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Review

The chemistry of $[M_3(CO)_{10}(\mu\text{-dppm})]$($M = Ru, Os$): Activating and maintaining the trinuclear core

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ABSTRACT

Ruthenium and osmium dodecacarbonyls, $M_3(CO)_{12}$ ($M = Ru, Os$), find extensive use as precursors towards a range of low-valent ruthenium and osmium compounds, being especially widely utilized in the area of cluster chemistry. However, especially in the case of $Ru_3(CO)_{12}$, the generally desired carbonyl loss competes with metal–metal bond cleavage such that a range of products of varying nuclearities result. In contrast, related complexes $[M_3(CO)_{10}(\mu\text{-dppm})]$ in which two equatorial carbonyls are replaced by the small bite-angle diphosphine, bis(diphenylphosphino)methane (dppm), are both relatively activated with respect to further carbonyl loss while also serving to maintain the integrity of the trinuclear core. This makes them attractive starting materials for a range of trinuclear cluster chemistry which is the subject of this review.

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1. Introduction

The ready availability of the binary carbonyls $M_3(CO)_{12}$ (M = Ru, Os) has lead to the extensive development of the cluster chemistry of ruthenium and osmium. While much of this is based on a trinuclear framework [1], the forcing conditions required for carbonyl loss, such as in reactions with hydrocarbons and other potential ligand sources, often results in a competitive metal–metal bond scission leading to products with nuclearities ranging from 1 to 20 [2]. For example, among a mixture of products generated from the extended thermolysis of $Ru_3(CO)_{12}$ in mesitylene is the decanuclear hydride cluster $[Ru_{10}(CO)_{24}(\mu\text{-}H)(\mu_6\text{-}C)]^-$ [3], while in contrast, the reaction of tetraethylthiuram disulfide with $Ru_3(CO)_{12}$ at 60 °C in chloroform rapidly and quantitatively affords mononuclear *cis*-$[Ru(CO)_2(S_2CNEt_2)_2]$ [4] (Scheme 1).

This difference stems in part from the relative strengths of the M–CO and M–M bonds within $M_3(CO)_{12}$. Hence for $Ru_3(CO)_{12}$, the ruthenium–ruthenium bond enthalpy have been estimated at 78 kJ mol^{-1} and the ruthenium–carbonyl bond enthalpy at 182 kJ mol^{-1}, while for $Os_3(CO)_{12}$ the respective values are 94 and 201 kJ mol^{-1} [5,6]. Thus it is clear that in both cases scission of a metal–metal bond is thermodynamically favorable to carbonyl loss. For cluster fragmentation at least two metal–metal bonds must be broken, but since the strength of the metal–carbonyl bond in both is greater than twice the metal–metal bond enthalpy, then metal–metal and metal–carbonyl bond scission processes are competitive.

Phosphines find widespread use in coordination chemistry primarily since both their steric and electronic properties are easily tunable. Diphosphines in turn are able to confer extra stability to their complexes as a result of their ability to chelate metal centers. Small bite-angle diphosphines are an important sub-class of diphosphines in which the two phosphorus atoms are linked *via* a single atom. The best known and ubiquitous example of small bite-angle diphosphines is bis(diphenylphosphino)methane (dppm) in which the phosphorus nuclei are linked *via* a methylene bridge [7–9]. Unlike most other diphosphines, the stability conferred *via* the formation of stable five-membered rings results in their propensity to bridge two metal atoms. In this capacity not only can the steric and electronic properties of the phosphine be tuned [10,11] but the diphosphine can also serve to retain the nuclearity of the system even if the metal–metal bond that it spans breaks at some stage during a reaction (to be reformed at a later stage). This is exemplified by comparison of the chemistry of $Fe_2(CO)_9$ with that of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ [12] (Scheme 2). While the reactivity of the former is dominated by the heterolytic cleavage of the iron–iron bond, in contrast the extensive chemistry developed from $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ is characterized by the almost exclusive formation of binuclear products [13–16].

In order to confer similar stability onto a trinuclear core, a tridentate phosphine is required which can bind to all three metal atoms concurrently. There is, however, a major problem with this approach since $M_3(CO)_{12}$ preferentially undergo substitution of carbonyls lying *trans* to the metal–metal bonds, that is those in the equatorial plane. Hence, use of a simple tridentate capping ligand would require the disfavored substitution of three axial carbonyl ligands. A common triphosphine ligand which is able to cap triangular metal faces is tris(diphenylphosphino)methane, $HC(PPh_2)_3$ (triphos). While reaction of triphos with $Ru_3(CO)_{12}$ does furnish small amounts of the desired $[Ru_3(CO)_9\{\mu_3\text{-}HC(PPh_2)_3\}]$ [17,18] a wide range of other products also result from competing ruthenium–ruthenium and carbon–phosphorus bond cleavage reactions.

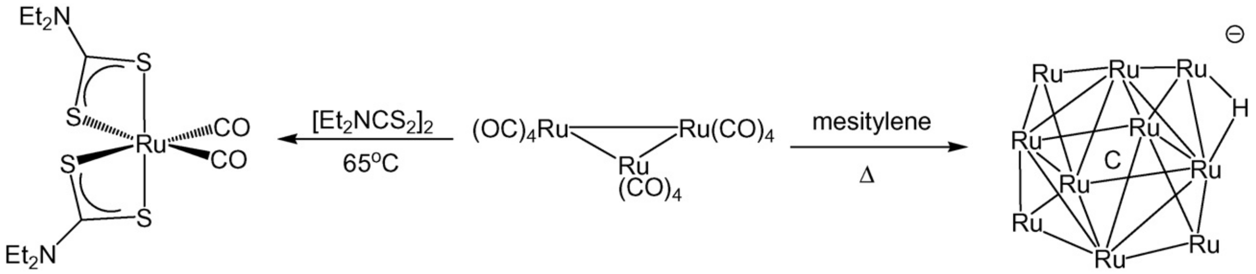
2. Synthesis and structure of $[M_3(CO)_{10}(\mu\text{-}dppm)]$ (M = Ru, Os) (1)

In 1977, Cotton and Hanson first reported the synthesis of $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ (**1**-Ru) from the reaction between $Ru_3(CO)_{12}$ and dppm in thf at 50 °C for 36 h [19]. It was isolated as a red-orange band upon chromatography with a 50:50 mixture of thf and hexanes, red-orange crystals forming upon concentration of the mixture. A characteristic IR pattern was recorded in CH_2Cl_2 showing carbonyl stretches at 2080m, 2040w, 2010s, 1988sh and 1960m cm^{-1}. No yield was given in this contribution, but in 1983 the electron-transfer-catalyzed reaction of $Ru_3(CO)_{12}$ and dppm by $[PPN][O_2CMe]$ was reported to give a 75% yield [20], while a similar process using sodium diphenylketyl catalyst in thf gave 91% [21]. This is now the accepted method of preparation of **1**-Ru, optimum conditions leading to a 95% yield [22,23]. A number of other synthetic methods have also been documented. The same reactants can be photochemically activated in cyclohexane to give an 80% yield [24], while addition of $Fe_2(CO)_9$ to the ruthenium(II) dimer $[\{RuCl_2(cymene)\}_2(\mu\text{-}\eta^1,\eta^1\text{-}dppm)]$ affords **1**-Ru in 15% yield, together with the mixed-metal analogue $[FeRu_2(CO)_{10}(\mu\text{-}dppm)]$ in 37% yield [25]. The latter is the only known example of a mixed-metal derivative of this type and characterization with the diphosphine bridging the ruthenium–ruthenium vector is made on the basis of the observation of a singlet at 20.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum. This compares with a phosphorus chemical shift of 17.2 ppm for **1**-Ru in $CDCl_3$ [25]. In the ^1H NMR spectrum the methylene protons of **1**-Ru are equivalent being observed as a triplet at δ 4.2 (J_{PH} 10.5 Hz).

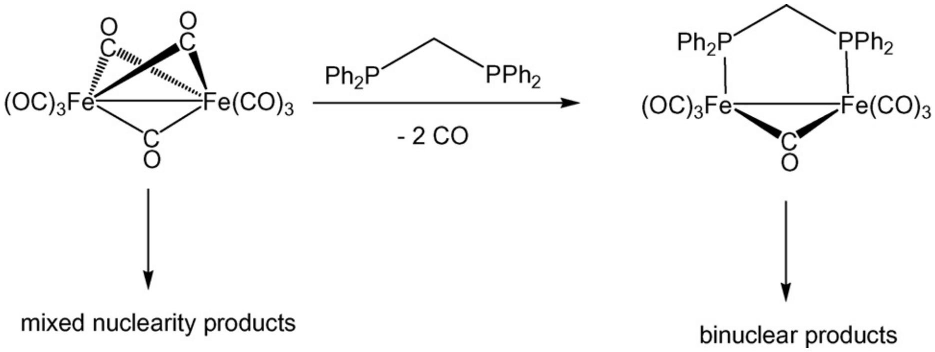
Three groups independently reported the synthesis of the osmium analogue **1**-Os in 1984 [26–29]. It can be prepared in 74% yield upon the dropwise addition of a methanol solution of two equivalents of $Me_3NO\cdot 2H_2O$ to a suspension of $Os_3(CO)_{12}$ and dppm in benzene and is recrystallised from an acetone–ethanol mixture to afford orange needles [26,28]. Other preparations involve the addition of dppm to $[Os_3(CO)_{10}(\eta^4\text{-}cis\text{-}C_4H_6)]$ [29,30] or $[Os_3(CO)_{10}(MeCN)_2]$ and *via* carbonyl loss from $[Os_3(CO)_{11}(\eta^1\text{-}dppm)]$ upon mild heating [27,30]. The IR spectrum in CH_2Cl_2 shows carbonyl stretches at 2090m, 2026sh, 2006vs, 2000vs, 1971m, 1954m and 1944m cm^{-1}, and a singlet is seen at −27.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a triplet at δ 5.09 (J_{PH} 10.7 Hz) in the ^1H NMR spectrum.

Poë and Sekhar have followed carbonyl loss from $[Os_3(CO)_{11}(\eta^1\text{-}dppm)]$ between 50 and 70 °C by UV–vis spectroscopy, the absorption maxima of $[Os_3(CO)_{11}(\eta^1\text{-}dppm)]$ at 410 nm ($\varepsilon = 6.4 \times 10^3\ M^{-1}\ cm^{-1}$) being replaced by peak at 417 nm ($\varepsilon = 5.2 \times 10^3\ M^{-1}\ cm^{-1}$) upon carbonyl loss [27]. Rate constants were found to be insensitive to the presence of oxygen and [complex], [dppm] and [CO] and activation parameters $\Delta H^{\#}$ 22.22 ± 0.44 kcal mol^{-1} and $\Delta S^{\#}$ -9.6 ± 1.3 cal $K^{-1}\ mol^{-1}$ were determined. The low value of the enthalpy of activation and negative entropy of activation both point strongly towards an associative process. No mechanism is directly suggested, however, one involving a transition state resulting from homolytic cleavage of a metal–metal bond being bridged by a carbonyl ligand seems sensible (Scheme 3).

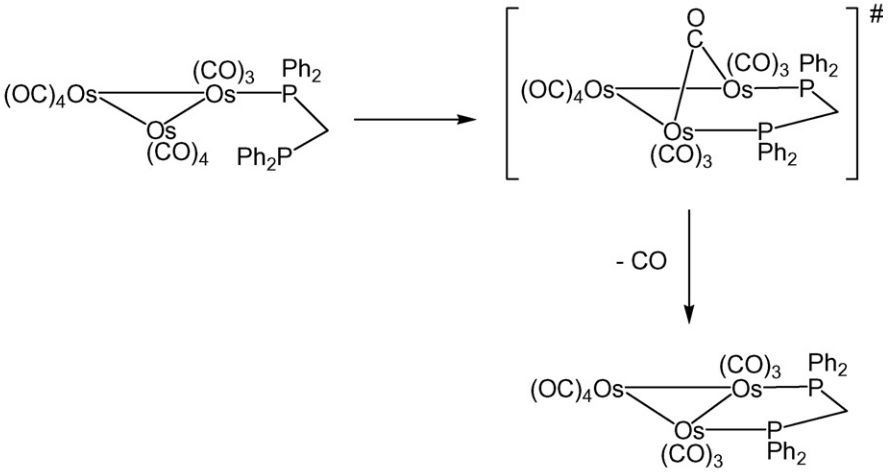
Somewhat surprisingly, the analogous ruthenium complex $[Ru_3(CO)_{11}(\eta^1\text{-}dppm)]$ has not been isolated in a pure state. Poë and Ambwani have looked at the kinetics of formation of **1**-Ru from $Ru_3(CO)_{12}$ the former showing an absorption maximum at 424 nm ($\varepsilon = 8.3 \times 10^3\ M^{-1}\ cm^{-1}$) in benzene. Overall formation of **1**-Ru is first order in [dppm] and the reaction is believed to proceed *via* initial formation of $[Ru_3(CO)_{11}(\eta^1\text{-}dppm)]$ and the authors state that its conversion to the bridged product is “virtually certain to be independent of [dppm]” but this is not proven [31].



Scheme 1.

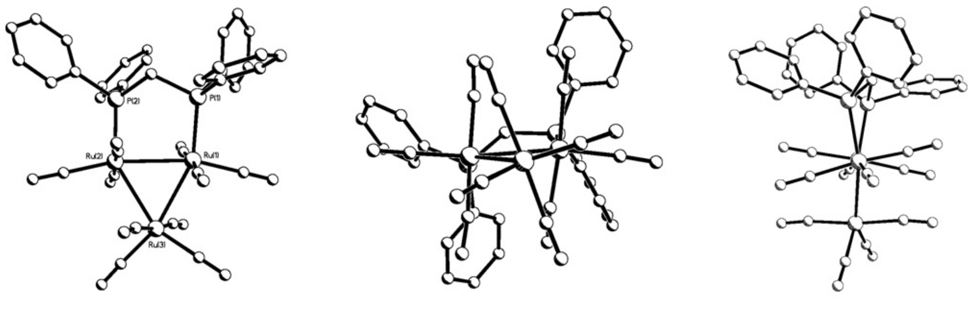


Scheme 2.



1-Os

Scheme 3.



(a) (b) (c)

Fig. 1. Three views of 1-**Ru** (data taken from J. Organomet. Chem., 655 (2002) 227, see ref. [58]).

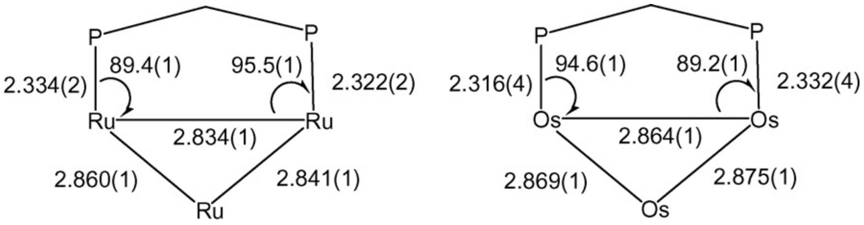


Fig. 2. Selected metric parameters for 1.

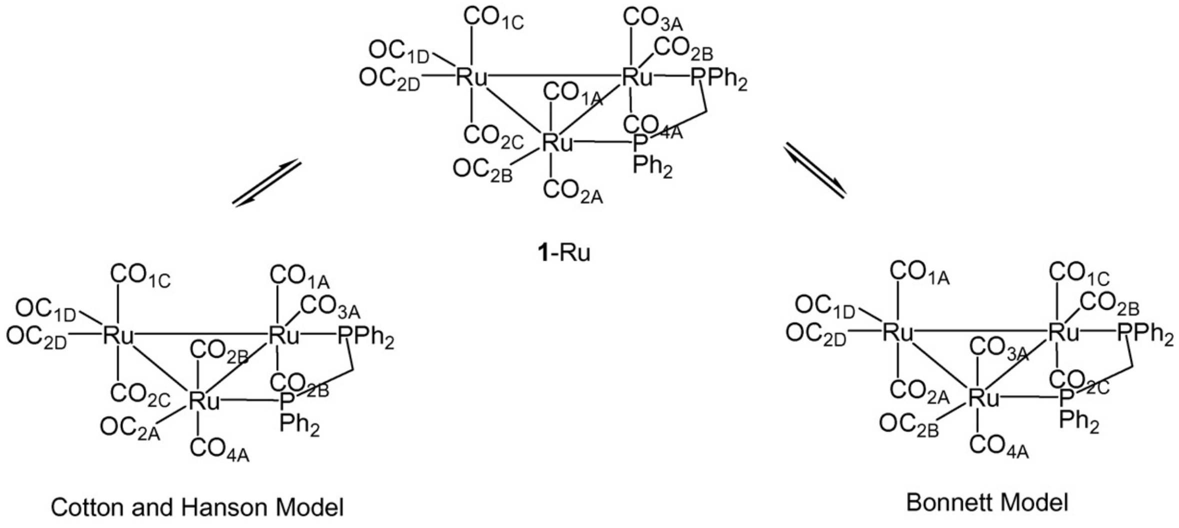
The X-ray structures of both **1**-Ru [25] and **1**-Os [32] have been reported. Views of **1**-Ru are given in Fig. 1 and key metric parameters are summarized in Fig. 2 (average values given for **1**-Os which contains two molecules in the asymmetric unit). In both the diphosphine is coordinated in equatorial sites, which introduces a significant distortion to the trinuclear core. The metal–metal vector spanned by the diphosphine is significantly shorter than the other two which more closely reflect the metal–metal bond lengths in $Ru_3(CO)_{12}$ [2.851(1)–2.859(1) Å] and $Os_3(CO)_{12}$ [2.8737(5)–2.8824(5) Å]. Metal–phosphorus bond lengths are within the expected ranges and the *trans* shortening of the phosphorus ligands can be clearly seen since in both structures the longest metal–metal bond length is associated with the longest ruthenium–phosphorus length. The most notable feature of the structures is the strain in the five-membered chelate rings which results in a significant twisting of the phosphorus atoms from the basal plane of the metal triangle. This results in the tilting of the axial carbonyls away from their expected positions orthogonal to the triangle, such that each is bent towards a metal–metal bond.

The solid-state structure is maintained in solution. Cotton and Hanson have studied the dynamic nature of **1**-Ru in solution *via* VT $^{13}C\{^1H\}$ NMR measurements of an isotropically enriched sample [19]. Monitoring changes to the carbonyl region of the spectrum has allowed three fluxional processes to be deconvoluted while a fourth is implied. At low temperature (−131 °C) four singlets are observed in the carbonyl region of the spectrum in a 2:1:1:1 ratio being assigned to the four different carbonyl types (Scheme 4A–D), suggesting that the puckered Ru_2P_2C ring flips rapidly even at this temperature. Upon warming the large singlet and one other collapse (T_c −80 °C, $\Delta G^{\#} = 8.5 \pm 0.1$ kcal mol^{-1}) to be replaced by a single sharp signal by −27 °C. Cotton and Hanson have attributed this to the interconversion of axial and equatorial carbonyls on the phosphine-bound ruthenium atoms possibly proceeding *via* a double carbonyl-bridged intermediate [19]. However, on the basis of the X-ray structure this was later queried by Bonnet and co-workers, who suggested that it arises due to the interconversion of all six axial carbonyls, which are found to be distorted in the solid-state [25].

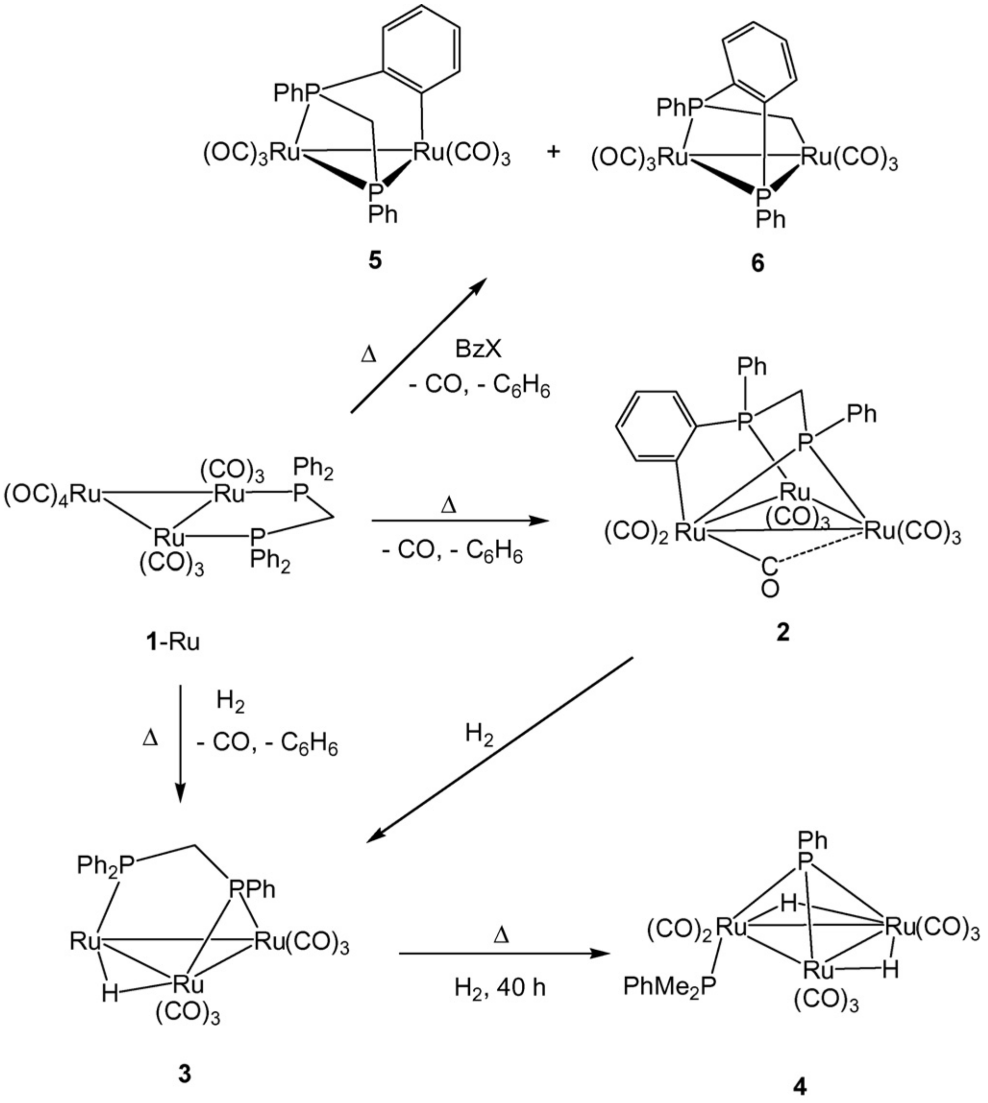
At higher temperatures the two remaining singlets collapse (T_c 71 °C) which Cotton and Hanson attribute to the local exchange at the $Ru(CO)_4$ centre, but could be ascribed to exchange of the four equatorial carbonyls on the Bonnet model. Above 100 °C, all signals broaden but the signal-noise increases and above 111 °C a facile transformation occurs (see below) which precludes further characterization of the fluxional behavior. As far as we are aware, related studies of **1-Os** have not been carried out. Aime and co-workers have used the ^{187}Os sub-spectrum of the $^{31}P\{^1H\}$ NMR spectrum of **1**-Os to measure both ^1J and ^2J Os–P coupling constants, values of 227 and 38 Hz, respectively being determined [33].

3. Thermal rearrangements of $[M_3(CO)_{10}(\mu\text{-dppm})]$ (1)

As alluded to above, **1**-Ru is unstable at temperatures above 110 °C. This was first appreciated concomitantly by the groups of Bonnet [34] and Bruce [35]. Heating **1**-Ru in cyclohexane for between 6 and 10 h leads to the high yield formation of $[Ru_3(CO)_9\{\mu_3\text{-}\eta^3\text{-PhPCH}_2\text{PPh}(C_6H_4)\}]$ (**2**) resulting from loss of both CO and benzene. Under similar conditions, in the presence of hydrogen, hydride **3** is formed, which also results upon hydrogenation of **2**. It exists as an interconverting mixture of two isomers, believed to differ in the relative positions of the hydride and diphos-



Scheme 4.

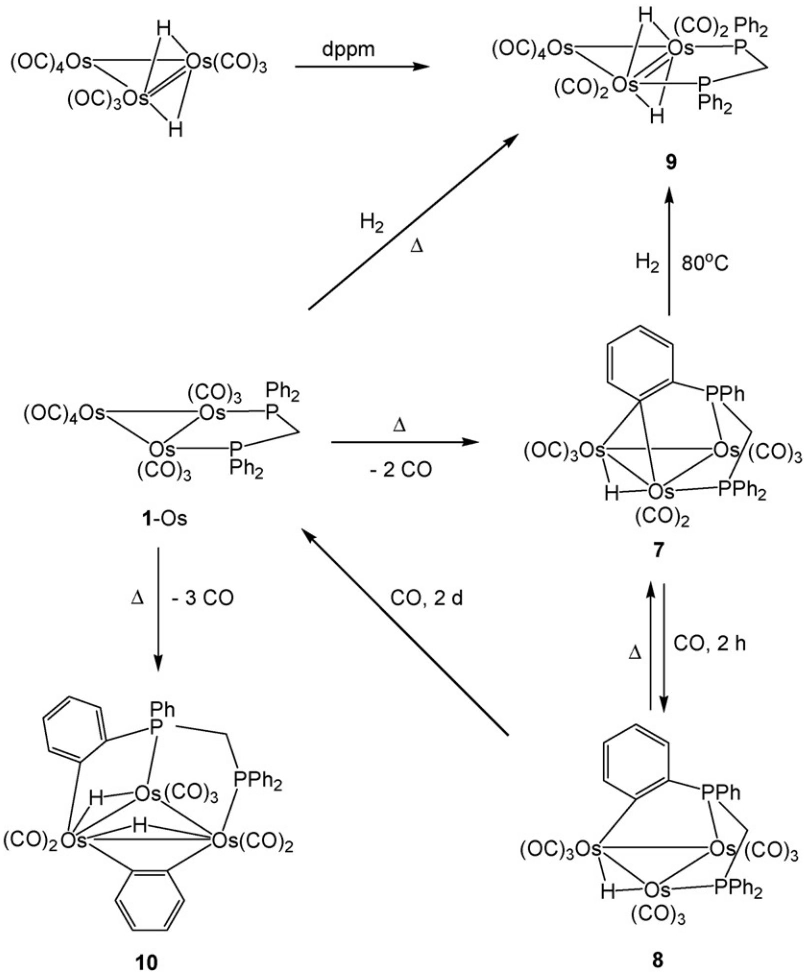


Scheme 5.

phine ligands. Prolonged hydrogenation of **3** results if the isolation of $[Ru_3(CO)_8(PMe_2Ph)(\mu\text{-}H)_2(\mu_3\text{-}PPh)]$ (**4**) in 45% yield, which results from a phosphorus–methylene cleavage of the diphosphine backbone. Two minor products of the thermolysis of **1**-Ru are binuclear **5**–**6** [36] which have also been isolated from the thermolysis of **1**-Ru and benzyl halides [37]. Both result from loss of benzene from the diphosphine but in **5** the backbone phosphorus–methylene bonds remain intact, while in **6** one is cleaved. Further, prolonged heating of **1**-Ru with benzothiophene affords low yields of hexanuclear $[Ru_6(CO)_{13}(\mu\text{-}CO)(\mu_6\text{-}C)(\mu_3\text{-}PhPC_6H_4PPh)]$ and tetranuclear $[Ru_4(CO)_9(\mu\text{-}H)(\mu_4\text{-}C_6H_4)(\mu_3\text{-}Ph_2PCH_2PPh_2)]$ degradation products, both of which have been crystallographically characterized [36]. Overall, these transformations (Scheme 5) represent an impressive series of rearrangements of the diphosphine ligand at the triruthenium centre. Clearly, upon development of the chemistry of **1**-Ru then it is necessary to make sure that reactions take place at lower temperatures than 110 °C, otherwise competing reactivity of **2** (and to a lesser extent **3**) must be considered.

The precise mode of formation of **2** from **1**-Ru is not known, however, it has been proposed to occur *via* initial CO loss and orthometalation to afford an intermediate which then eliminates benzene [34]. Support for this comes from the thermally induced transformation of the analogous osmium cluster **1**-Os [38]. Heating **1**-Os in toluene affords $[Os_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^4\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ (**7**) resulting from loss of two carbonyls and orthometalation of the diphosphine. This is electronically unsaturated and shows a diverse range of reactivity (see later) which includes the facile and reversible carbonylation to afford saturated **8** which in turn adds further CO to regenerate **1**-Os (Scheme 6). A second important transformation is the addition of hydrogen. This affords a further unsaturated cluster **9** [38], which is the dppm-derivative of the well-known unsaturated osmium cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. The same product also results from the hydrogenation of **1**-Os at 85 °C [39,40].

The reversible nature of the orthometalation of a phenyl ring in **7** is very important in the subsequent development of the chemistry of the dppm-2stabilized triosmium centre. Thus, while reactions of **1**-Os with a variety of reagents generally require thermal activation, **7** reacts with the same reagents at room temperature resulting in both addition of the new ligand(s) and reformation of the dppm ligand. Hence, in the development of triosmium dppm chemistry it is often **7** which is the preferred starting material.



Scheme 6.

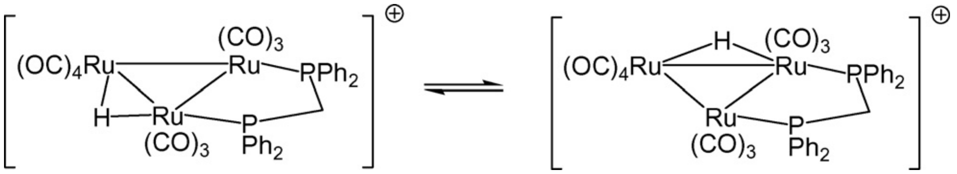
Koridze et al. have reported the isolation of a second reaction product from the thermolysis of **1**-Os in toluene. Thus, $[Os_3(CO)_7(\mu\text{-}H)_2(\mu\text{-}C_6H_4)\{\mu_3\text{-}Ph_2PCH_2PPh(C_6H_4)\}]$ (**10**) was isolated in 30% yield after heating for 10 h in toluene [41]. The cluster contains a benzyne ligand, the origin of which is unclear. Characterization was made on the basis of NMR and X-ray crystallographic studies. The latter suggests that it is a 47-electron cluster and hence should be paramagnetic. This is clearly not the case and from the NMR data given it is not possible to reason why this should be so. It readily protonates to give a trihydride which shows three inequivalent hydride signals, ruling out the possibility that **10** is a trihydride. The color of **10** is variously described as “yellow” and “green” in different sections of the publication throwing up the real possibility that it is actually a mixture.

A true 47-electron cluster is produced upon reduction of **7** [42]. This process is facile (−1.18 V) and the radical nature of the product is confirmed by EPR spectroscopy. The transformation is reversible at low temperatures or rapid scan rates but a chemical transformation occurs under other conditions, the nature of which is not known, but EPR spectra suggest a highly delocalized system.

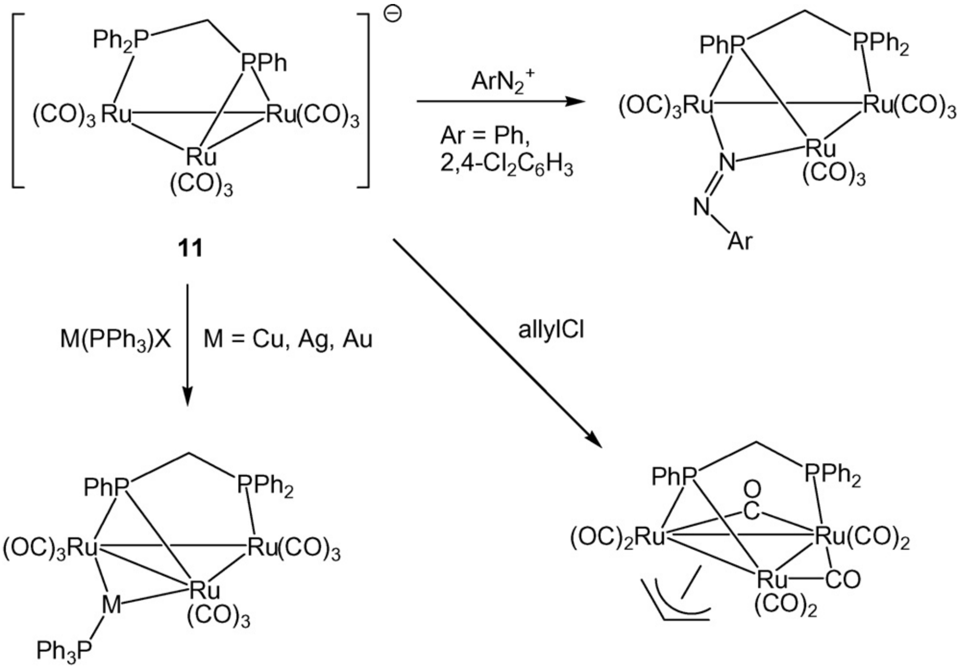
4. Reactivity towards acids and bases

Low valent transition metal clusters are generally prone to protonation across metal–metal bonds and $[M_3(CO)_{10}(\mu\text{-dppm})]$ are no exception to this. Addition of excess CF_3CO_2H to **1**-Os affords $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-dppm})][O_2CCF_3]$ in which the hydride bridges a non-diphosphine supported edge, as characterized by the presence of a doublet resonance at δ −19.45 (J_{PH} 13.6 Hz) [40]. This differs from the behavior of longer chain diphosphine complexes, $Ph_2P(CH_2)_nPPh_2$ (n = 2–4), whereby the proton bridges the diphosphine-supported edge. The latter is expected to be the more basic site, however, the reduced flexibility of the dppm ligand and the resulting relatively high energy barrier required to increase the Os–Os–P angle (which is generally seen upon protonation) may be the reason why the preferred product is that with the hydride bridging a less basic edge. Addition of excess CF_3CO_2H to **1**-Ru similarly affords $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-dppm})][O_2CCF_3]$ characterized by a high field triplet at δ −18.68 (J_{PH} 6.6 Hz) [43]. At first sight the triplet nature suggests protonation across the more basic diphosphine-supported edge but low temperature NMR studies reveal that this is not the case. Hence at −50 °C, the signal becomes a doublet of doublets at δ −18.68 (J_{PH} 17.7, 3.5 Hz) an observation which is consistent with the rapid movement of the hydride from one non-supported edge to the other at room temperature (Scheme 7). Addition of weak bases to both cationic hydrides results in the rapid regeneration of the neutral clusters and neither protonated cluster has been isolated in the solid-state.

The methylene protons of coordinated dppm ligands are known to be relatively acidic, with one being easily removed upon addi-



Scheme 7.



Scheme 8.

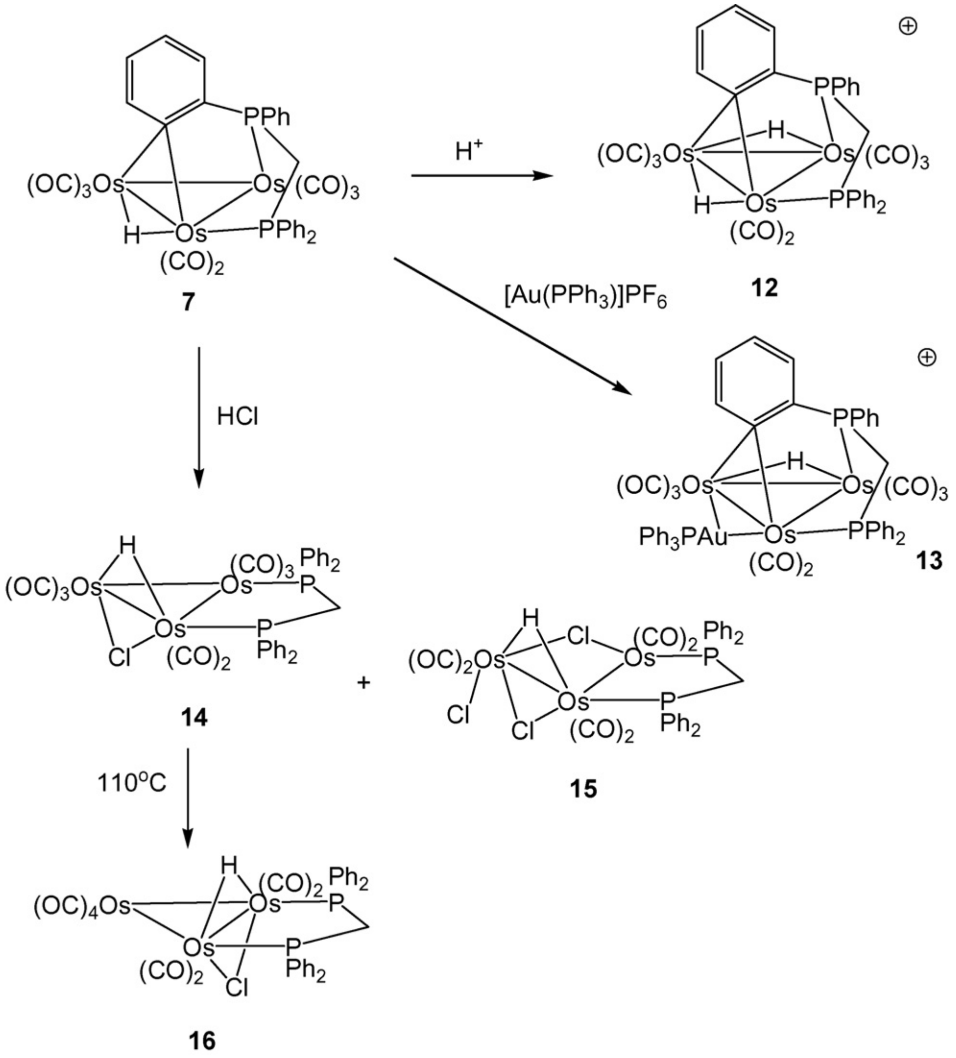
tion of strong bases [7–11], however, a quite different reactivity is observed for **1**-Ru. Hence treating **1**-Ru with potassium selectride, $K[BHBu^{s}_3]$, in thf at room temperature affords $K[Ru_3(CO)_9(\mu_3\text{-}PhPCH_2PPh)]$ (**11**) resulting from both CO loss and dephenylation of the dppm ligand [44]. The precise nature of this transformation remains unknown, but it has been proposed to proceed *via* initial attack of hydride at a carbonyl, the resulting formyl complex losing CO to give $K[Ru_3(CO)_8(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}dppm)]$ which subsequently eliminates benzene. Evidence for the intermediate formation of the latter comes from the observation of a medium intensity absorption at 1665 cm^{-1} in the IR spectrum of the reaction mixture, being similar to that found in $[HRu_3(CO)_{11}]^-$ [44]. Anion **11** displays high reactivity (Scheme 8), protonating readily on work-up to afford **3**, and acting as precursors to aryldiazo [45] and allyl [46] complexes, together with heterometallic clusters upon reaction with $[M(PPh_3)X]$ [44].

A somewhat similar reaction of **1**-Ru with silver trifluoroacetate in CD_2Cl_2 at low temperature resulted in the proposed formation of $[Ru_3(CO)_{10}(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$ on the basis of the $^{31}P\{^1H\}$ NMR spectrum. All attempts to isolate this failed, however, the more basic $[Ru_3(CO)_8(\mu\text{-}dppm)_2]$ reacted similarly to afford crystallographically characterized $[Ru_3(CO)_8(\mu\text{-}dppm)_2(\mu\text{-}AgO_2CCF_3)]$ [47].

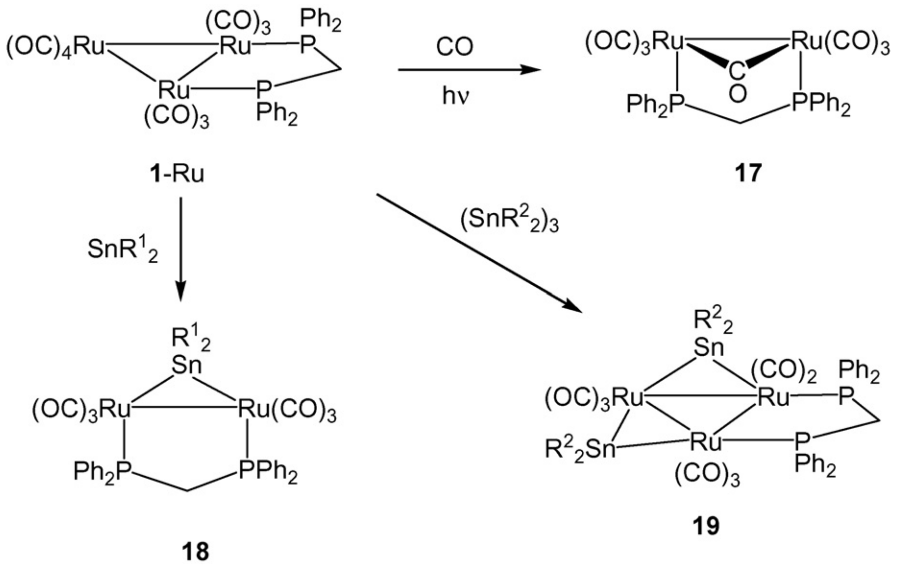
The orthometalated cluster **7** is also readily protonated upon addition of acids with non-coordinating anions to give a cationic dihydride **12** with the orthometalated dppm ligand remaining intact [48,49] (Scheme 9). Addition of $[Au(PPh_3)]PF_6$ affords a related cation **13** with the gold bridging the osmium–osmium vector spanned by the metalated phenyl ligand, while the proton bridges across the diphosphine ligated edge [48]. Addition of acids with coordinating anions leads to neutral products. Thus when HCl gas is bubbled through a dichloromethane solution of **7** an instantaneous reaction takes place to give predominantly $[Os_3(CO)_8(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}dppm)]$ (**14**) but also small amounts of the open 50-electron cluster $[Os_3(CO)_7Cl(\mu\text{-}H)(\mu\text{-}Cl)_2]$ (**15**) [49]. Addition of HBr and CF_3CO_2H to **7** affords products analogous to **14**. Complex **14** also results upon addition of HCl to the lightly stabilized cluster $[Os_3(CO)_9(MeCN)(\mu\text{-}dppm)]$ [50] and at 110 °C it isomerizes to give **16**, in which all three bridging ligands span the same osmium–osmium vector, while in contrast the analogous bromide is stable under these conditions.

5. Reactivity towards two-electron donor ligands

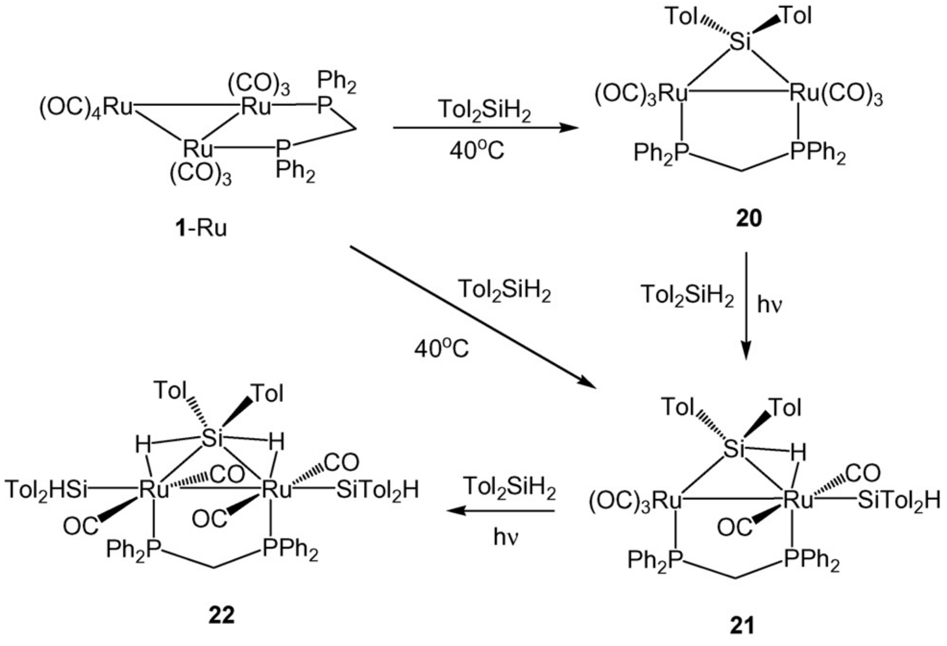
Except for reactions with phosphines (see Section 6) the reactivity of **1** towards simple two-electron donor ligands has not been widely explored. Photolysis ($\lambda > 280$ nm) of **1**-Ru in pentane under a CO atmosphere leads to the formation of $[Ru_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**17**) (82% yield) and $Ru(CO)_5$ resulting from cleavage of two ruthenium–ruthenium bonds [51]. Likewise, reaction with the tin (II) compound, $SnR^1{}_2$ ($R^1 = CH(SiMe_3)_2$) gives the related diruthenium complex $[Ru_2(CO)_6(\mu\text{-}SnR^1{}_2)(\mu\text{-}dppm)]$ (**18**). In contrast, trimeric $(SnR^2{}_2)_3$ ($R^2 = 2,4,6\text{-}{}^iPr_3C_6H_2$) affords only $[Ru_3(CO)_8(\mu\text{-}SnR^2{}_2)_2(\mu\text{-}dppm)]$ (**19**) [52]. Complex **18** has been crystallographically characterized and the tin atom lies in the plane of the Ru_2P_2 unit. This is in contrast to $[Ru_2(CO)_6(\mu\text{-}CO)(\mu\text{-}$



Scheme 9.



Scheme 10.

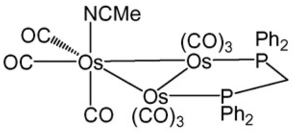


Scheme 11.

dppm)] in which (based on the structure of the analogous iron complex) the bridging carbonyl lies perpendicular (Scheme 10). While pentanuclear **19** is diamagnetic, the related osmium complex $[Os_3(CO)_8(\mu\text{-}SnR_2)_2(\mu\text{-dppm})]$ $[R = CH(SiMe_3)_2]$, formed from the reaction of **7** with two equivalents of SnR_2 is paramagnetic [53]. This is a very unusual situation where the cluster as a whole is electron-precise (48-electrons) but individual metal atoms are not. An ESR signal was noted and a magnetic moment of $2.4\mu_B$ measured using the Evans method.

Reaction of **1**-Ru with Tol_2SiH_2 (Tol = *p*-MeC_6H_4) at 40 °C affords a mixture of dinuclear products, $[Ru_2(CO)_6(\mu\text{-}SiTol_2)(\mu\text{-dppm})]$ (**20**) and $[Ru_2(CO)_5(SiHTol_2)(\mu\text{-}SiTol_2)(\mu\text{-}H)(\mu\text{-dppm})]$ (**21**). Under thermal conditions, **20** does not react with further Tol_2SiH_2 to give **21**, however, when the same reaction is carried out photochemically **21** is formed as an intermediate en-route to $[Ru_2(CO)_4(SiHTol_2)_2(\mu\text{-}SiTol_2)(\mu\text{-}H)_2(\mu\text{-dppm})]$ (**22**) [54] (Scheme 11). In all three complexes, the silicon lies in the Ru_2P_2 plane and in **21** and **22** the hydrides bridge ruthenium–silicon vectors appearing at δ −8.87 (d, J_{PH} 34.2 Hz) and −8.84 (m, J_{PH} 31.0 Hz) in **21** and **22**, respectively.

Replacement of a metal-bound carbonyl by acetonitrile upon oxidation of the cluster by Me_3NO is a common method for preparing activated ruthenium and osmium clusters. Given this, it is somewhat surprisingly that $[Ru_3(CO)_9(MeCN)(\mu\text{-dppm})]$ appears to be unknown. The osmium analogue is, however, readily prepared upon addition of Me_3NO to an acetonitrile solution [50]. IR spectra indicate that the reaction is both immediate and quantitative but attempts to isolate $[Os_3(CO)_9(MeCN)(\mu\text{-dppm})]$ (**23**) led only to extensive decomposition. It can, however, be used *in situ* as a precursor to a range of other substituted products. For example, addition of Bu^tNC affords $[Os_3(CO)_9(Bu^tNC)(\mu\text{-dppm})]$ in good yield. In both of these complexes, on the basis of spectroscopic data, the new substituent is believed to occupy an axial site on the non-phosphorus-coordinated osmium atom. This is significantly different from the equatorial substitution of all phosphine and phosphite ligands (see below) and may result due to steric effects; the shorter osmium–carbon versus osmium–phosphorus bonds not allowing relief of the adverse steric interactions with the diphosphine when placed in an equatorial site. The only product isolated upon thermolysis of **1**-Ru and an excess of CyNC is the open cluster **24**. This results from addition of three equivalents of isonitrile and also cleavage of one of the phosphorus–phenyl bonds thus increasing the valence electron count to 50. Two of the CyNC ligands bind in the expected terminal fashion, while the third bridges all three metal atoms acting as a net four-electron donor ligand [55].



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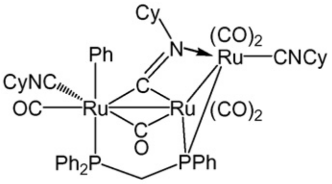

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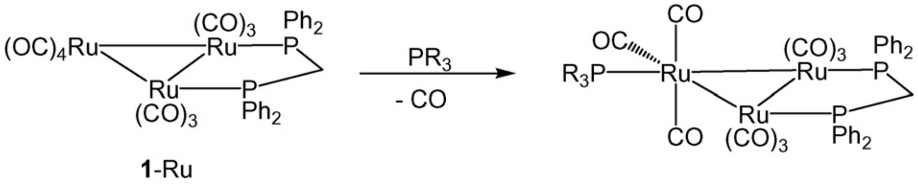
6. Reactivity towards phosphorus donor ligands

The reactivity of **1**-Ru towards simple phosphines has been extensively studied, most reacting cleanly and selectively in a slow reaction (*ca.* 24–36 h) at room temperature to give $[Ru_3(CO)_9(PR_3)(\mu\text{-dppm})]$ (Scheme 12). Reactions can be accelerated by heating and also upon addition of Me_3NO [56–59]. In all cases the new phosphine is attached to the previously unsubstituted ruthenium atom and lies in the equatorial plane. Koutsantonis and co-workers have characterized a number of these adducts by X-ray crystallography comparing them with the structure of **1**-Ru [58]. All contain two short and one relatively long ruthenium–ruthenium vectors, the latter invariably lying adjacent to the introduced phosphine. The difference between these bond lengths appears to be correlated with the steric encumbrance of the latter, with larger ligands inducing the greatest lengthening. The facile nature of the substitution process has been attributed to the relief of steric congestion between the equatorial carbonyls on the unique ruthenium atom and the bulky diphosphine, the longer ruthenium–phosphorus bonds allowing this to be partially alleviated. **1**-Ru also reacts with phosphites [59,60] and $SbPh_3$ [61] to give products in which the new ligand occupies an equatorial site on the previously unsubstituted ruthenium atom.



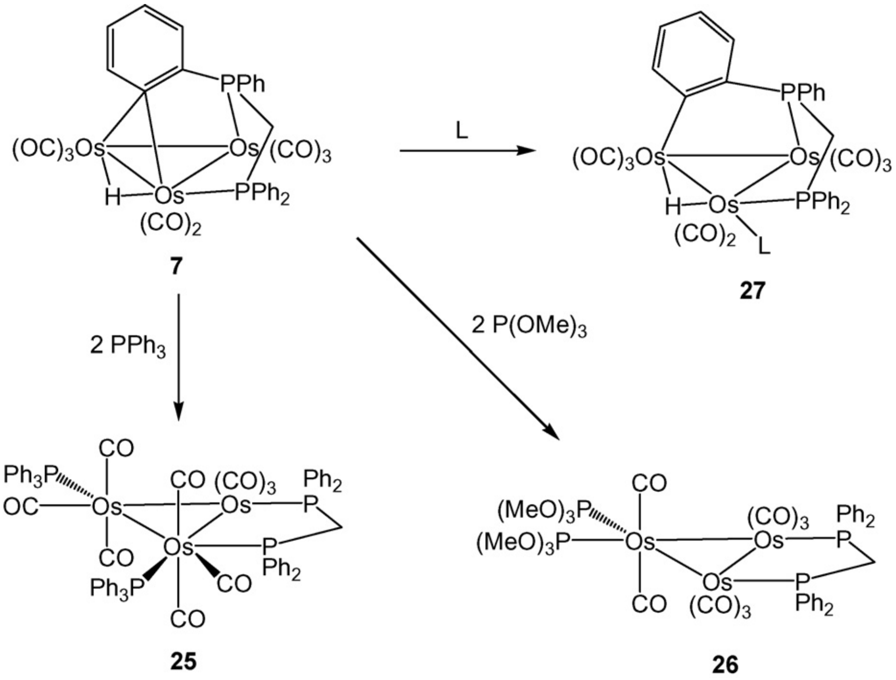
Scheme 12.

The reactivity of **1**-Os towards simple phosphines and phosphites has been less widely studied [50]. Addition of PPh_3 and $P(OMe)_3$ to the acetonitrile adduct **23** affords simple phosphorus-substituted complexes, and here the substituted also occupies an equatorial site. The NMR spectra of $[Os_3(CO)_9(PPh_3)(\mu\text{-dppm})]$ are temperature dependent, the fluxionality being associated with the movement of the monodentate phosphine between equatorial sites.

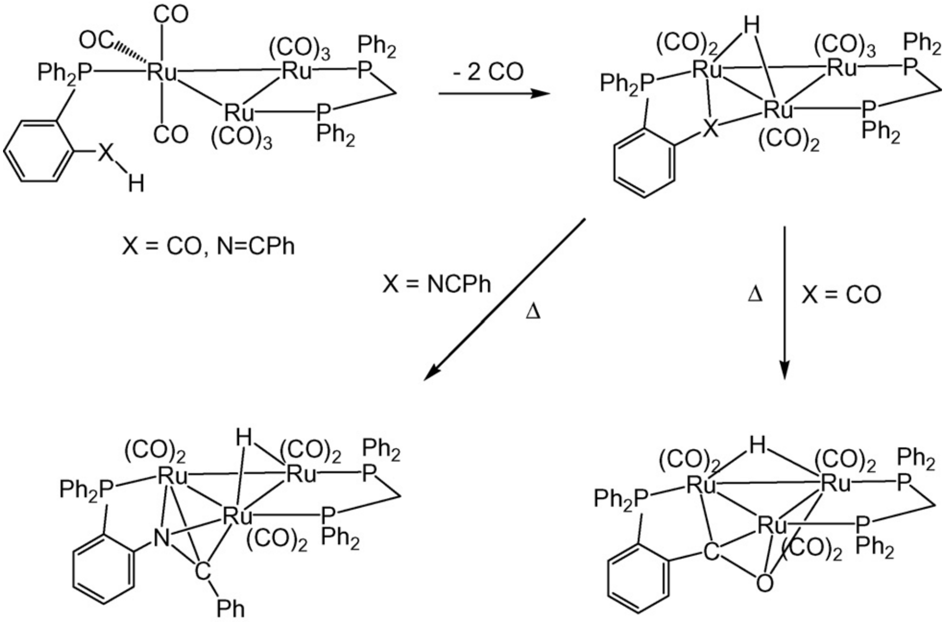
The unsaturated orthometalated cluster **7** acts as a precursor to complexes of the type $[Os_3(CO)_8L_2(\mu\text{-dppm})]$ [62,63]. Thus reaction with excess PPh_3 or $P(OMe_3)$ at room temperature affords moderate yields of $[Os_3(CO)_8(PPh_3)_2(\mu\text{-dppm})]$ (**25**) and $[Os_3(CO)_8\{P(OMe)_3\}_2(\mu\text{-dppm})]$ (**26**), respectively, together with the monosubstituted orthometalated complexes (**27**) (Scheme 13). The latter do not react further with two-electron donor ligands suggesting that formation of the disubstituted dppm complexes proceeds *via* an unsaturated $[Os_3(CO)_8L(\mu\text{-dppm})]$ [L = PPh_3 or $P(OMe_3)$]intermediate, most likely containing one bridging carbonyl. Complex **25** comprises a single isomeric form, shown by X-ray crystallography to have one phosphine attached to the unique osmium atom and a second to one of the dppm-coordinated atoms. For phosphite derivative **26**, this is a minor form, the major isomer having both phosphites coordinated at the non-dppm coordinated osmium atom. In all cases the phosphorus ligands occupy equatorial coordination sites.

Poë and co-workers [64,65] have studied the kinetics of phosphine and phosphite substitution of **1**-Ru. The diphosphine is found to be less labilizing than two PPh_3 groups in terms of rate constants but more labilizing in terms of $\Delta H^{\#}$. For relatively weak nucleophiles (PPh_3, $AsPh_3$, PCy_3, $P(OEt)_3$) and at low nucleophile concentrations, the first order rate constants and retardation by CO are characteristic of a simple CO dissociative mechanism [65]. This supports the idea that there is strain within the molecule caused by the small bite-angle diphosphine which might be removed upon CO loss. However, an alternative whereby a metal–metal bond is cleaved in the transition state cannot be totally ruled out. With more nucleophilic phosphorus-donor ligands, kinetic measurements reveal an associative term [64].

Bruce and co-workers have detailed the reactivity of **1**-Ru towards a range of functional phosphines including 2-substituted triphenylphosphines and keto-phosphines [66,67]. Initial reaction generates the expected equatorially substituted products but secondary transformations then occur resulting in oxidative-addition of the substituent to the trinuclear core. This is exemplified by $Ph_2P(2\text{-}HCOC_6H_4)$ and $Ph_2P(2\text{-}PhNCC_6H_4)$]; oxidative-addition of the X–H bond resulting in loss of two carbonyls and formation of new hydride complexes, while heating in toluene leads to the facile loss of one further carbonyl and coordination of the previously uncoordinated atom (C or N) (Scheme 14).

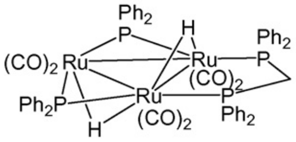


Scheme 13.



Scheme 14.

Kabir and co-workers have detailed the reactivity of **1**-Ru towards diphenylphosphine [68,69]. Heating **1**-Ru and Ph_2PH in heptane for 1.5 h leads to the formation of four new products **28**–**31**. All retain the trinuclear framework and in **28**–**29** the integrity of the diphosphine is also maintained. Cluster **28** results from the oxidative-addition of two equivalents of phosphine to the trinuclear cluster, while **29** contains two phosphido and one phosphinidene ligand resulting from cleavage of a phosphorus–carbon bond of one equivalent of PPh_2H. Both **30**–**31** result from addition of two equivalents of Ph_2PH together with phosphorus–carbon bond cleavage of the diphosphine; phosphorus–methylene and phosphorus–aryl bonds being cleaved, respectively. While it is not easy to predict the route *via* which each of these products has been formed, **31** can be independently synthesized upon addition of Ph_2PH to **3** a thermolysis product of **1**-Ru alone. Other products are likely to proceed *via* initial formation of $[Ru_3(CO)_9(PPh_2H)(\mu\text{-dppm})]$, but the latter has not been isolated or identified spectroscopically. The key driving force for these reactions is probably the formation of the metal–hydride bonds.



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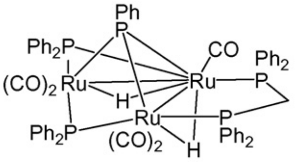

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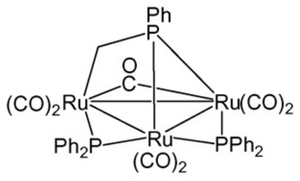

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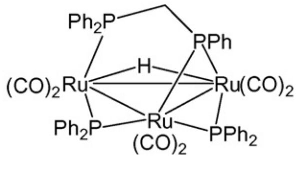

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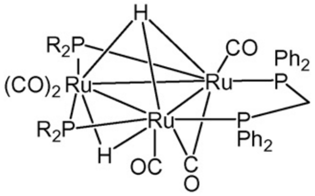
With **1**-Os, the simple adduct $[Os_3(CO)_9(PPh_2H)(\mu\text{-dppm})]$ is formed in high yields from the reaction with Ph_2PH at 110 °C [63]. A second minor product of this reaction is $[HOs_3(CO)_7(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ (**33**), presumed to be formed *via* the intermediate $[Os_3(CO)_8(PPh_2H)_2(\mu\text{-dppm})]$ (**32**). Indeed, this is the case, equatorially disubstituted **32** being prepared from the addition of two equivalent of PPh_2H to **7** (see above) and heating at 110 °C affords **33** together with two further trinuclear products **34**–**35** (Scheme 15).

Böttcher et al. have reported the reactions of **1**-Ru with secondary phosphines, R_2PH ($R = Bu^t$, Ad, Cy) [70]. All initially afford the nonacarbonyl complexes $[Ru_3(CO)_9(PR_2H)(\mu\text{-dppm})]$ but on heating to 100 °C in the presence of further phosphine they rearrange to afford phosphido-bridged complexes $[Ru_3(CO)_4(\mu\text{-CO})(\mu\text{-H})(\mu_3\text{-H})(\mu\text{-PR}_2)_2(\mu\text{-dppm})]$ (**36**) ($R = Bu^t$, Ad) and $[Ru_3(CO)_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$ (**37**). While the latter are electron-precise, **36** are electron-deficient 46-electron clusters. Only the reactivity of $Bu^t{}_2PH$ with **1**-Os has been reported [71]; prolonged heating in diglyme affording unsaturated $[Os_3(CO)_5(\mu\text{-H})(\mu_3\text{-H})(\mu\text{-PBu}^t{}_2)_2(\mu\text{-dppm})]$ (**38**) in 50% yield, which while is related to **36**, but does not contain a bridging carbonyl.



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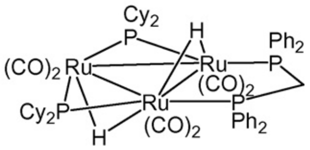

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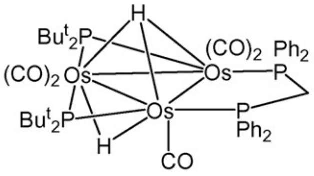

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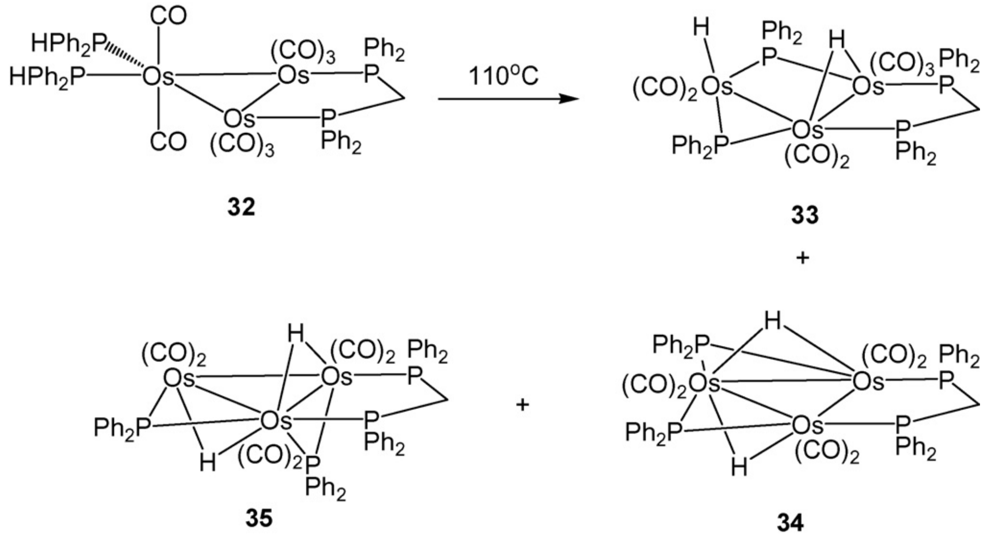
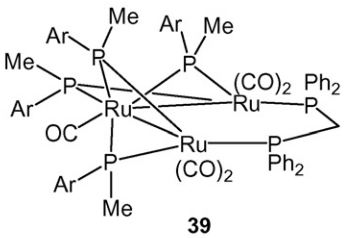
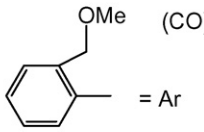
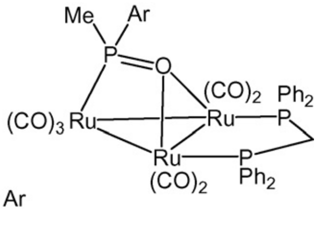
The major product from reaction of **1**-Ru with the functionalised secondary phosphine, MePHAr ($Ar = C_6H_4\text{-o-}CH_2OMe$), varies from reaction to reaction, probably due to presence of differing amounts of the phosphine oxide [72]. Thus in one instance the multi-phosphine addition product **39** was isolated, while in another the major product was the oxide **40**.



Scheme 15.







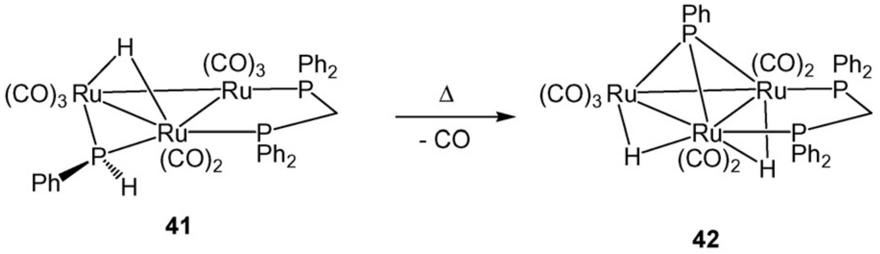
Thermolysis of **1**-Ru and the primary phosphine, $PhPH_2$, in thf initially affords the phosphido-bridge complex $[Ru_3(CO)_8(\mu\text{-}PPhH)(\mu\text{-}H)(\mu\text{-}dppm)]$ (**41**) which rearranges smoothly upon further heating to phosphinidene $[Ru_3(CO)_7(\mu_3\text{-}PPh)(\mu\text{-}H)_2(\mu\text{-}dppm)]$ (**42**) (Scheme 16) [73]. The reactivity of **1**-Os towards primary phosphines has not been assessed but reactions of both $PhPH_2$ and $CyPH_2$ with the electron-deficient orthometalated cluster **7** have been reported [74]. The reactivity observed is exactly analogous to that seen for **1**-Ru, with both affording the phosphido-bridged complexes $[Os_3(CO)_8(\mu\text{-}RPH)(\mu\text{-}H)(\mu\text{-}dppm)]$ at room temperature which rearrange to phosphinidene complexes $[Ru_3(CO)_7(\mu_3\text{-}PCy)(\mu\text{-}H)_2(\mu\text{-}dppm)]$ upon heating at 128 °C.

Reaction of **1**-Ru and $PhPCl_2$ follows a quite different course to that with $PhPH_2$ with $[Ru_3(CO)_8(\mu\text{-}H)(\mu\text{-}Cl)_2(\mu\text{-}dppm)]$ being the only isolated product (10% yield). The same complex is also formed upon heating **1**-Ru in CCl_4 under a hydrogen atmosphere [75].

Reactions of **1** with diphosphines have not been so extensively investigated. Early studies centered on the synthesis of $[Ru_3(CO)_8(\mu\text{-}dppm)_2]$ [28,76] and $[Os_3(CO)_8(\mu\text{-}dppm)_2]$ [77] (Scheme 17). Both can be prepared directly from the parent dodecacarbonyls, in reactions that proceeds *via* **1**. In the case of **1**-Os, the intermediate $[Os_3(CO)_9(\eta^1\text{-}dppm)(\mu\text{-}dppm)]$ has been isolated and crystallographically characterized, all three phosphorus atoms occupying equatorial sites [28]. Both $[M_3(CO)_8(\mu\text{-}dppm)_2]$ have been crystallographically characterized [77,78], with all four phosphorus atoms occupying equatorial sites. Smith and co-workers have also reported the synthesis of $[Ru_3(CO)_6(\mu\text{-}dppm)_3]$ but no crystallographic study was carried out [28]. Poë and co-workers have followed the reaction of **1**-Ru and dppm by UV–vis spectroscopy. The rate of formation of $[Ru_3(CO)_9(\eta^1\text{-}dppm)(\mu\text{-}dppm)]$ was found to independent upon [dppm] and retarded by addition of CO, suggesting that this step proceeds *via* reversible CO dissociation. The coordination of the second phosphorus atom takes place in a slower step and involves two paths of approximately equal importance, neither of which is dependent upon [dppm]. One is inhibited by added CO while the second is unaffected. This latter path has parameters characteristic of a dissociative mechanism and formation of the chelate follows rapidly. The former is less clearly defined but may involve reversible loss of CO followed by transfer of the unsaturation from one metal atom to another [31].

1-Ru reacts with bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)ferrocene (dppf) to afford clusters in which the two triruthenium units are linked *via* the diphosphine [59]. The unsaturated diphosphine, bis(diphenylphosphino)acetylene (dppa) also forms a complex of this type, $[\{Ru_3(CO)_9(\mu\text{-}dppm)\}_2(\eta^1,\eta^1\text{-}dppa)]$ along with trinuclear $[Ru_3(CO)_9(\eta^1\text{-}dppa)(\mu\text{-}dppm)]$ (**43**) [79–81]. Heating either of these dppa complexes affords a mixture of trinuclear clusters with supporting phosphorus-containing ligands resulting from a series of phosphorus–carbon bond cleavage reactions. For example, thermolysis of **43** affords **44** as the major product resulting from phosphorus–carbon bond activation of both dppm and dppa ligands (Scheme 18) [79]. Three equivalents of **43** have also been reacted with $[Ru_3(CO)_9(MeCN)_3]$ to afford low yields (6%) of $[Ru_3(CO)_9\{Ru_3(CO)_9(\mu\text{-}dppm)_2(\eta^1,\eta^1\text{-}dppa)\}_3]$ [81].

Reaction of **1**-Os with dppf affords $[Os_3(CO)_9(\eta^1\text{-}dppf)(\mu\text{-}dppm)]$ which at 110 °C eliminates a further carbonyl and gives $[Os_3(CO)_8(\eta^2\text{-}dppf)(\mu\text{-}dppm)]$ [82]. Similar behavior is observed for **1**-Ru and 1,8-bis(diphenylphosphino)naphthalene



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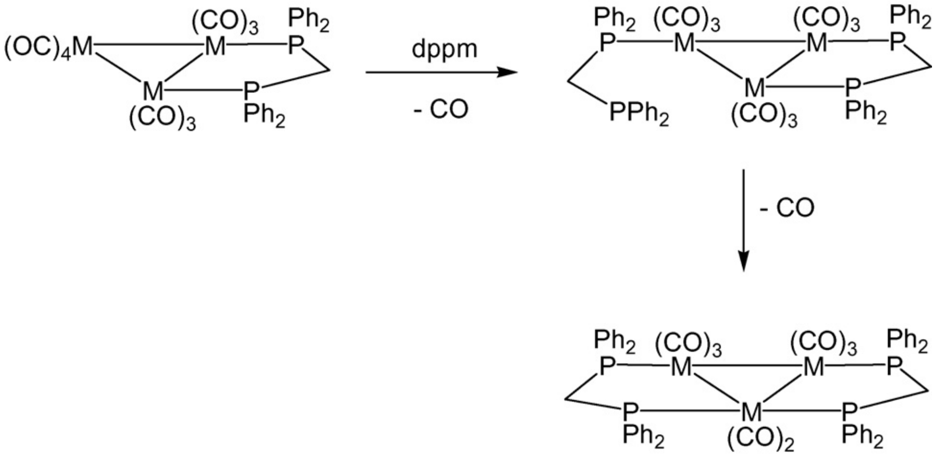
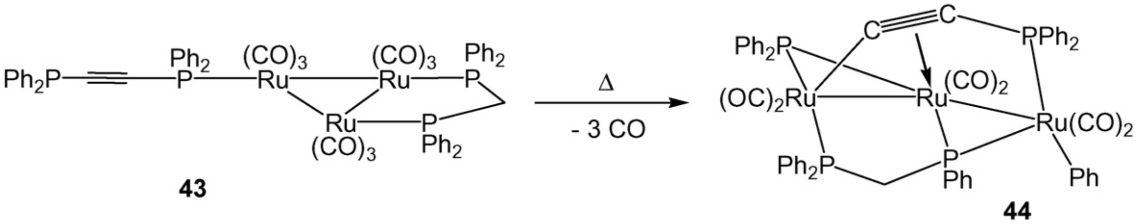
Scheme 16.



Scheme 17.



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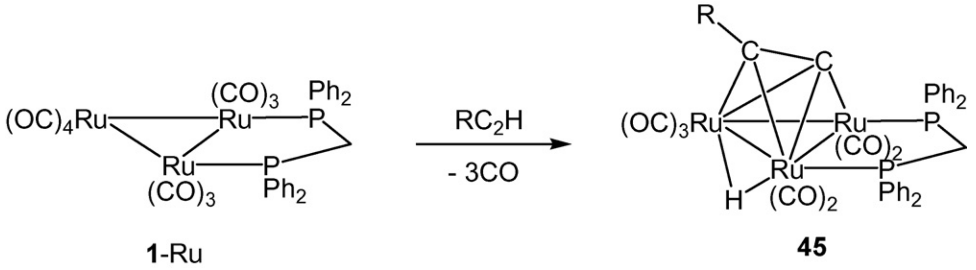
Scheme 18.

(dppn), initial formation of [$Ru_3(CO)_9(\eta^1$-dppn)(μ-dppm)] leading to the low yield generation of [$Ru_3(CO)_8(\eta^2$-dppn)(μ-dppm)] under more forcing conditions [83]. The structures of these chelate complexes are as expected with all four phosphorus atoms occupying equatorial sites. With the related diphosphine, 1,8-bis(dimethylphosphino)naphthalene (dmpn), the major product upon reaction with **1**-Ru is a monosubstituted derivative in which one PMe_2 group has been replaced by a proton [84].

7. Reactivity towards alkynes

Reactions of both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with alkynes have been extensively studied and numerous exotic products have been isolated. While the reactivity of **1**-Ru towards alkynes has been quite thoroughly studied, surprisingly that of **1**-Os remains virtually unexplored. Reactions of **1**-Ru and alkynes depend critically on the nature of the alkyne. With primary alkynes, RC_2H, the initial product is almost invariably the alkynyl cluster [$Ru_3(CO)_7(\mu$-H)(μ_3-C_2R)(μ-dppm)] (**45**) [85–88] (Scheme 19). The alkynyl and hydride ligands in **45** are fluxional on the NMR scale moving to equivalence the two phosphorus-coordinated ruthenium atoms. While the trinuclear framework is maintained, addition of iodine (R = Ph) leads to rapid elimination of one metal atom to afford binuclear [$Ru_2(CO)_4(\mu$-I)(μ-C_2Ph)(μ-dppm)] [85]. From the reaction with $HC\equiv CCO_2Me$ [89] a μ_3-alkyne complex (see **49** Scheme 21) is initially observed but this rearranges to **45** (R = CO_2Me), upon heating (although in only modest yields). Reactions with primary alkynes are not, however, always clean, heating **1**-Ru with $HC\equiv C$-CPh_2OH leads to the generation of at least 10 products (by tlc) [87].

The reaction of **1**-Ru with ethyne either in boiling THF or at room temperature in the presence of $Me_3NO{\cdot}2H_2O$ affords a mixture of products **46**–**48** resulting from the addition of three or four alkyne ligands to the trinuclear core [90] (Scheme 20). No complexes were isolated with one or two alkynes although such

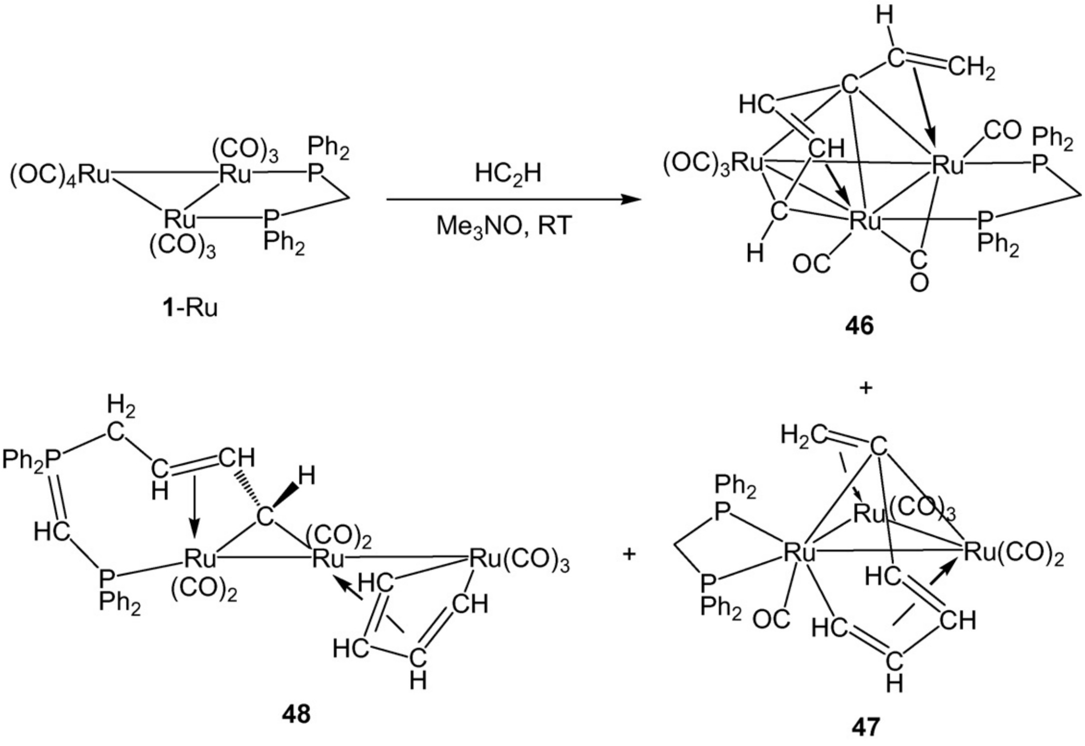


Scheme 19.

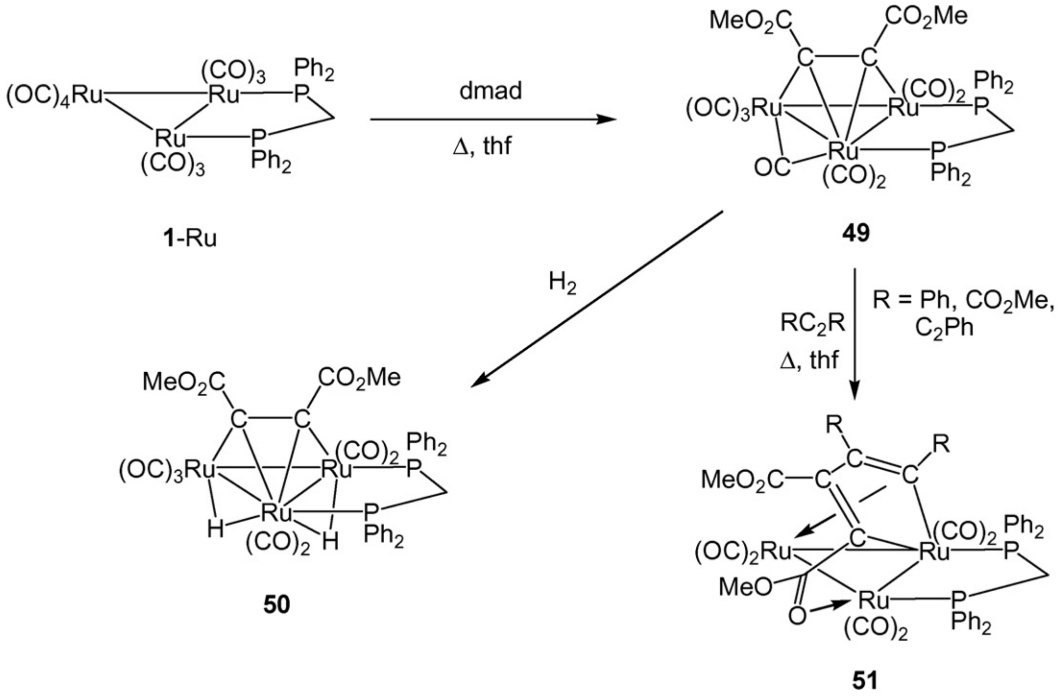
species may be intermediates en-route to the final products. Clusters **46** and **47** are isomers and differ in the coordination of both the diphosphine and hydrocarbyl ligands. In **46** the initial diphosphine bridging mode is maintained, while in **47** it has switched to chelate a single ruthenium atom. The hydrocarbyl ligands also differ although both contain one methylene and one naked carbon atom. The third product, **48**, consists of an open array of three ruthenium atoms and results from addition of four molecules of ethyne. Here the diphosphine bridges between ruthenium and carbon atoms. Hence, while all three products maintain the triruthenium framework the coordination of the diphosphine differs in each. As far as we are aware this is a unique feature of the chemistry of **1**-Ru.

The reactivity of **1**-Ru towards disubstituted alkynes appears to be limited to that with dimethylacetylene dicarboxylate (dmad) [91]. Heating the two in thf for 1 h leads to the formation of a number of products, the major component of which is **49** (Scheme 21). This in turn reacts with hydrogen to afford the dihydride **50** and further dmad to give **51** (R = CO_2Me) which contains two equivalents of alkyne. Likewise, PhC≡CPh, PhC≡C—C≡CPh and $HC{\equiv}CCO_2Me$ also react with **49** to afford analogues of **51** [89]. All of the products so far mentioned from the reactions of **1**-Ru with alkynes are trinuclear, but from the reaction with dmad low yields (1–2%) of two tetranuclear mono-alkyne complexes have also been isolated and crystallographically characterized [91]. The reduced reactivity of secondary as compared to primary alkynes probably relates to the inability of the former to easily afford metal–hydride complexes.

The reactivity of **1**-Os towards alkynes appears not to have been reported but that of unsaturated **7** has been probed. Smith and co-workers [92,93] have shown that a range of disubstituted alkynes add to **7** to afford unsaturated 46-electron clusters **52** in which the alkyne adopts a perpendicular μ_3-η^2-⊥ binding mode rather than the more common μ_3-η^2-∥ mode. The latter can be achieved, however, upon addition of CO to afford **53** or upon two-electron reduction, while hydrogen adds readily to **52** to afford dihydrides **54** (Scheme 22). Analogous chemistry has been shown to occur at



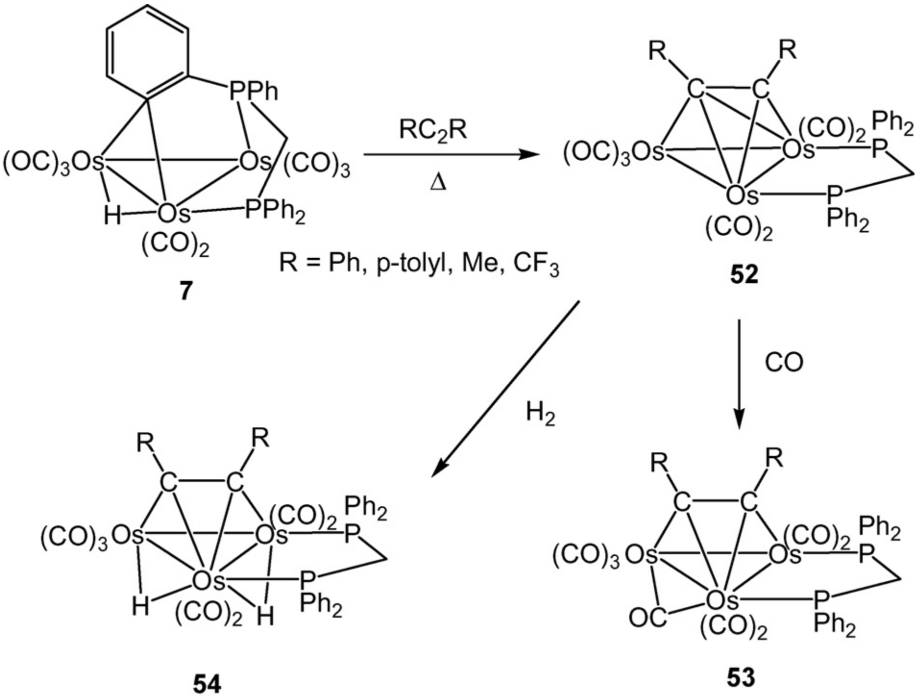
Scheme 20.



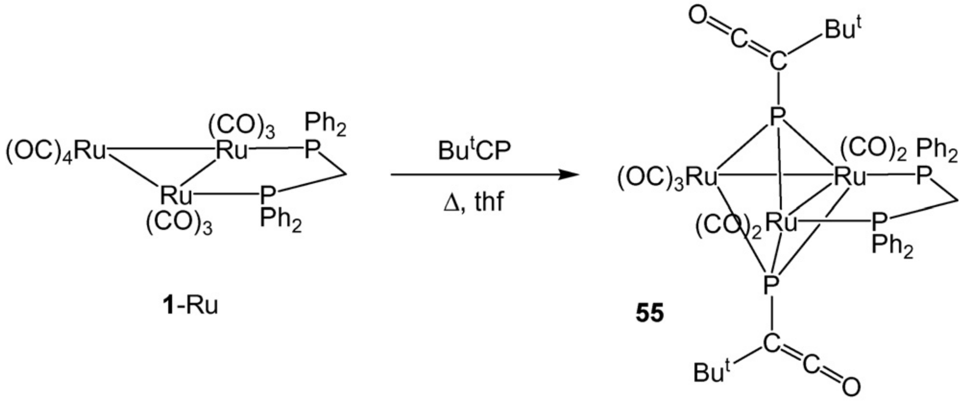
Scheme 21.

the triruthenium centre, the unsaturated cluster $[Ru_3(CO)_7(\mu_3\text{-}PhC_2Ph)(\mu\text{-dppm})]$ being formed upon addition of dppm to $[Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}Cl)][PPN]$ [94]. Neither reactions of **1**-Os nor **7** appear to have been studied with ethyne itself or primary alkynes.

Koutsantonis and co-workers have reported that **1**-Ru reacts with an excess of the phospha-alkyne, $Bu^tC{\equiv}P$, to the give bis(phosphinidene) cluster **55** [95] (Scheme 23). No further products were isolated and hence the mode of formation of **55** remains unknown.



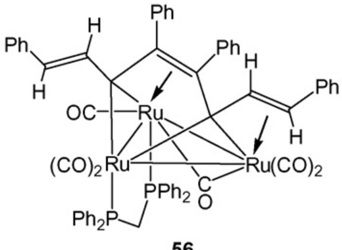
Scheme 22.



Scheme 23.

8. Reactivity towards eneynes and diynes

Koridze et al. have shown that **1**-Ru reacts with the eneynes, $RCH{=}CH{-}C{\equiv}CR$ (R = Ph, ferrocenyl), at 55 °C in thf to give a bewildering array of strange products **56**–**60** all characterized (R = Ph) on the basis of X-ray crystallographic studies [96–98].



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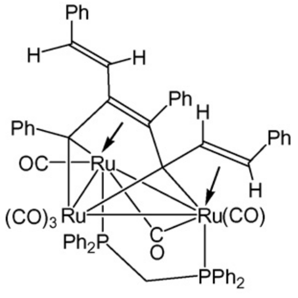

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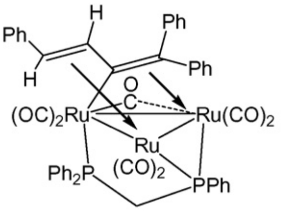

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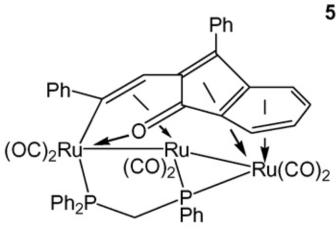

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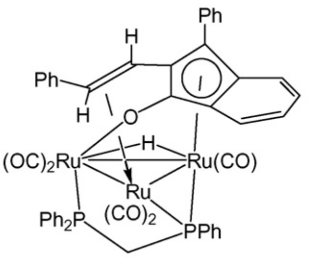


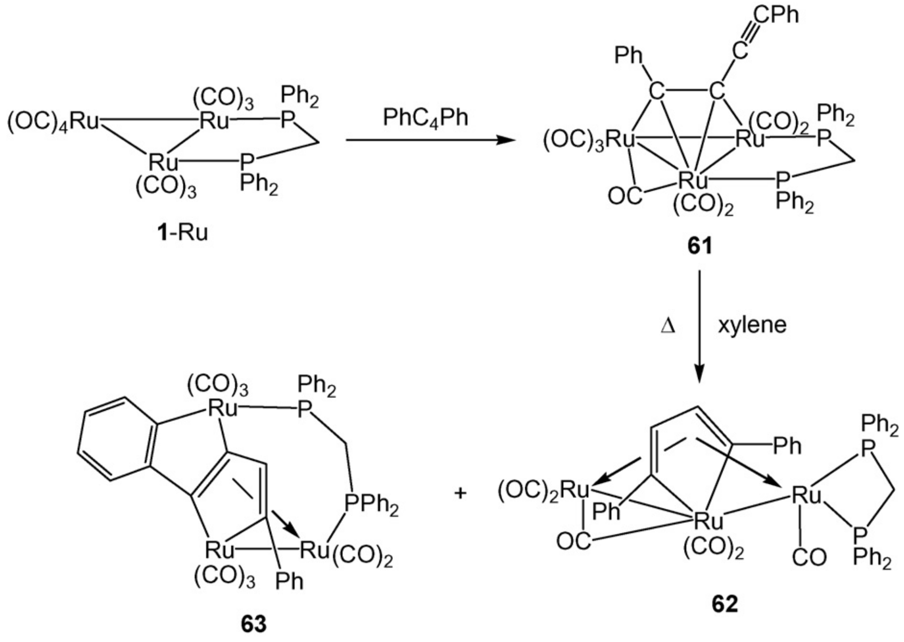
60

Isomers **56** and **57** are low yielding products in which the diphosphine remains intact. They result from the coupling of two eneynes and differ with respect to the relative orientations of the diphosphine and hydrocarbyl ligands, and also the position of the free alkenyl moiety in the latter. The other three products all contain a dephenylated diphosphine. The indenone complex **59** is the major product after short heating times (3 h) and results from the coupling of an eneyne, CO and the cleaved phenyl group. The trinuclear core is open and thus the hydrocarbyl ligand donates a total of 9-electrons in order to satisfy the EAN of 50-electrons. Cluster **60** is closely related to **59** but contains a closed triangle of ruthenium atoms and a bridging hydride ligand. The alkenyl complex **58** results from the coupling of the eneyne and the cleaved phenyl group. The precise mode of formation of these products remains unknown; however, heating a thf solution of **59** affords **58** in moderate yields suggesting that all three dephenylated products are interrelated and may be formed *via* a single pathway.

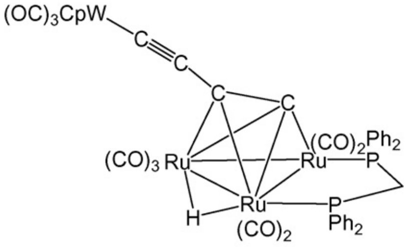
Reactions of **1**-Ru with a number of diynes has been carried out [88,99] with $PhC{\equiv}C{-}C{\equiv}CPh$ being representative [99]. Initial reaction at room temperature in the presence of Me_3NO affords the alkyne complex **61** as the major product, together with smaller amounts of what is believed to be a diyne-coupled product. Cluster **61** is fairly stable but rearranges upon heating in xylene to give a number of products, two of which **62** and **63** have been crystallographically characterized (Scheme 24). The former is notable since the diphosphine chelates a single metal centre, while the latter results from the metalation of one of the phenyl groups of the diyne.

9. Reactivity towards metal–alkynyl and diynyl complexes

As seen above, **1**-Ru is reactive towards carbon–carbon triple bonds. This reactivity extends into the domain of metal–alkynyl and metal–diynyl complexes as first demonstrated by Bruce et al. [100,101]. Thus, reaction of **1**-Ru and $CpW(CO)_3C{\equiv}C{-}C{\equiv}C{-}H$ results in the facile oxidative-addition of the carbon–hydrogen bond to give **64** in high yield. It exists as a mixture of isomers being related by the well-known “windshield wiper” fluxionality of the metal-bound alkynyl group. This behavior is analogous to that previously noted for related alkynyl complexes **45**. Related chemistry has also been carried out with *cis*-$PtL_2(C{\equiv}C{-}C{\equiv}C{-}H)_2$ (L = PEt_3, L_2 = dppe, dppp) and in each case only one of the diynyl ligands adds to the triruthenium centre [102]. Low and co-workers have recently demonstrated similar reactivity with a range of gold–phosphine alkynyl complexes such as $Ph_3P{-}Au{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}C_6H_4X$ which oxidatively add the gold-carbon bond to the cluster to yield heterometallic clusters **65** [103,104]. Developing this scheme further, Bruce has added two equivalents of **1**-Ru to $Tol_3P{-}Au{-}C{\equiv}C{-}C{\equiv}C{-}H$ to give **66** in which two triruthenium units are linked *via* a C_4 ligand [105].



Scheme 24.



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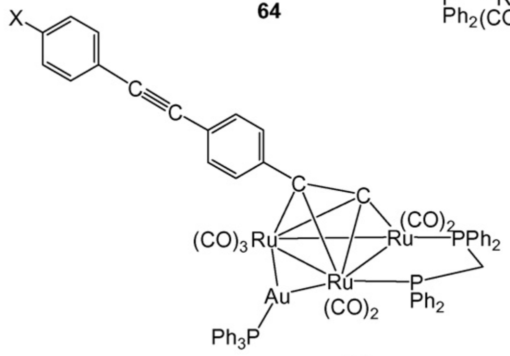

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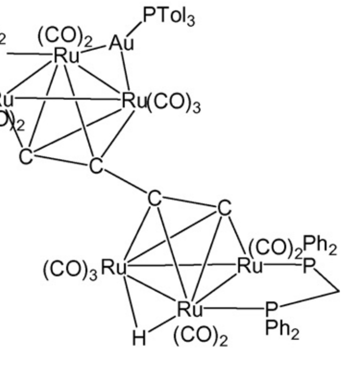
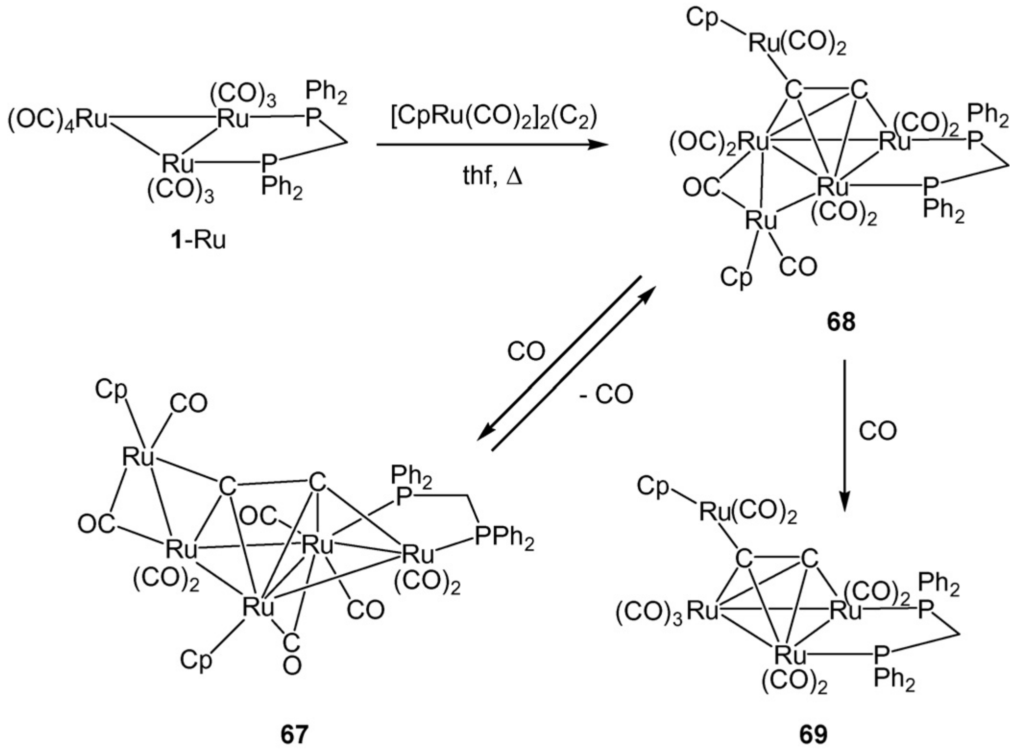


66

Closely related to this work, Kountsantonis and co-workers have reported the high yield synthesis of pentaruthenium **67** upon heating **1**-Ru and the ethyne-1,2-diyl complex [$\{CpRu(CO)_2\}_2C{\equiv}C$] in thf, the analogous methylcyclopentadienyl complex reacting in the same way [106,107]. The cluster contains an unusual spiked-butterfly framework of ruthenium atoms which is held together by the C_2 unit. When the reaction was carried out on a large scale, two further products were isolated, one of which was the CO addition product **68**, shown in a separate reaction to lose CO to give **67** [107]. This transformation is reversible but **68** reacts further with CO to eliminate one of the ruthenium–cyclopentadienyl groups to afford tetranuclear **69** (Scheme 25).

10. Reactivity towards unsaturated organics

Reactions of **1**-Ru and **7** towards diazomethane lead to very different end products. Heating **1**-Ru and a slight excess of diazomethane in toluene for a short time results in the formation of the ketene cluster **70** in moderate yields [108]. This results from addition of two methylene groups, one coupling with a carbonyl to afford the ketene. A key feature of **70** is the chelating nature of the diphosphine and retention of the trinuclear core. Both of these change upon carbonylation which leads to the high yield formation of binuclear **71**. This contains the more

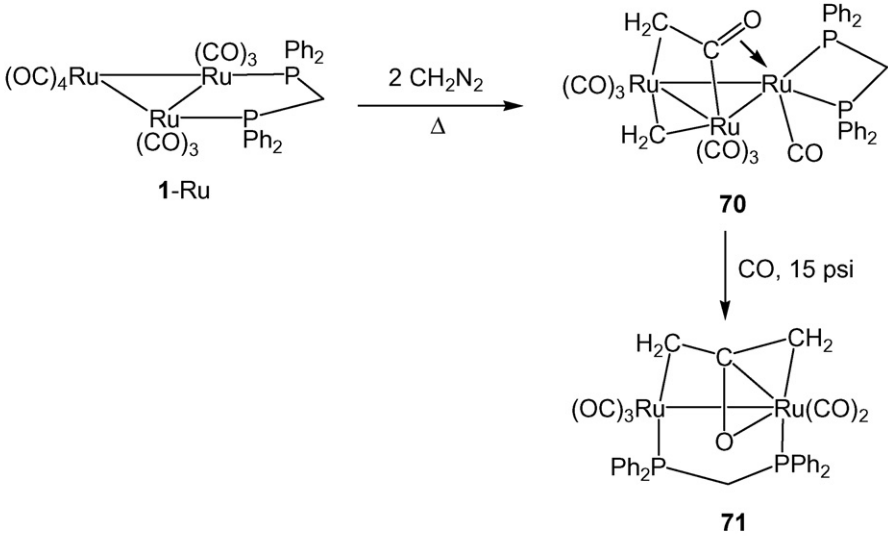


Scheme 25.

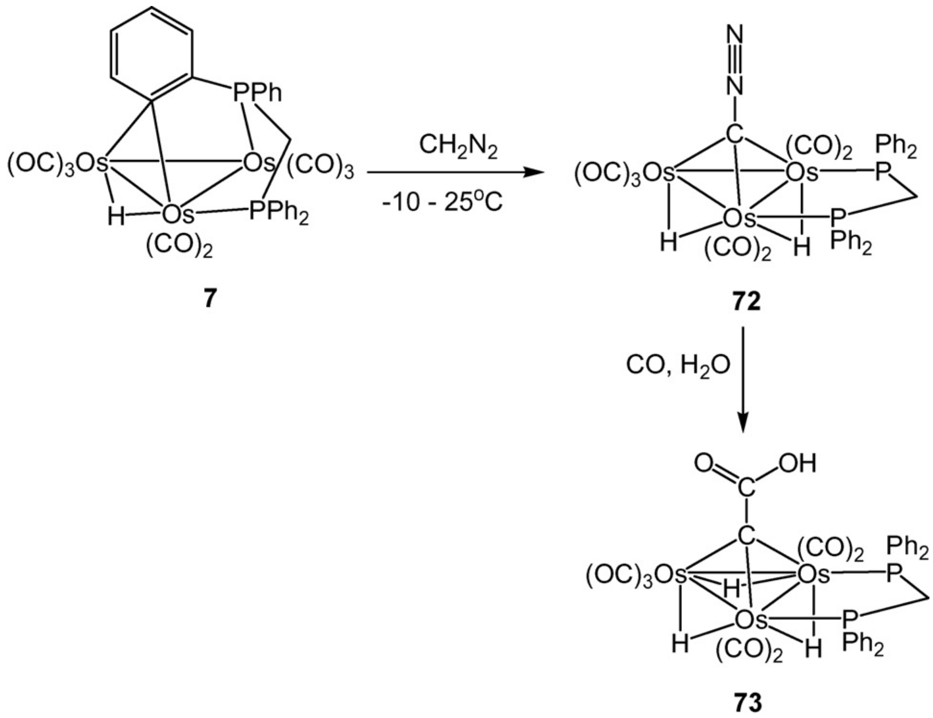
familiar bridging dppm ligand together with a bridging oxa-allyl ligand formed from the coupling of methylene and ketene moieties (Scheme 26).

The reactivity of **7** towards diazomethane follows a different and quite unique path [109]. At low temperatures the reaction is facile with dihydride **72** being formed in moderate yields. This results from the oxidative-addition of the two carbon–hydrogen bonds to the cluster while the carbon–nitrogen bond is retained. Reaction of **72** with CO and water results in the instantaneous and quantitative formation of trihydride **73**, resulting from loss of dinitrogen (Scheme 27). This in turn can be hydrogenated to give a mixture of **1**-Os and $[Os_3(CO)_8(\mu\text{-}H)_2(\mu\text{-dppm})]$ (**9**).

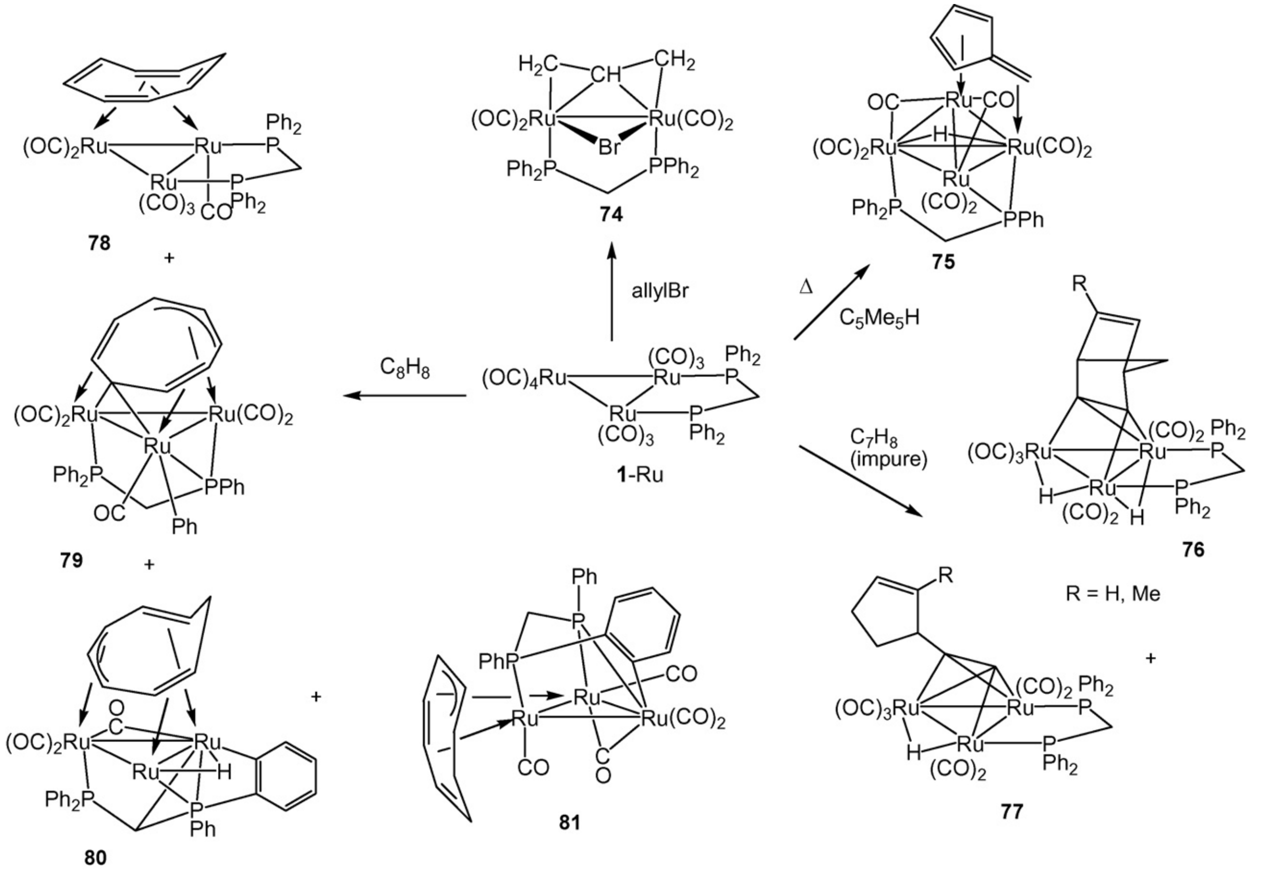
Reactions of **1**-Ru and **1**-Os with simple alkenes do not appear to have been explored but the reactivity of **1**-Ru towards other unsaturated organics has received some attention (Scheme 28). Addition of allylbromide leads to the clean formation of binuclear **74** [59], while with pentamethylcyclopentadiene, the tetraruthenium fulvalene complex **75** is the major (although still low yield) product [110]. Heating **1**-Ru and an impure sample of cycloheptatriene led to the isolation of mixtures of C_7 and C_8 hydrocarbyl complexes **76** and **77** [111]. In **76** the hydrocarbyl binds as an alkyne, while in **77** it adopts a μ_3-alkynyl coordination geometry. It is noteworthy that when the cycloheptatriene was purified then none of these products were obtained. Cycloocta-1,3,5,7-tetraene (cot) reacts with **1**-Ru to give



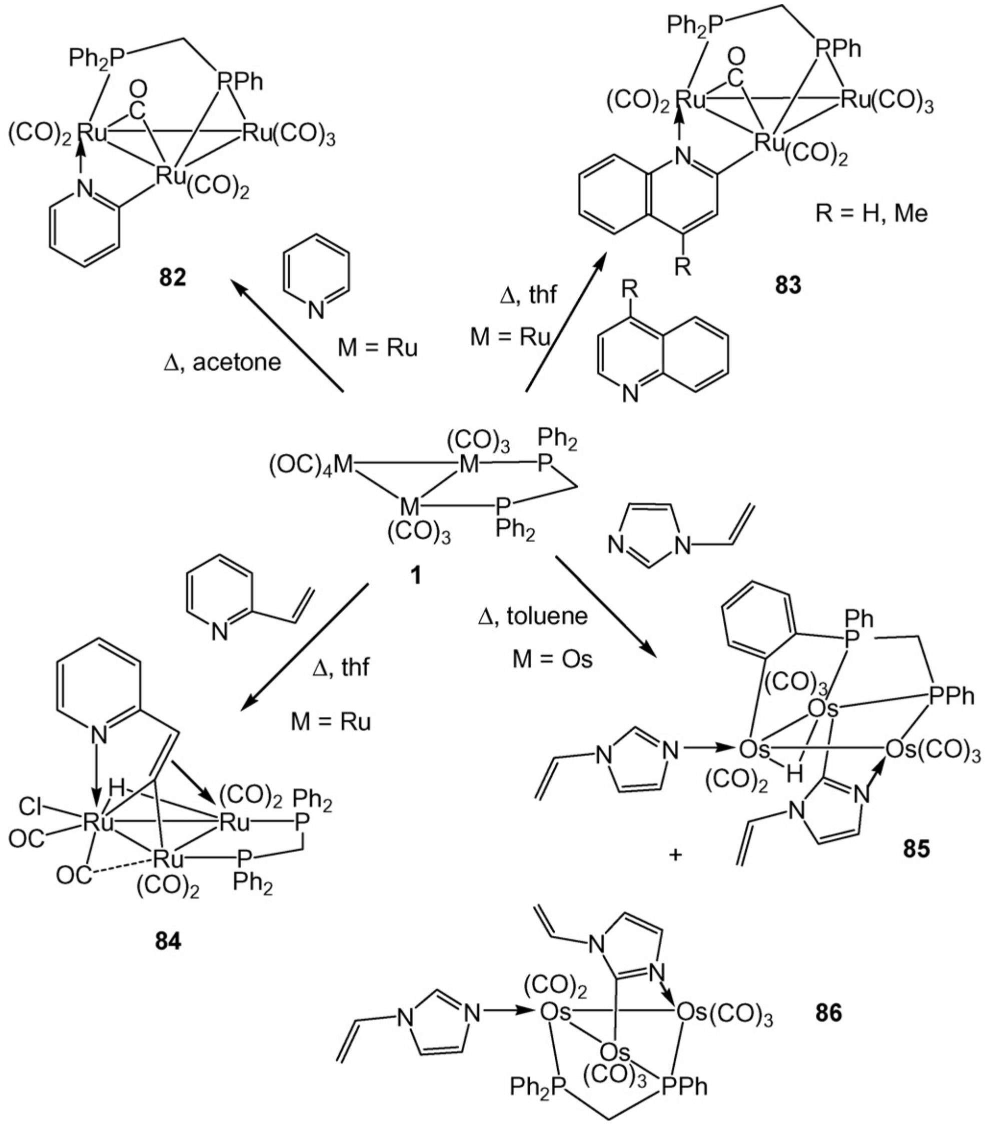
Scheme 26.



Scheme 27.



Scheme 28.



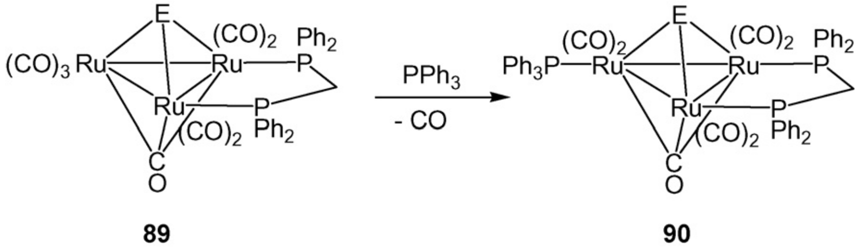
Scheme 29.

a mixture of four complexes **78**–**81** all of which have been characterized crystallographically [112]. Each contains a triruthenium core but only **78** retains an intact dppm ligand. Here the bonding with in the cot ligand is highly delocalized and it acts as a total eight-electron donor. Cluster **79** has all of the components of the dppm ligand but one of the phenyl groups has been cleaved from phosphorus and is now σ-bonded to a ruthenium atom and the cot ligand binds to the triruthenium core in an $\eta^1,\eta^2,\eta^2,\eta^3$-manner. Both **80** and **81** contain very unusual diphosphine ligands. In the former, a methylene proton has been removed and the backbone carbon is now metal-bound, while one of the phenyl groups is orthometalated. The cot ligand has picked up a proton and binds in an η^2,η^2,η^3-manner to the metal atoms. In **81**, benzene has been lost from the dppm ligand. As also observed in **78**, the cot ligand binds only to two of the three metal atoms but now it binds in an η^3,η^5-fashion, rather than the η^4,η^4 binding mode seen in **78**.

11. Reactivity towards amines

The reactivity of **1** towards simple primary or secondary amines appears not to have been probed. Reaction of **1**-Ru with pyridine (boil in acetone) gives low yields of $[Ru_3(CO)_7(\mu\text{-}CO)(\mu_3\text{-}Ph_2PCH_2PPh)(\mu\text{-}NC_6H_4)]$ (**82**) resulting from elimination of benzene [113], while quinolines afford similar orthometalated products **83** in slightly better yields (boil in thf) [114] (Scheme 29). With 1-vinylpyridine, triruthenium $[Ru_3Cl(CO)_5(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_3\text{-}NC_5H_4CH{=}C)(\mu\text{-}H)]$ (**84**) is isolated in 30% yield after chromatography [115]. Here it is the β-carbon of the vinyl group that is activated, dimetalation resulting in the isolation of a unique ligand type. The origin of the chloride remains unclear, but it most likely results upon chlorination of an initially formed terminal hydride complex.

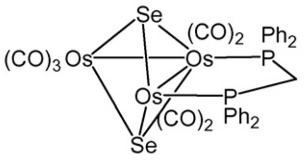
Thermolysis of **1**-Os and a slight excess of 1-vinylimidizole in toluene leads to the isolation of two trinuclear products, **85** and **86**. In contrast to the vinylpyridine chemistry described above, no activation of the vinyl group is noted. Both clusters contain a single orthometalated 1-vinylimidizole ligand which spans a non-bonded osmium–osmium vector and an intact 1-vinylimidizole group terminally bonded through nitrogen. The clusters differ in the nature of the diphosphine ligand. Both contain dephenylated dppm moieties which cap the triosmium unit and in **85** one of the phenyl groups is also orthometalated [116].



Scheme 30.

12. Reactivity towards chalcogenides and chalcogenide sources

Low-valent ruthenium and osmium clusters are known to be chalcogenophilic and **1** are no exceptions to this, showing an extensive chemistry towards chalcogen-containing compounds. Somewhat surprising given this, the reactivity towards elemental sulfur has not been reported. **1**-Ru reacts with elemental selenium in boiling thf to afford a mixture of products including **89** (E = Se), $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}Se)(\mu\text{-}dppm)]$, $[Ru_3(CO)_6(\mu\text{-}CO)(\mu_3\text{-}Se)\{\mu_3\text{-}PhPCH_2PPh(C_6H_4)\}]$ and cubane $[Ru_4(CO)_8(\mu_3\text{-}Se)_4(\mu\text{-}dppm)]$ [117]. The reaction of selenium with **1**-Os appears not to have been reported but orthometalated **7** reacts with elemental black selenium to afford a mixture of three selenium capped clusters [118]. These include the known trinuclear complexes **87** and **88**, together with a very small amount of the cubane $[Os_4(CO)_{10}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)]$.



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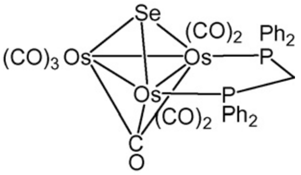

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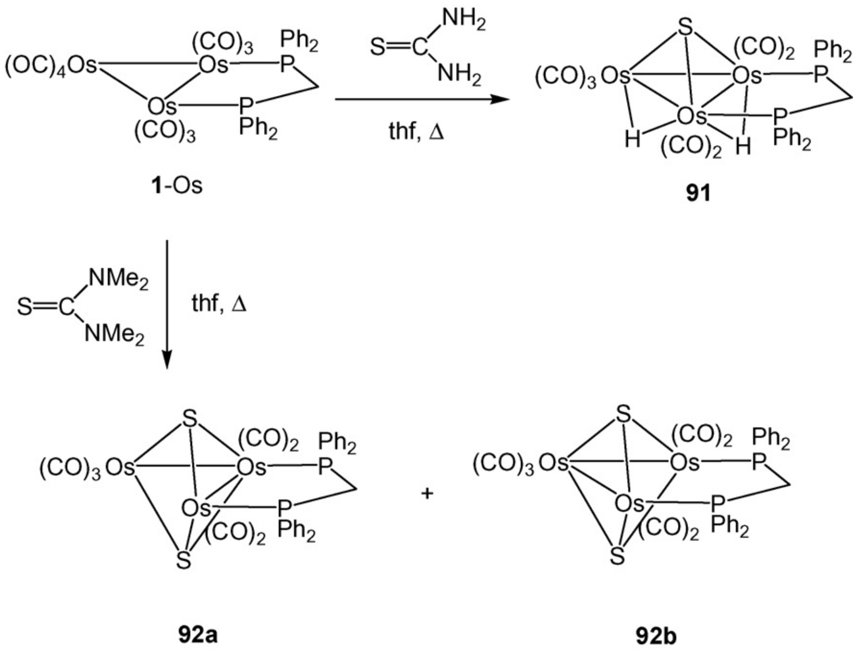
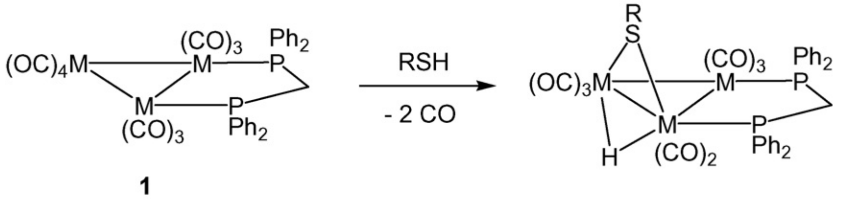
Triarylphosphine sulfides and selenides have been widely utilized as precursors to phosphine-substituted sulfido- and selenido-capped clusters, respectively owing to the ready cleavage of the phosphorus–chalcogenide bond [119]. **1**-Ru reacts with $Ph_3P=S$ at room temperature in thf to give a mixture of chalcogen-capped clusters **89** and **90**. Addition of $Ph_3P=Se$ to **1**-Ru proceeds in an analogous fashion. In separate experiments, addition of PPh_3 to **89** has been shown to produce **90** suggesting that chalcogen addition occurs prior to carbonyl substitution (Scheme 30) [120,121].

Reactions of **1**-Ru have also been carried out with dppm(E) leading to mixtures of up to five products [122]. These include $[Ru_3(CO)_8(\mu\text{-}dppm)_2]$, **89**, $[Ru_3(CO)_5(\mu_3\text{-}CO)(\mu_3\text{-}E)(\mu\text{-}dppm)_2]$, $[Ru_3(CO)_6(\eta^1\text{-}dppmO)(\mu_3\text{-}CO)(\mu_3\text{-}E)(\mu\text{-}dppm)]$ and $[Ru_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ 122].

Thioureas have been utilized as a source of sulfur [117,123]. Reaction of **1**-Ru with thiourea in boiling thf affords mixtures of $[Ru_3(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}dppm)]$ (30%) and $[Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)]$ (7%) resulting from cleavage of both carbon-sulfur and hydrogen–nitrogen bonds [117], while a similar treatment of **1**-Os affords $[Os_3(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}dppm)]$ (**91**) in 70% yield. Reaction of **1**-Os with tetramethylthiourea results in the formation of $[Os_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ (**92**) in 80% yield, resulting from the selective transfer of sulfur to the cluster [123] (Scheme 31). Cluster **92** is formed as mixture of two isomers (**92a**–**b**) which can be separated chromatographically and both have been crystallographically characterized.

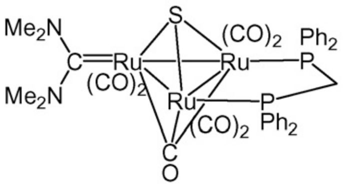


Scheme 31.



Scheme 32.

The reaction of **1**-Ru with tetramethylthiourea is more complex giving up to five products depending upon the reaction times and stoichiometry used [117]. Most significantly two of them, **93**–**94**, bear a terminally bonded diaminocarbene ligand, showing that in many respects the reactivity is analogous to that of $Ph_3P=S$. In a separate experiment, [$Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)$] is shown to be a precursor to **94**.



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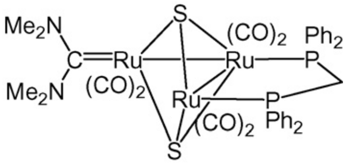

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13. Reactivity towards thiols

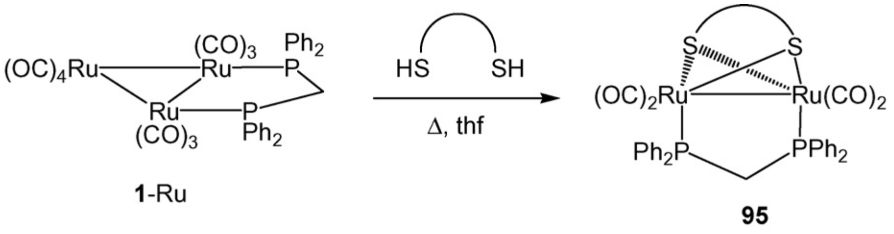
Both **1**-Ru and **1**-Os show high reactivity towards thiols, the dominant feature of which is the facile oxidative-addition of the sulfur–hydrogen bond, as first reported by Bonnet and co-workers who studied the reaction of thiophenol with **1**-Ru. This proceeds smoothly upon gentle heating to give thiolate-bridged [$Ru_3(CO)_8(\mu\text{-}H)(\mu\text{-}SPh)(\mu\text{-}dppm)$], prolonged heating of which results in further sulfur–carbon bond cleavage to afford the known sulfido-capped cluster [$Ru_3(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}S)(\mu\text{-}dppm)$] [124]. A similar addition of thiophenol is noted for **1**-Os [125] and this appears to be a quite general reaction (Scheme 32) [50,59,125,126] which also works for phenylselenol [127].

Hydrogen sulfide reacts with **1**-Os in boiling toluene to give sulfido-capped clusters (**91**) and [$Os_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)$], the latter being the major product. No bridging thiolate complexes were observed suggesting that initial sulfur–hydrogen bond addition is rate-limiting [123]. A similar reaction with **1**-Ru likewise affords [$Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)$] in 80% yield [128].

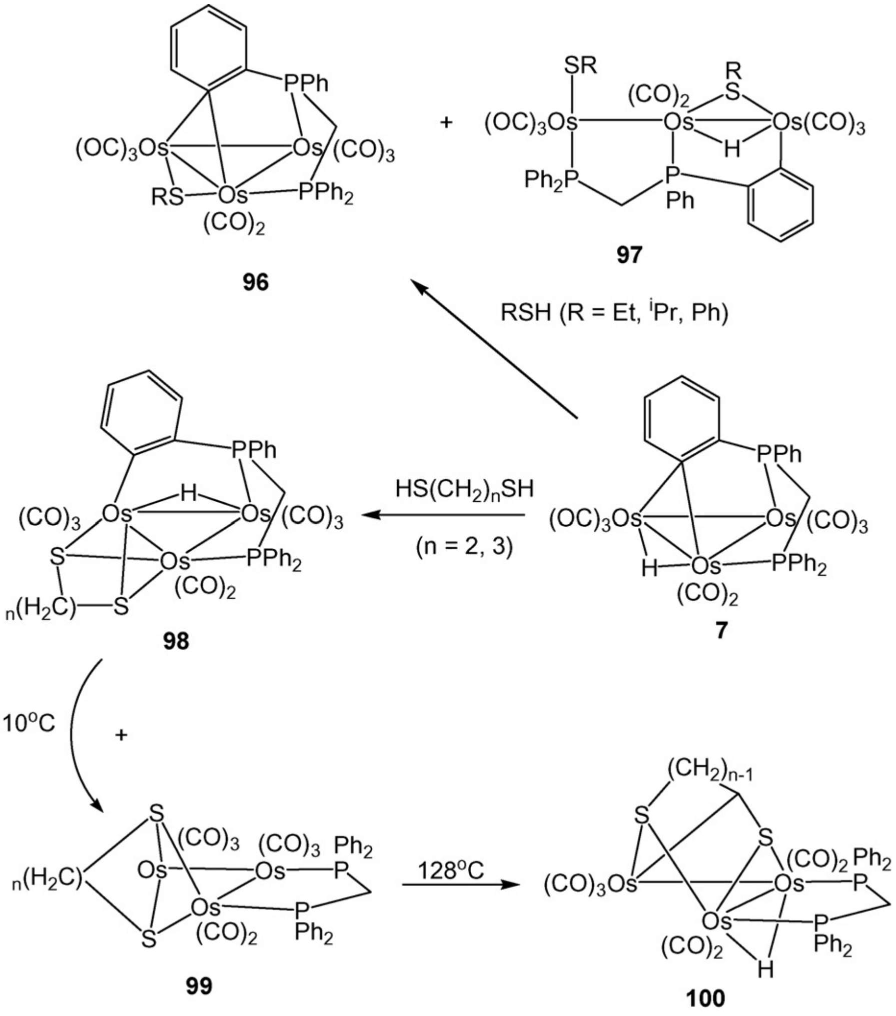
While the trinuclear framework is invariably retained upon reactions with simple thiols, addition of dithiols generally leads to the formation of binuclear products. Thus, **1**-Ru reacts with a range of alkane and arene dithiols in boiling thf to afford the dithiolate-bridged complexes **95** (Scheme 33) [129,130]. With benzene-1,2-dithiol a second product results believed to be trinuclear [$Ru_3(CO)_8(\mu\text{-}SC_6H_4S)(\mu\text{-}dppm)$] [130].

Orthometalated **7** also reacts readily with both thiols and dithiols [131,132]. Thiols add at room temperature to give mixtures of products including the previously discussed [$Os_3(CO)_8(\mu\text{-}H)(\mu\text{-}SR)(\mu\text{-}dppm)$], together with the orthometalated clusters **96** and **97** (Scheme 34). The latter contain an open triosmium core and result from the addition of two equivalents of thiol. Two isomers are observed in solution being attributed to the hydride bridging different osmium–osmium vectors. Alkane dithiols, $HS(CH_2)_nSH$ ($n=2$, 3) also add to **7** at room temperature to give mixtures of **98** and **99**. The former still retains the orthometalated diphosphine, while the latter contains a dppm ligand. It is noteworthy that in both the triosmium core is retained. Heating **98** at 110 °C results in conversion into **99** which in turn rearranges at 128 °C to give the unusual complexes **100** in which one of the backbone methylene groups has been orthometalated [132].

The reactivity of a number of functionalised thiols has been reported [133–135]. With **1**-Os they generally react in an analogous manner to non-functionalised thiols (see Scheme 32). For example, 2-mercapto-1-methylimidazole adds to orthometalated **7** at room temperature of **1**-Os at 110 °C to give a thiolate-bridged complex [133]. In contrast, addition to **1**-Ru affords only [$Ru_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}S)(\mu\text{-}dppm)$]. Reaction of **7** with pyridine-2-thiol also proceeds at room temperature to give the expected thiolate-bridged **101** together with the open 50-electron cluster **102** (Scheme 35) [135]. The latter contains both terminal and bridging hydrides and the nitrogen of the pyridine ligand



Scheme 33.



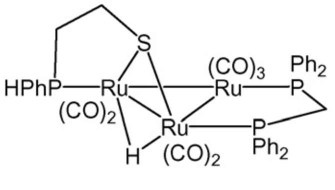
Scheme 34.

is also metal-bound. When the reaction is carried out at higher temperatures a third product **103** is also isolated. In a separate experiment the latter has been shown to result from the reductive-elimination of hydrogen from **102**, a process which can be reversed.

The difunctional thiol-secondary phosphine, $HS(CH_2)_2PPhH$, adds to **1**-Ru to give two products, **104** and **105** [72]. They result from oxidative-addition of the sulfur–hydrogen bond and coordination of the phosphine, differing *via* the intra- and intermolecular nature of the latter. It is noteworthy that for both the phosphorus–hydrogen bond remains intact showing its relative strength with respect to the sulfur–hydrogen bond.

14. Reactivity towards RE-ER (E = S, Se, Te)

The binuclear $[M_2(CO)_4(\mu\text{-ER})_2(\mu\text{-dppm})]$ framework is extremely stable and hence there is a strong thermodynamic driving force behind its formation. This may account for the observation that, unlike in the majority of the chemistry described in this review, reactions of **1**-Ru with dichalcogenide reagents, RE-ER, almost invariably leads to cluster fragmentation and formation of $[Ru_2(CO)_4(\mu\text{-ER})_2(\mu\text{-dppm})]$ (Scheme 36) [59,122,136–138]. This was first shown by Bruce et al. who reported that heating a thf solution of **1**-Ru and MeS–SMe in thf affords $[Ru_2(CO)_4$



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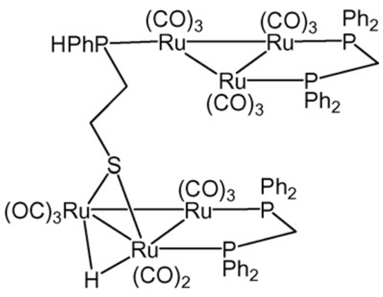

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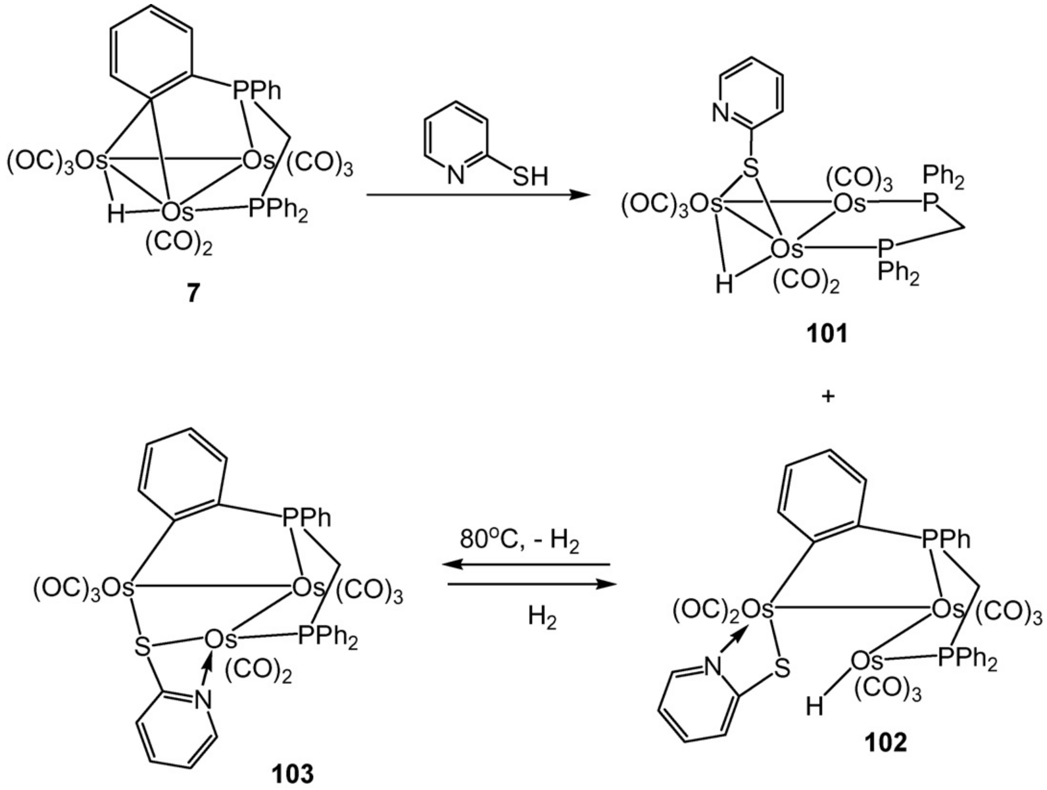
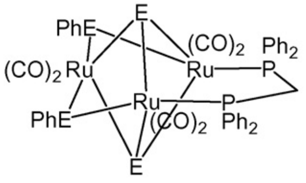


Scheme 35.

(μ-SMe)$_2$(μ-dppm)] as the major product (40% yield), a second minor product being trinuclear [$Ru_3(CO)_8(\mu$-H)(μ-SMe)(μ-dppm)] [59].

Reactions of PhE–EPh (E = S, Se, Te) with **1**-Ru all afford [$Ru_2(CO)_4(\mu$-EPh)$_2$(μ-dppm)] along with a mixture of non-metal–metal bonded triruthenium clusters **106** and **107**. These result from oxidative-addition of both E–E and E–Ph bonds, the phenyl group being captured in **107** (it is COPh when E = Te) [136]. With ArTe–TeAr (Ar = *p*-C_6H_4OEt), tetranuclear [$Ru_4(CO)_9(\mu$-CO)(μ_4-Te)$_2$(μ-dppm)] [137] and mononuclear [$Ru(CO)_4(TeAr)_2$] are also produced [138] lending further insight into the fate of the cleaved ruthenium atoms.



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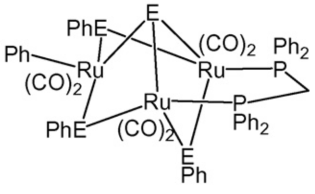

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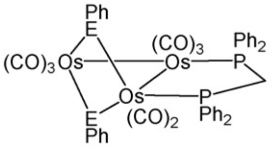
The reactivity of **1**-Os towards PhE–EPh (E = S, Se, Te) results in the formation of large numbers of products [139,140]. Binuclear thiolate-bridged [$Os_2(CO)_4(\mu$-EPh)$_2$(μ-dppm)] are formed for selenium and tellurium, but they are not the major products, and no related complex is formed for sulfur. These observations reflect the stronger osmium–osmium bonds in **1**-Os versus the ruthenium–ruthenium bonds in **1**-Ru. With PhS–SPh, triosmium complexes **108** (E = S) and **109**–**110** are formed in approximately equal amounts [139]. Bis(thiolate)-bridged **108** are also formed for selenium and tellurium along with isomers **111** (E = Se, Te) and **112** (E = Se), while the benzyne cluster **113** is unique to selenium.



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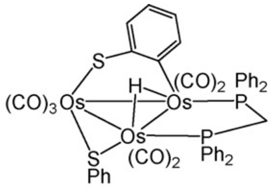

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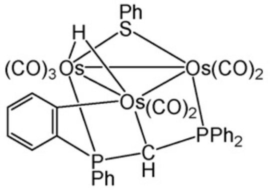

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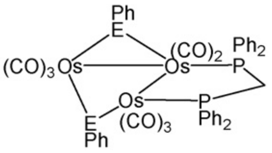

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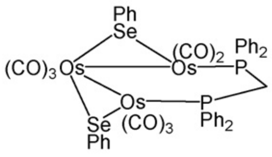

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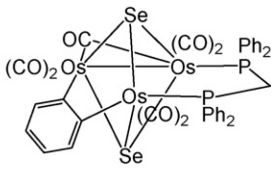

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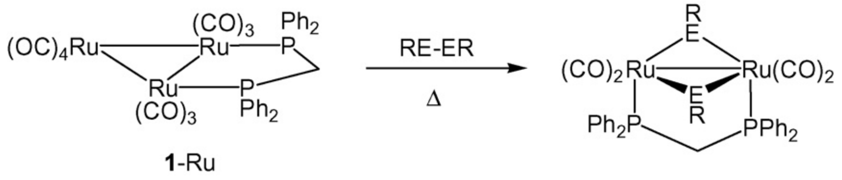
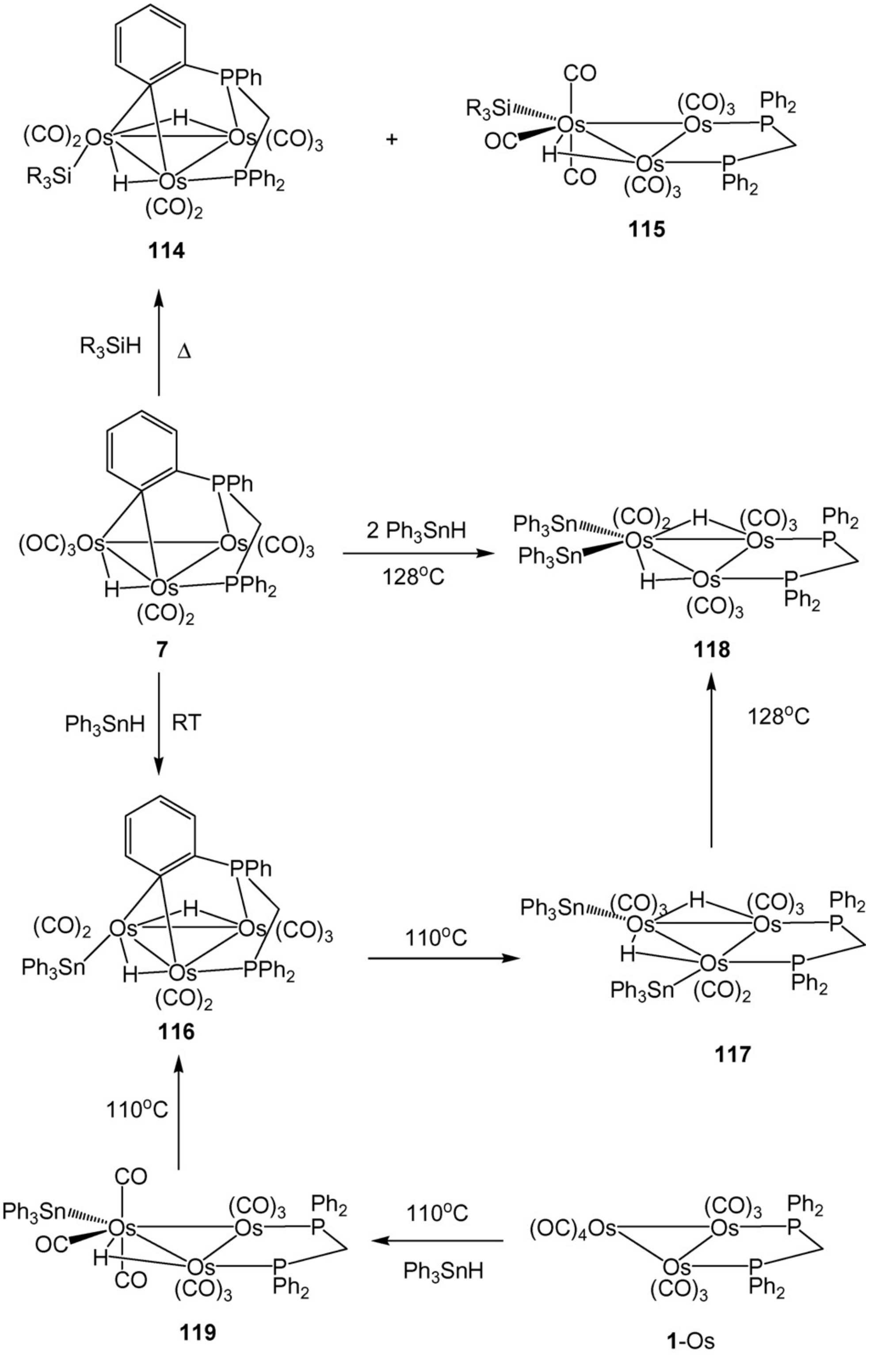
15. Reactivity towards group 14 hydrides

Oxidative-addition of the silanes R_3SiH (R_3 = Ph_3, Et_3, $EtMe_2$) to unsaturated **7** produce a mixture of saturated and unsaturated silyl clusters **114** and **115**, respectively [141] (Scheme 37). The latter are fluxional in solution, being attributed to the migration of

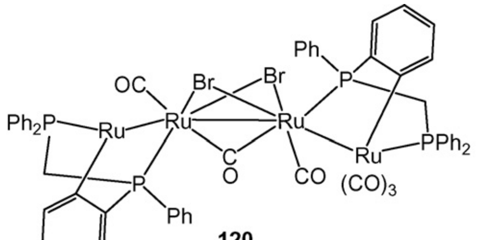


Scheme 36.



Scheme 37.

the hydride from one unsupported osmium–osmium bond to the second with a concomitant movement of the silyl group between the two equatorial sites. Thermolysis of **7** and an excess of Ph_3SnH in xylene affords the bis(triphenyltin) complex **118** as a result of the oxidative-addition of two tin–hydrogen bonds and reductive-elimination of the hydride and orthometalated diphosphine ligand [142]. These transformations were shown to occur in a stepwise manner, initial room temperature oxidative-addition affording **116** in which the orthometalated diphosphine remains intact. The latter can also be prepared upon heating **119** in toluene, itself formed upon addition of Ph_3SnH to **1**-Os. Heating **116** and excess Ph_3SnH in toluene affords **117** in which the two triphenyltin ligands bind to different metal atoms, while both occupy equatorial sites. Finally, heating **117** at 128 °C results in the migration of a triphenyltin unit to afford **118** in which both occupy equatorial sites at the non-dppm coordinated osmium atom. These transformations are summarized in Scheme 37. Somewhat surprisingly given the rich chemistry described above for the triosmium centre, analogous reactions of group 14 hydrides with **1**-Ru have not yet been reported.



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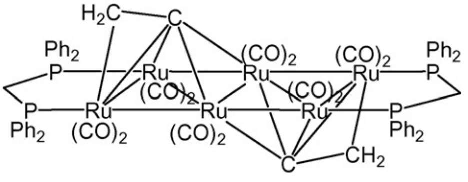

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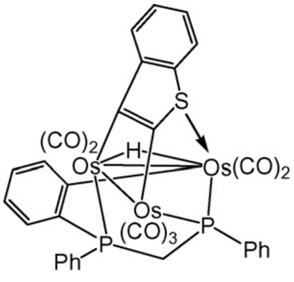

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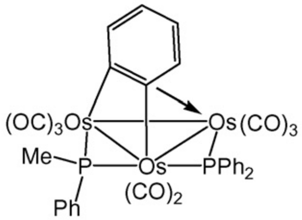
16. Assorted reactions

A few further reactions of **1** and **7** have been reported that do not fit into the above sections. Johnson and co-workers have reported that $[Os_3(CO)_9(MeCN)(\mu\text{-dppm})]$ (**23**) slowly loses acetonitrile in methanol or water to give **7**, and under these conditions addition of the oxygen–hydrogen bonds does not occur. The expected product of the addition of water, namely $[Os_3(CO)_8(\mu\text{-H})(\mu\text{-OH})(\mu\text{-dppm})]$ can, however, be prepared upon addition of dppm to $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ highlighting a limitation to the oxidative-addition of E–H bonds to the triosmium centre [50].

A minor product of the reactions of benzyl bromides, $C_6X_5CH_2Br$ (X = H, Me, F) with **1**-Ru is tetranuclear **120** [37]. This contains two fragmented diphosphine ligands and presumably results from initial scission of a ruthenium fragment from **1**-Ru followed by dimerisation of the resulting binuclear products. It has been crystallographically characterized and contains a linear tetraruthenium core held together by three ruthenium–ruthenium bonds. The only product isolated from the reaction of **1**-Ru and calcium carbide in the presence of tmeda is hexanuclear **121** [143], also the major product of the addition of potassium fluoride to $[Ru_3(CO)_7(\mu\text{-H})(\mu_3\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-dppm})]$ in methanol [90]. It results from the fusion of two Ru_3dppm fragments each being capped by a vinyl ligand. The source of the protons in the latter is not clear but they may derive from adventitious water.

Thermolysis of **7** in *m*-xylene in the presence of benzothiophene affords a mixture of three triosmium clusters. One, **122**, contains a doubly metalated benzothiophene ligand while the other two, **123**–**124** contain no trace of benzothiophene derived ligands. Indeed, heating **7** alone in *m*-xylene for 4 h was shown to afford these clusters in 10 and 27% yields, respectively [144]. In **123**, a backbone phosphorus–methylene bond has been cleaved to generate two phosphido-bridges and one face of the triosmium unit is capped by a benzyne ligand, presumably generated from a cleaved phenyl group, while **124** results from the elimination of benzene.



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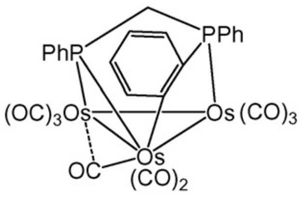

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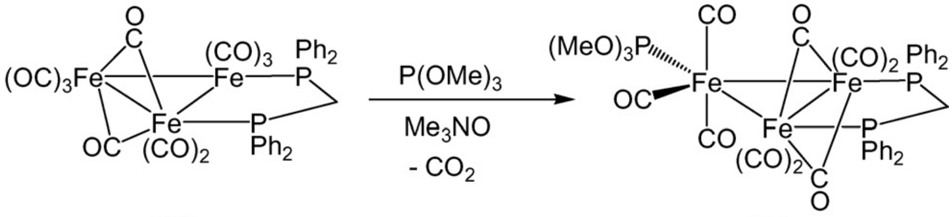
17. Applications in catalysis

No catalytic studies have been carried out using **1**-Os or **7**, but **1**-Ru has been shown to be an active catalyst for a number of organic transformations. Thus, the reductive carbonylation of nitrobenzene to $PhNH(CO_2Me)$ in MeOH–toluene mixtures proceeds at 170 °C for 3 h with 60 atm of CO gives a 24% conversion, although it is noteworthy that $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ gives a 45% conversion under the same conditions [145]. **1**-Ru has been tested in the hydroformylation of cyclohexene using CO_2 as a reactant. At 140 °C and CO_2 and H_2 pressures of 4.0 MPa, a 94% conversion results after 30 h to give a 66% yield of alcohol and 23% yield of cyclohexane. No aldehydes were recovered and the overall activity was lower than that with $Ru_3(CO)_{12}$ [146]. **1**-Ru is more successful as a catalyst for the isomerisation of hex-1-ene to *cis*-hex-2-ene at low hydrogen pressures and also catalyses the hydrogenation to n-hexane at higher hydrogen pressures [22]. In both respects it is found to be more active than $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ [147] and $Ru_3(CO)_{12}$. Although it is not possible to completely rule out fragmentation to mononuclear species during the catalysis, turnover frequency studies strongly suggest that the trinuclear framework remains intact throughout.

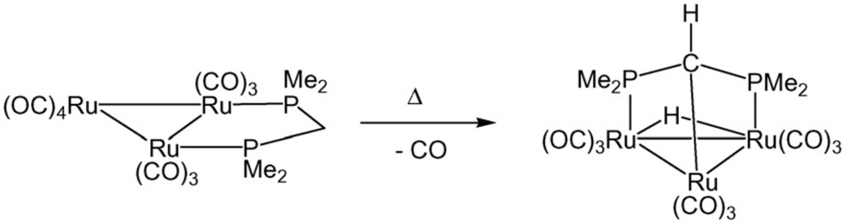
18. Related $[M_3(CO)_{10}(bridge)]$ complexes

Somewhat surprisingly given the rich chemistry demonstrated for **1**-Ru and **1**-Os, only a single report details $[Fe_3(CO)_{10}(\mu\text{-dppm})]$ (**125**) [148]. It is prepared from the Me_3NO-activated reaction of $Fe_3(CO)_{12}$ and dppm at −78 °C in dichloromethane. The crystal



125 **126**

Scheme 38.



127 **128**

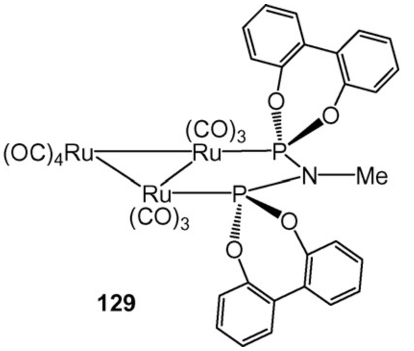
Scheme 39.

structure reveals the presence of two bridging carbonyls in the solid-state, although the IR spectrum in dichloromethane shows only terminal carbonyl absorptions. Low temperature addition of $P(OMe)_3$ to **125** affords $[Fe_3(CO)_9\{P(OMe)_3\}(\mu\text{-dppm})]$ (**126**) (Scheme 38) which has also been characterized by X-ray crystallography. Here the phosphite occupies an equatorial position at the unique iron atom, and now the two carbonyls bridge the dppm-supported iron–iron vector. Cluster **125** is highly fluxional in solution, changes in $^{13}C\{^1H\}$ NMR spectra being explained by a combination of concerted bridge – opening bridge – closing, merry-go-round and trigonal twist mechanisms.

A number of related small bite-angle diphosphine complexes, $[Ru_3(CO)_{10}(\mu\text{-diphosphine})]$, are known including $[Ru_3(CO)_{10}(\mu\text{-}Me_2PCH_2PMe_2)]$ (**127**) [24,149]. Heating **127** in benzene or toluene leads to metalation of the backbone methylene group to give **128** (Scheme 39) [150,151]. The analogous osmium complex $[Os_3(CO)_{10}(\mu\text{-}Me_2PCH_2PMe_2)]$ has also been prepared and reacts with Me_3NO in MeCN to give lightly stabilized $[Os_3(CO)_9(MeCN)(\mu\text{-}Me_2PCH_2PMe_2)]$, the acetonitrile ligand being readily displaced by $P(OMe)_3$ or ethylene [50].

Triruthenium dodecacarbonyl reacts with bis(diphenylphosphino)amine in the presence of a catalytic amount of sodium benzophenone to afford $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(H)PPh_2\}]$ in quantitative yields [152]. The solid-state structure closely resembles that of **1**-Ru, the edge supported by the diphosphine being slightly shorter than the other two. The related complex $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ has been prepared from $Ru_3(CO)_{12}$ under photochemical conditions [24]. Here the difference in ruthenium–ruthenium bridging and non-bridges distances of 0.055(7) Å is even greater than that seen in **1**-Ru (0.017 Å) reflecting the smaller bite-angle of the amino-diphosphine ligand. Krishnamurthy and co-workers have used the sodium benzophenone electron-transfer catalyst route to prepare a range of triruthenium complexes containing axially chiral diphosphazane ligands [153]. This affords chiral triruthenium clusters, a number of which, such as **129**, have been crystallographically characterized.

Bis(diphenylarseno)methane ($Ph_2AsCH_2AsPh_2$ = dapm) reacts with $Ru_3(CO)_{12}$ to afford $[Ru_3(CO)_{10}(\mu\text{-dapm})]$ (**130**) [154] which has been crystallographically characterized [155]. The chemistry has been fairly well developed and very closely models that of **1**-Ru. Reaction with dppm in the presence of an electron-transfer catalyst affords $[Ru_3(CO)_8(\mu\text{-dppm})(\mu\text{-dapm})]$ which has been crystallographically characterized [154]. The ruthenium–ruthenium vector spanned by dppm [2.8653(7) Å] is longer than that spanned by dapm [2.8301(6) Å] and both are longer than the non-bridged vector [2.8873(7) Å].



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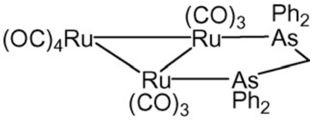

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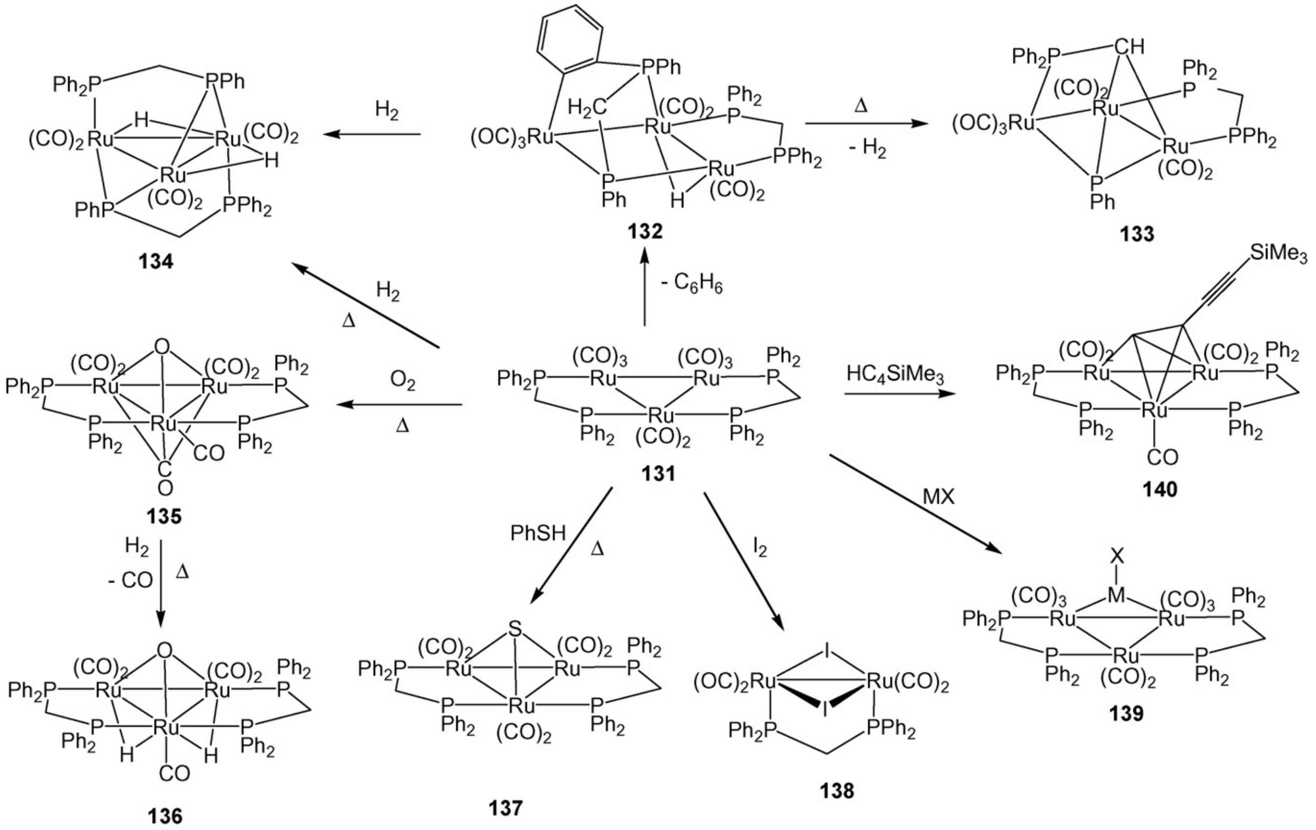
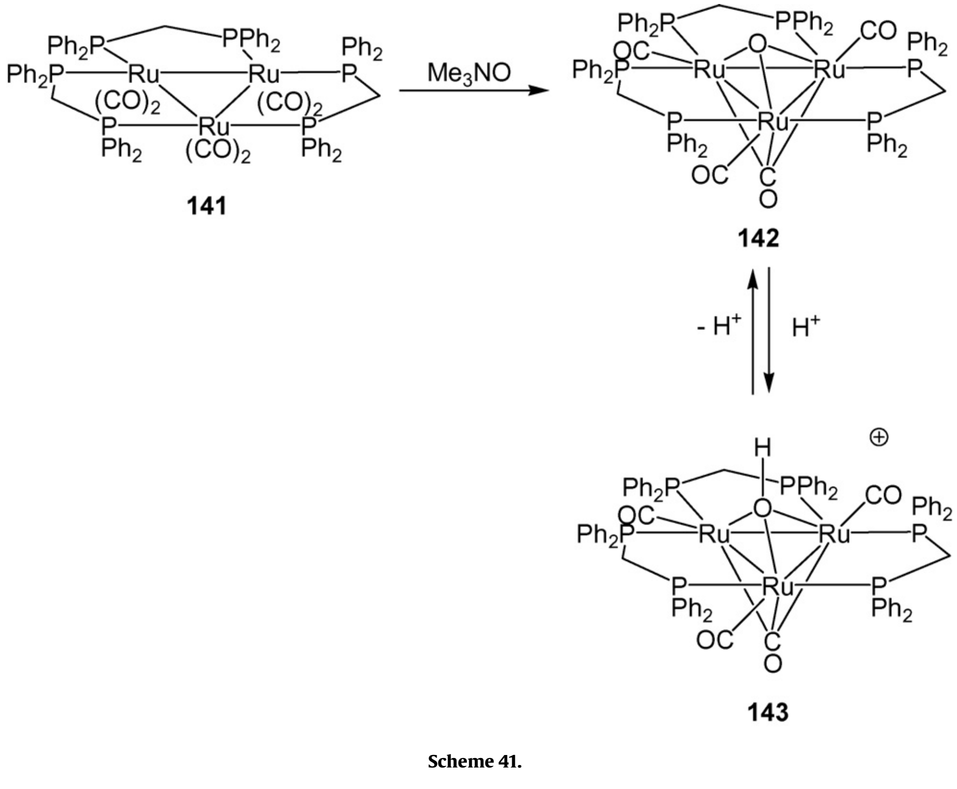
19. Chemistry of $[M_3(CO)_8(\mu\text{-dppm})_2]$ and $[Ru_3(CO)_6(\mu\text{-dppm})_3]$

As early as 1981, Lavigne and Bonnet reported the synthesis of $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ (**131**) upon heating $Ru_3(CO)_{12}$ and two equivalents of dppm in xylene between 80 and 85 °C [76] and the



Scheme 40.

crystal structure reveals the expected equatorial substitution pattern of the phosphorus atoms [78]. The chemistry of **131** has not been explored to the extent of **1**-Ru but broadly follows that of the latter (Scheme 40). Thermolysis of **131** in ethoxyethanol under a slow stream of nitrogen affords **132** as a result of benzene loss, which rearranges further to **133** upon prolonged thermolysis. The latter results from cleavage of a phosphorus–methylene bond with concomitant reductive-elimination of one of the methylene pro-



Scheme 41.

tons. It is noteworthy that in both **132** and **133** the second dppm ligand remains intact [76,156]. When **131** is heated at 85 °C in the presence of hydrogen, activation of both dppm ligand occurs to afford **134**, this also being the product of hydrogenation of **132** [157]. It is noteworthy that under similar conditions the related arsenic complex $[Ru_3(CO)_8(\mu\text{-dapm})_2]$ also transforms into the analogue of **134** but here an intermediate mono-hydride with one dapm ligand remaining intact can also be isolated. When **131** is heated in the presence of oxygen a quite different transformation takes place to yield the oxo-capped cluster **135** [158,159], which is itself quite reactive, for example, oxidative-addition of hydrogen occurs to give dihydride **136** [159]. Heating **131** with thiophenol leads directly to a related sulfido-capped cluster **137** which also undergoes facile oxidative-addition of dihydrogen [124].

Oxidation of **131** occurs upon addition of iodine resulting in cluster fragmentation and formation of binuclear **138** and mononuclear $[RuI_2(CO)_2(\eta^2\text{-dppm})]$, the latter having a *cis* arrangement of carbonyls and *trans* arrangement of halides [160]. As might be expected given the presence of two phosphines, **131** is more basic than **1**-Ru and forms weakly bound adducts **139** with a range of Lewis acids, MX (MX = $Ag(O_2CCF_3)$, $Hg(O_2CCF_3)_2$, $[Cu(NCMe)_4][BF_4]$), one of which, $[Ru_3(CO)_8(\mu\text{-dppm})_2(\mu\text{-AgO}_2CF_3)]$, has been crystallographically characterized [47]. Cluster **131** also reacts with trifluoroacetic acid to give the corresponding cationic hydride [47]. Little organometallic chemistry of **131** has been reported, but Bruce et al. have shown that it reacts readily with the diyne $HC{\equiv}C{-}C{\equiv}C{-}SiMe_3$ to give the alkynyl cluster **140** [161] and the facile nature of this reaction suggests that the organometallic chemistry of **131** could be quite rich.

The osmium analogue, $[Os_3(CO)_8(\mu\text{-dppm})_2]$ has been independently prepared by two groups upon heating **1**-Os and dppm [28,77]. The only chemistry detailed is its ready protonation by trifluoroacetic acid to afford $[Os_3(CO)_8(\mu\text{-H})(\mu\text{-dppm})_2][CF_3CO_2]$ which on the basis of NMR data is assigned a structure in which the hydride bridges the unsupported osmium–osmium edge [77].

The tris(dppm) complex $[Ru_3(CO)_6(\mu\text{-dppm})_3]$ (**141**) has been prepared in low yields from the reduction of ruthenium(III) acetate by $NaBH_4$ in the presence of excess dppm and CO [162] and from $Ru_3(CO)_{12}$ and dppm in benzene [28]. It can be oxidized by silver(I) and oxygen or Me_3NO to give the oxo-capped cluster **142** which itself undergoes reversible protonation to the related hydroxide cluster **143** (Scheme 41) [163].

20. Concluding remarks

A large variety of reactions have been described in the preceding sections, highlighting the versatility of **1** and **7** as synthons to a wide range of triruthenium and triosmium chemistry. In comparison with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, the small bite-angle dppm ligand activates **1** towards carbonyl loss allowing reactions to be carried out at lower temperatures and also leading to better product selectivity. This activation is believed to result from adverse steric interactions in the ground state, since the rigidity of the five-membered M_2P_2C ring does not allow the cluster to relieve steric strain by twisting the ML_4 units. The latter, in contrast, is a common feature of the parent carbonyls and simple monodentate phosphine-substituted derivatives. In **1** there is a substantial adverse steric interaction between the bulky dppm and the equatorial carbonyls on the non-substituted metal atom leading to the relatively facile loss of one of these.

In the vast majority of cases, the dppm ligand serves to maintain the integrity of the trinuclear core. Notable exceptions are when potential three-electron donor ligands are involved as exemplified by the formation of binuclear complexes upon reactions with RE-ER (E = chalcogenide). Other examples of scission of one metal atom are found in addition of some two-electron donor ligands such as CO. In only a very few instances are higher nuclearity complexes formed, an observation that is in stark contrast to the chemistry of $Ru_3(CO)_{12}$. Further, in no instance does complete fragmentation of the cluster occur to give only mononuclear products.

The dppm ligand is not always an innocent bystander. This is best exemplified by the reversible formation of **7** resulting from orthometalation of one of the phenyl substituents. This provides an excellent staring material for triosmium chemistry as **7** is effectively a masked synthon of the highly unsaturated 44-electron cluster $[Os_3(CO)_8(dppm)]$. In a limited number of instances the diphosphine also remains intact but changes its coordination mode from bridging to chelating. Indeed in one instance this can later be reversed. Formation of a highly strained four-membered ring is likely to be energetically unfavorable and thus a significant driving force for the transformation must be provided by the other metal-bound ligands.

The most notable feature of the non-innocent behavior of the dppm ligand is the numerous carbon–hydrogen and carbon–phosphorus bond activation processes noted. These are apparent when **1** are heated alone or in the presence of hydrogen leading to a wide array of ligand transformations while maintaining the trimetallic core. When other ligands are coordinated to the cluster core then the coupling of these with the fragmented diphosphine subunits gives rise to novel transformations and the generation of new and otherwise inaccessible ligands. Currently most of these are in the domain of laboratory novelties since their chemistry has not been explored but some may become valuable in their own right.

Acknowledgements

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