster precursors being available in all sorts of composition.

Another interesting combination of metals in the synthesis of mixed-metal cluster systems is osmium and rhodium. Similar to palladium, the rhodium ion tends to have a stable, co-ordinatively unsaturated 16-electron configuration and has a well established background of catalytic applications. An established route to Os–Rh mixed-metal clusters is *via* nucleophilic addition of rhodium reagents to the co-ordinatively unsaturated

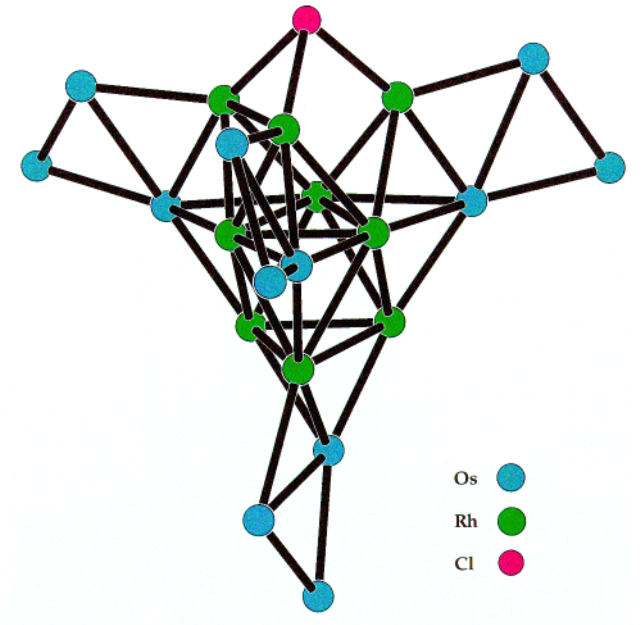


Fig. 3 The metal core of $[Os_{12}Rh_9(CO)_{44}(\mu_3\text{-}Cl)]$

cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[76] Recently we were able to prepare some high nuclearity mixed-metal clusters of Os–Rh in good yield *via* the redox condensation of the $[Rh(nbd)]^+$ (nbd = norbornadiene, bicyclo[2.2.1]hepta-2,5-diene) cation and the $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ anion. An example of these clusters is $[Os_{12}Rh_9(CO)_{44}(\mu_3\text{-}Cl)]$, shown in Fig. 3.[77]

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