Phosphane-Substituted Selenido−(carbonyl)iron and −(carbonyl)ruthenium Clusters: Structures, Fluxionality and Reactivity

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Keywords: Crystal structures / Fluxional behaviour / Iron clusters / Ruthenium clusters / Selenium compounds

Selenium-transfer reactions from tertiary phosphane and diphosphane selenides to the carbonyl clusters $[M_3(CO)_{12}]$ (M = Fe or Ru) provide a simple, stepwise synthetic route to phosphane-substituted, mono- and diselenido–(carbonyl)iron and –(carbonyl)ruthenium clusters. Four families of clusters are generally obtained: (*i*) the $M_2Se_2L_6$ tetrahedral species (only for iron), (*ii*) the M_3SeL_{10} capped triangular species, (*iii*) the $M_3Se_2L_9$ square-pyramidal *nido* species (for iron and ruthenium), and (*iv*) the $M_4Se_2L_{11}$ octahedral *closo* species (only for ruthenium), with L being a phosphane or carbonyl ligand. When the tertiary phosphane selenide contains heterocyclic fragments, the reaction is not only limited to the transfer of the selenium atom, but proceeds by P–C and, sometimes, C–H bond cleavages, affording new selenidophosphido carbonyl clusters bearing coordinated heterocyclic fragments. Many clusters show fluxional behaviour in solution because of either ligand mobility or M–M bond migration. Furthermore, dimetallic substituted carbonyl clusters have been prepared by two different synthetic approaches: (1) MM′ + PSe (reactions between preformed dimetallic clusters and tertiary phosphane selenides) and (2) MSeP + M′ [cluster growth reactions from preformed chalcogenido–(carbonyl)metal clusters and suitable organometallic fragments]. In particular, from the tetrahedral clusters $[HMCo_3(CO)_{12}]$ (M = Fe or Ru) monoselenido clusters $[MCo_2(\mu_3\text{-}Se)]$ with a tetrahedral core have been obtained. The second type of approach has been applied to the open-triangular *nido* clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_{9-n}L_n]$ (L = tertiary phosphane, *n* = 1 or 2), which can add zero-s.e.p.'s organometallic fragments, such as $M(CO)_3$ (M = Mo or W), giving the corresponding *closo* clusters $[MRu_3(\mu_4\text{-}Se)_2(CO)_{12-n}L_n]$.

I. Introduction

Transition metal species may combine with main group elements or related molecular fragments to afford a variety

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of interesting cluster compounds. Apart from their fundamental significance as a class of complexes owning peculiar-chemical and structural properties, the growing interest in these species derives from their potential applications as catalysts, electrocatalysts and precursors for semiconductors.[1−3] Very recently, chalcogenido−ruthenium derivatives have shown interesting catalytic activity in oxygen reduction reactions in polymer electrolyte fuel cells (PEMFC),[4−7] suggesting their application as cathodes for these devices. The presence of chalcogenide species, in particular Se, appears to catalyse processes that lead to reduction of oxygen through the formation of selenido−transition metal cluster materials.[8] In addition, it is well known that sulfur and selenium atoms are found in active sites of a large number of proteins.[9]

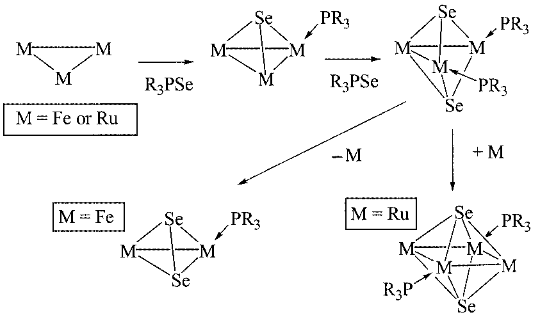
The availability of substituted chalcogenido−metal clusters offers the opportunity to exert a stoichiometric control in those processes that lead from molecular metal chalcogenides, such as $[M_xE_y(PR_3)_z]$, to extended inorganic solids, like M_xE_y. The stoichiometric control, combined with kinetic control, which derives from low activation energies of these processes, often allows the preparation of otherwise inaccessible solid phases or microinhomogeneous materials, such as nanocomposites.[10]

Different synthetic routes are presently available for the preparation of selenido−transition metal clusters, such as those involving diphenyl diselenide,[11,12] phenylselenyl chloride,[13] selenophene,[14] trialkylsilyl selenides,[15−17] polyselenide anions,[18,19] and phosphane selenides [20−23] as starting materials. Furthermore, small selenido clusters, such as $[M_2(\mu\text{-}Se_2)(CO)_6]$ and $[M_3(\mu_3\text{-}Se)_2(CO)_9]$, can be used conveniently to prepare larger mono- and dimetallic species.[24,25]

II. Synthesis of Selenido Clusters from Phosphane Selenides

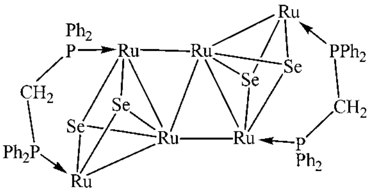
The reactions of tertiary phosphane selenides with (carbonyl)metal species provide a simple synthetic procedure to form selenido clusters through transfer of selenium atoms to low-valent metal centres, taking advantage of the frailty of the P=Se bond. Despite the synthetic potential of the phosphane selenides, their reactions with (carbonyl)metal compounds have been explored only to a limited extent prior to the last few years. For this reason, we began studying the reactions of tertiary phosphane and diphosphane selenides with $[M_3(CO)_{12}]$ (M = Fe or Ru)[26,27] with the aim to obtain new phosphane-substituted selenido carbonyl clusters, whose structural characterization, fluxional behaviour and reactivity are the central issues of this Microreview.

The carbonyl clusters $[M_3(CO)_{12}]$ (M = Fe or Ru) react with tertiary phosphane selenides through transfer of selenium atoms to the metal cluster, giving a variety of phosphane-substituted selenido carbonyl clusters, whose structural frameworks are shown in Scheme 1. The open-triangular, variously substituted, *nido* clusters with the M_3Se_2 core are the major products for both metals, but significant amounts of clusters with dinuclear M_2Se_2, trinuclear M_3Se, and tetranuclear M_4Se_2 cores are also obtained. The product distribution is strongly dependent on the reaction conditions, on the nature of the phosphane and on the cluster/phosphane molar ratio. In the case of iron, the reaction takes place rapidly upon gentle warming, whereas, in the case of ruthenium, the presence of Me_3NO as a decarbonylation reagent is required to increase the reaction rate. Most of those clusters are air-stable and can be separated and recognized by silica gel chromatography[28] and recovered by TLC.



Scheme 1

Moreover, the reactions with bis(diphenylphosphanyl)methane diselenide ($dppmSe_2$) lead to the formation of other less common compounds, which can be obtained by condensation processes, such as the hexanuclear clusters containing M_6Se_4 cores[29] shown in Scheme 2 and the compound $[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)]$, shown in Figure 1, which is the first reported 72-electron Ru_4Se_4 cubane-like cage complex.[30] This complex should be regarded as a secondary product, probably formed by the self-assembly of two dinuclear Ru_2Se_2 groups, derived from *nido*-Ru_3Se_2 by loss of a mononuclear metal fragment. Despite the presence of the bridging diphosphane, the overall geometry of the Ru−Se cubane is very similar to those of the unsubstituted Fe−S and Fe−Se cubanes $[Fe_4E_4(CO)_{12}]$ (E = S, Se).[31,32]



Scheme 2

On the basis of our results we have suggested that the reactions between $[M_3(CO)_{12}]$ and R_3PSe proceeds through two consecutive steps. The monoselenido clusters $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_8PR_3]$, obtained by the stoichiometry-controlled reaction of phosphane selenide R_3PSe with $[Ru_3(CO)_{12}]$, undergo a second attack by R_3PSe affording the corresponding diselenido derivatives $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PR_3)_2]$. To demonstrate the stepwise selenium transfer,

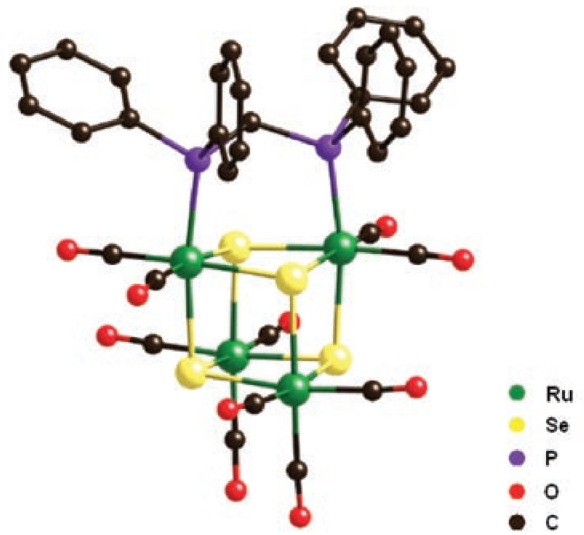


Figure 1. Perspective view of cage compound [$Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)$]

we have treated the monoselenido clusters with another equivalent of phosphane selenide, obtaining the corresponding diselenido species quantitatively.[33] The process, occurring at 60−70 °C, in the presence of Me_3NO, can be monitored by IR spectroscopy.

The structure of the monoselenido-disubstituted cluster [$Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2$] is shown in Figure 2. The triangle of ruthenium atoms is capped on one side by a selenium atom and on the other by a carbonyl group. The two PPh_3 ligands coordinate through the P atoms to two Ru atoms in pseudo-equatorial and pseudo-axial positions, respectively. The μ_3-Se ligand is practically equidistant from the three Ru atoms, whereas the μ_3-CO group bridges, in a slightly asymmetrical way, the two shortest Ru−C distances involving the ruthenium atoms coordinated by the two phosphane groups. This slight asymmetry has also been observed in the case of the unsubstituted cluster [$Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9$].[34]

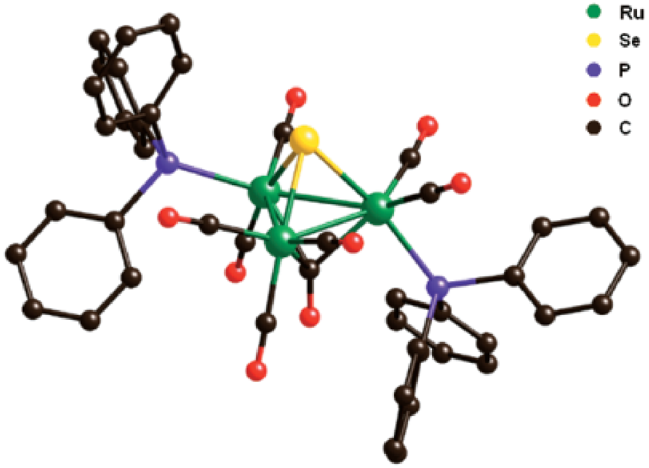


Figure 2. Perspective view of cluster [$Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2$]

The structure of the diselenide cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppy)_2$] [dppy = diphenyl(pyridyl)phosphane] (Figure 3) contains an Ru_3Se_2 core that can be described as a square pyramid with one Ru atom at the apex and two Ru and Se atoms alternating at the base. In this structure, the two phosphane groups coordinate the Ru atoms in pseudo-equatorial and pseudo-axial positions, as in the triphenylphosphane derivative,[35] although, with other ligands, we have obtained analogous clusters with both phosphane groups in equatorial positions.[36] The values of the Ru−P bond lengths, 2.326(3) and 2.371(4) Å, differ remarkably because of the influences of the *trans* Ru−Ru and Ru−Se bonds.

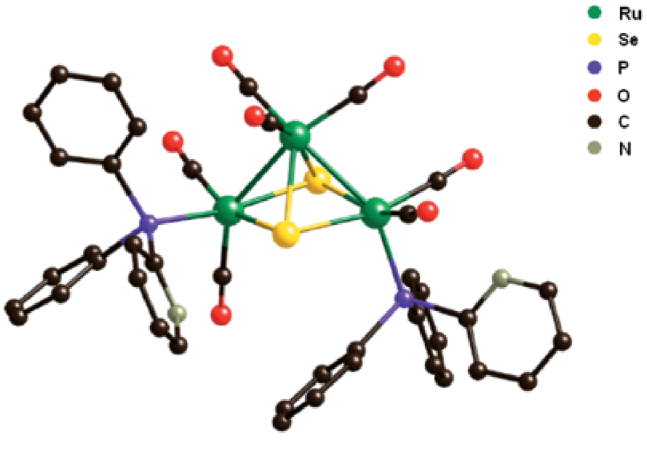


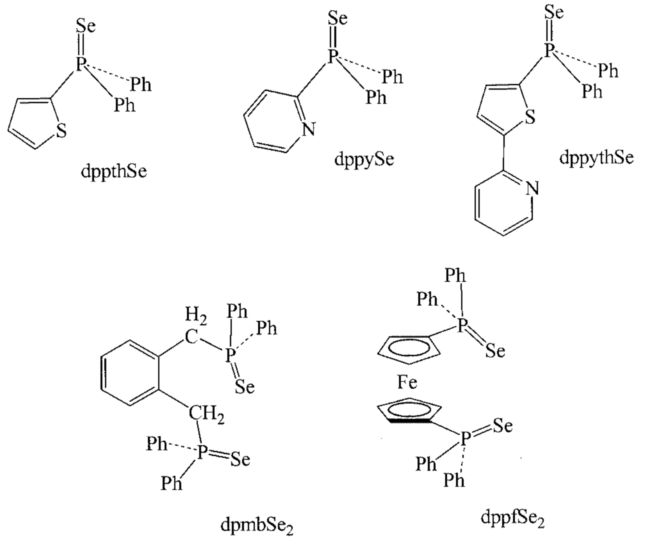
Figure 3. Perspective view of cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppy)_2$]

III. Multiple Fragmentation of the Phosphane Selenide Leading to Selenido-Phosphido Clusters

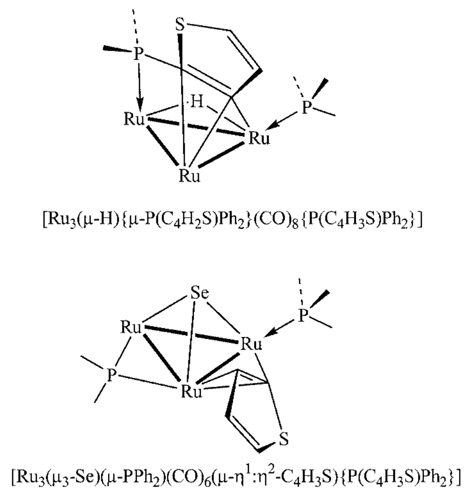
Recently, we observed that tertiary phosphane selenides bearing heterocyclic fragments, such as 2-thienyl (th),[37] 2-pyridyl (py),[38] and 5-(2-pyridyl)-2-thienyl (pyth),[39] (see Scheme 3) can undergo P−C bond cleavage by reaction with (carbonyl)iron and -ruthenium compounds, affording selenido-phosphido clusters. In fact, the heterocyclic moiety was introduced to drive new reactivity patterns in cluster-growing processes, because of the possible release of heterocyclic fragments and the coordinating ability of the heteroatoms.

The cluster [$Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_3S)\{P(C_4H_3S)Ph_2\}$], obtained by reaction between [$Ru_3(CO)_{12}$] and diphenyl(2-thienyl)phosphane selenide, was identified only after the determination of its crystal structure by diffraction methods because of its structural singularity. In the structure, shown in Figure 4, the Se atom caps the metal triangle, two sides of which are bridged by a phosphido and a thienyl ligand, which derive from the multiple fragmentation of the parent diphenyl(2-thienyl)phosphane selenide.

The bonding of the thienyl group is rather unusual, since it interacts through the double bond forming a σ-bond with



Scheme 3



Scheme 4

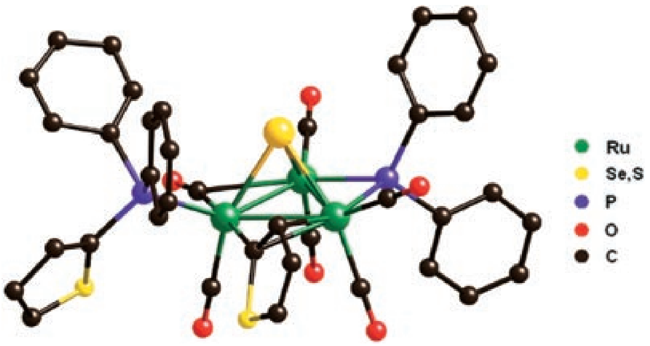


Figure 4. Perspective view of cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_3S)\{P(C_4H_3S)Ph_2\}]$

an Ru atom and a π-bond with another Ru atom. The coordination mode ($\mu\text{-}\eta^1{:}\eta^2$) of the 2-thienyl fragment is similar to that observed in $[Ru_3(\mu\text{-}H)\{\mu\text{-}P(C_4H_2S)Ph_2\}(CO)_8\{P(C_4H_3S)Ph_2\}]$ for the $Ph_2(C_4H_3S)P$ ligand.[40] The most important difference, however, between the two coordination modes is the position of the bridging thienyl moiety with respect to the metal triangle. In fact, in $[Ru_3(\mu\text{-}H)\{\mu\text{-}P(C_4H_2S)Ph_2\}(CO)_8\{P(C_4H_3S)Ph_2\}]$ the thienyl ring overhangs the metal triangle, whereas in $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(CO)_6(\mu\text{-}\eta^1{:}\eta^2\text{-}C_4H_3S)\{P(C_4H_3S)Ph_2\}]$ it approaches the triangle laterally, in such a way that the α-carbon atom is almost lying in the cluster plane, as shown in Scheme 4.

The structure of the cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(CO)_6(\mu\text{-}pyth)\{P(pyth)Ph_2\}]$, obtained by reaction between $[Ru_3(CO)_{12}]$ and diphenyl[5-(2-pyridyl)-2-thienyl]phosphane selenide, is very similar to that with the thienyl ligand.

In the case of the pyridyl group, the ligand $Ph_2(2\text{-}C_5H_4N)PSe$ undergoes multiple fragmentation by reaction with $[Ru_3(CO)_{12}]$ to afford the cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ that does not contain any Ru−Ru bond and is built up through the unique synergy of five bridging ligands. The structure of this polynuclear species (Figure 5) is characterized by the presence of a nearly planar array of eleven atoms forming two roughly coplanar fused rings; i.e., the heptaatomic RuPRuPRuCN cycle and one pyridyl ring [dihedral angle 6.9(1)°].

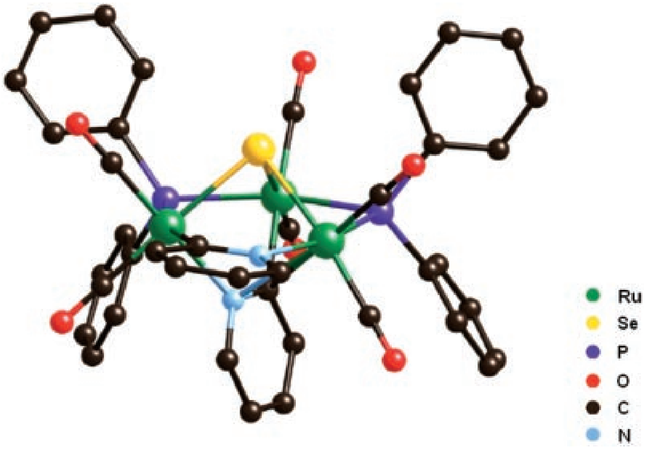


Figure 5. Perspective view of compound $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$

The μ_3-Se bridging mode, connecting three non-interacting ruthenium atoms, has only a few precedents in other trinuclear ruthenium derivatives.[38] This cluster has been obtained from $Ph_2(2\text{-}C_5H_4N)PSe$ through P=Se and P−C(Py) bond cleavages. It contains two differently bridging pyridyl groups, the former connects two Ru atoms through σ bonds, lying on the plane defined by the three metal atoms, the latter is σ-bonded to the same two Ru atoms, being nearly perpendicular to the metal plane, in such a way that it appears to be involved in a weak π interaction with the third metal atom, which completes its coordination sphere. Moreover, if we consider that the capping pyridyl group donates two π electrons to Ru(1), the whole set of ligands contributes 30 electrons to the structure, attaining the expected count of 54 electrons. This arrangement would be an unprecedented type of bridging mode for the pyridyl group.

Multiple fragmentations involving P−Se and P−C bond cleavages have been observed also with the two following diphosphane diselenides: the 1,2-bis[(diphenylphosphanyl)methyl]benzene diselenide[41] (dpmbSe_2) and the 1,1′-bis(diphenylphosphanyl)ferrocene diselenide[42] (dppfSe_2) (see Scheme 3). The reactions between $[M_3(CO)_{12}]$ (M = Ru or Fe) and the 1,2-bis[(diphenylphosphanyl)methyl]benzene diselenide were carried out with the aim of investigating the use of dpmbSe_2 as an effective precursor for selenido−(carbonyl)ruthenium and −(carbonyl)iron clusters containing the scarcely studied 1,2-bis[(diphenylphosphanyl)methyl]benzene ligand. The reaction of $[Ru_3(CO)_{12}]$ with dpmbSe_2 in hot toluene affords a variety of phosphane-substituted selenido carbonyl clusters. Along with substituted clusters with Ru_3Se_2, Ru_3Se, and Ru_2Se_2 cores, we have obtained workable amounts of an unprecedented and interesting complex $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}H)\{\mu_2\text{-}PPh_2)(CO)_6(\mu_2\text{-}CHC_6H_4CH_2PPh_2)]$ with an Ru_3Se core bound to phosphido, hydrido, and carbene moieties, whose structure (Figure 6) has been fully elucidated by X-ray diffraction methods.

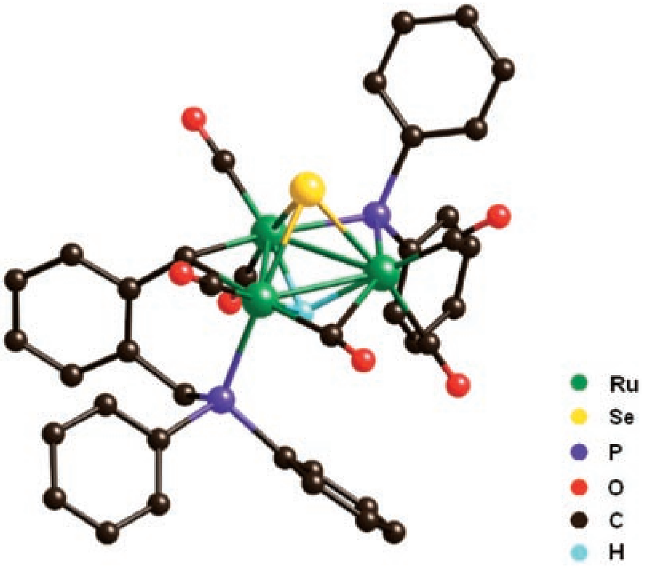
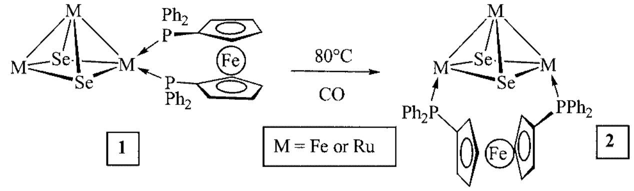


Figure 6. Perspective view of cluster $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}H)\{\mu_2\text{-}PPh_2)(CO)_6(\mu_2\text{-}CHC_6H_4CH_2PPh_2)]$

This cluster is the first example of a triruthenium triangular cluster capped on one side by a μ_3-Se unit and on the other by a μ_3-H atom. The diphosphane has undergone multiple fragmentations, namely P=Se, P−C, and C−H activations. This fragmentation produces a bridging carbene on an Ru−Ru edge resulting from a hydride migration from the Ar-CH_2 group to the cluster. (Carbene)ruthenium complexes have been used widely in the last few years as models, precursors and effective catalysts for olefin metathesis, ring-opening polymerization and alkyne oligomerization.[43] The $^{31}P\{^1H\}$ NMR spectrum, recorded at room temperature, shows two sharp singlets for the σ-coordinated phosphorus atoms and the phosphide group bridging one side of the metal triangle, respectively. The complete proton assignment has been achieved by two-dimensional NMR experiments (COSY, NOESY, TOCSY). The μ_3-hydride signal is found as a doublet of doublets at $\delta = -14.62$ ppm, because of coupling with the two non-equivalent phosphorus atoms. From the 2D NOESY spectrum, a correlation is detected between the hydride and a proton of a methylene group, which, in the solid-state structure, points towards the hydride group at a distance of 2.67(6) Å. The carbene hydrogen atom gives a sharp singlet at $\delta = 10.13$ ppm.

The reactions between dppfSe_2 at 60 and 110 °C afford the two isomeric *nido* clusters $[Ru_3(\mu_3\text{-}Se)_2(dppf)(CO)_7]$ (**1**) and $[Ru_3(\mu_3\text{-}Se)_2(\mu\text{-}dppf)(CO)_7]$ (**2**) which contain dppf as chelating and bridging ligand, respectively. Clusters **1** and **2** belong to the family of numerous open-triangular phosphane-substituted Ru_3Se_2 *nido* clusters, which are the primary products of the attack of 2 equiv. of P=Se groups to the starting triangular cluster. The chelated derivative **1**, obtainable under kinetic control, can be converted into the more stable bridged cluster **2** by thermal treatment in toluene solution as shown in Scheme 5. This conversion can be monitored by IR spectroscopy.[42]



Scheme 5

The cluster $[Ru_3Se\{\mu\text{-}P(Ph)C_5H_4FeC_5H_4PPh_2\}(\mu\text{-}OCPh)(CO)_6]$ (whose structure is depicted in Figure 7) was isolated as a minor product in the reaction between $[Ru_3(CO)_{12}]$ and dppfSe_2 at 60 °C.[42] The core consists of a metal triangle capped by a selenium atom and bridged on two sides by a phosphido ligand and by a benzoyl group, respectively, both deriving from multiple fragmentation of dppf diselenide and migratory insertion of a Ph ring into an Ru−C bond of a terminal carbonyl group.

Because of the loss of a phenyl ring, the phosphane-phosphido ligand is coordinated to one side of the Ru−Ru bond in an unusual manner: the phosphido P atom bridges two Ru atoms asymmetrically and participates with the other P atom in the chelation of one of them. The migratory insertion of a phenyl ring into a carbonyl group causes the formation of a benzoyl ligand that bridges two Ru atoms in a $\mu_2\text{-}\eta^1\text{:}\eta^1$-fashion through the C and O atoms. Only few examples are known of a μ_2-benzoyl group bridging two metal atoms in the same $\mu_2\text{-}\eta^1\text{:}\eta^1$-fashion.[42]

IV. Fluxional Behaviour

Two types of fluxional behaviour have been observed: (*i*) ligand mobility and (*ii*) M−M bond migration.

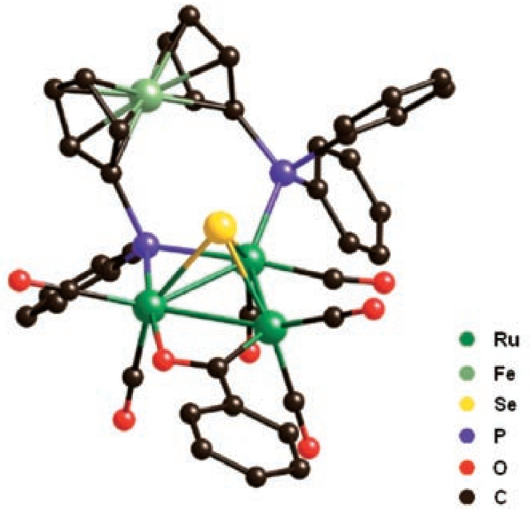
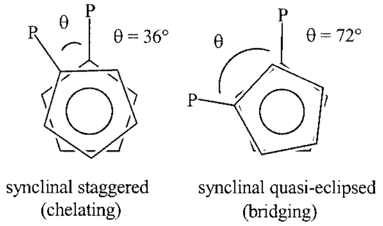


Figure 7. Perspective view of cluster [$Ru_3Se\{\mu$-$P(Ph)C_5H_4FeC_5H_4PPh_2\}(\mu$-$OCPh)(CO)_6$]

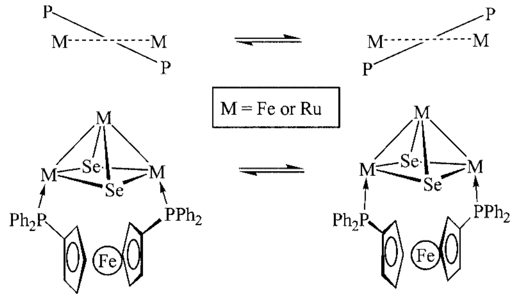
The ferrocenediphosphane ligand can assume different coordination modes in cluster chemistry. This feature derives from the possibility of the cyclopentadienyl rings twisting about their axis. In fact, the P···P separation between the two donor atoms depends on the θ torsional angle, ranging from 3.30 ($\theta = 0°$) to 6.90 Å ($\theta = 180°$). Scheme 6 shows the preferred conformations adopted in the case of chelating ($\theta = 36°$) and in the case of bridging ($\theta = 72°$) over one side of a (carbonyl)metal cluster. To gain an insight into the structures of these molecules in solution, we performed ^1H NMR investigations on clusters [$M_3(\mu_3$-$Se)_2(\mu$-dppf$)(CO)_7$]. At room temperature, the proton pattern of [$Fe_3(\mu_3$-$Se)_2(\mu$-dppf$)(CO)_7$] shows a featureless broad band in the cyclopentadienyl region, suggesting the onset of a fluxional behaviour. At 258 K, four singlets are visible in the same region, which indicate the equivalence of the two cyclopentadienyl rings. It has been demonstrated that the fluxional behaviour consists of the concerted twisting of the two equivalent rings around their axis ($\Delta G^{\ddagger} = 58.2\ kJ\cdot mol^{-1}$, $T_c = 303\ K$)[44] as shown in Scheme 7.



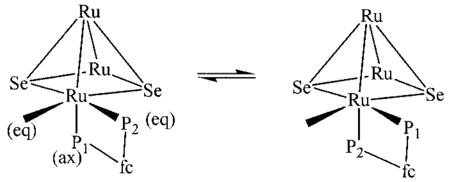
Scheme 6

The pattern of the signals of the protons of the Ru analogue parallels that of the corresponding Fe derivative at 273 °C, indicating that the fluxional behaviour of the ligand, observed for the Fe species, exhibits a higher energy barrier in the Ru congener.

The dynamic behaviour of [$Ru_3(\mu_3$-$Se)_2$(dppf)$(CO)_7$] (**1**) is quite different (see Scheme 8). At room temperature the ^1H NMR spectrum exhibits four singlets for the Cp protons, indicating the equivalence of the two rings. At 213 K, the two rings become inequivalent, with the proton spectrum showing eight singlets that were assigned by 2D NMR spectra. The fluxional behaviour of **1** consists of the localized scrambling of the chelating ligand around Ru, namely the exchange of the axial and equatorial positions of the two $Ph_2(C_5H_4)P$ moieties. This dynamic behaviour makes the two rings equivalent, but the four protons of each ring remain unequal.[44]

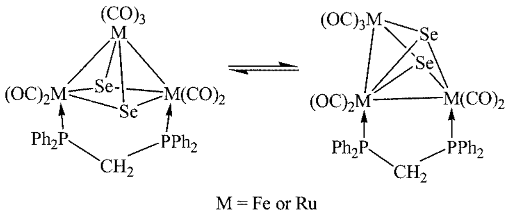


Scheme 7



Scheme 8

The cluster [$Ru_3(\mu_3$-$Se)_2(\mu$-dppm$)(CO)_7$] has the well-known bicapped open-triangular 50-electron core and is the expected primary product of the attack of dppmSe$_2$ on the starting carbonyl cluster. The structure in the solid state is the same as that observed for other phosphane-disubstituted Ru_3Se_2 derivatives, which exhibit two P donor groups coordinated (in axial positions) to the two non-bonded, basal metal atoms. Nevertheless, its NMR spectra in solution suggest fluxional behaviour. In fact, the ^{31}P NMR spectrum shows a singlet and two doublets at lower frequency. The ^{13}C NMR spectra, as well as the ^{77}Se NMR spectra, show a couple of signals, consistent with the presence of two isomers in solution: the first is the symmetrical cluster with the two phosphorus atoms equivalent, as found in the solid state, and the other is that obtained by migration of the M−M bond from a side of the square pyramid to the base, as depicted in Scheme 9.[29]



Scheme 9

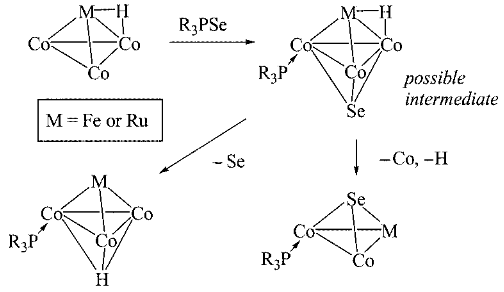
Also, the disubstituted Ru_3Se_2 clusters with monophosphanes exhibit ^{31}P NMR spectra in solution indicative of the same fluxional motion observed for the dppm.[35,36]

V. Dimetallic Clusters

Recently, we have extended our interest in the search for new synthetic routes to phosphane-substituted selenido−mixed-metal clusters by considering that the presence of different metals can influence the selectivity of certain processes and can lead to the formation of compounds presenting new, and not always easily predictable, structures.

Two different synthetic strategies have been developed for the synthesis of dimetallic substituted carbonyl clusters: (1) MM′ + PSe (reactions between preformed dimetallic clusters and tertiary phosphane selenides) and (2) MSeP + M′ [cluster growth reactions from preformed chalcogenido−(carbonyl)metal clusters and suitable organometallic fragments].

As a first approach for the synthesis of dimetallic selenido clusters, we have treated different phosphane selenides with the tetrahedral clusters $[HMCo_3(CO)_{12}]$ (M = Fe or Ru) and obtained two classes of products:[45] (*i*) trinuclear selenido clusters possessing an $MCo_2(\mu_3\text{-Se})$ core and (*ii*) tetranuclear hydrido clusters with an $HMCo_3$ core obtained by simple substitution of carbonyl groups by phosphane ligands (Scheme 10).



Scheme 10

Both classes are *nido* species and probably are derived from a trigonal-bipyramidal intermediate. While compounds of type (*ii*) have been reported already in the literature, the triangular dimetallic clusters of type (*i*), capped by a μ_3-selenide unit and substituted by a phosphane ligand, have been obtained and fully characterized for the first time. One possible hypothesis for the formation of these clusters is that the reactions proceed first with an addition of the phosphane selenide, giving an intermediate species in which the phosphane group and the selenium atom are coordinated. This intermediate would then loose a cobalt atom and a hydride ligand or a selenium atom to afford type (*i*) or (*ii*), respectively.

As an example of the structure of type (*i*), Figure 8 shows the structure of $[RuCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppy})]$ in which an MCo_2 triangle is capped by a μ_3-Se ligand. The bidentate phosphane ligand bridges the Co−Co edge through the phosphorus and nitrogen atoms. The bidentate bridging phosphane group forms a five-membered ring that is fused with the metal triangle on one side and with the pyridyl ring on the other.

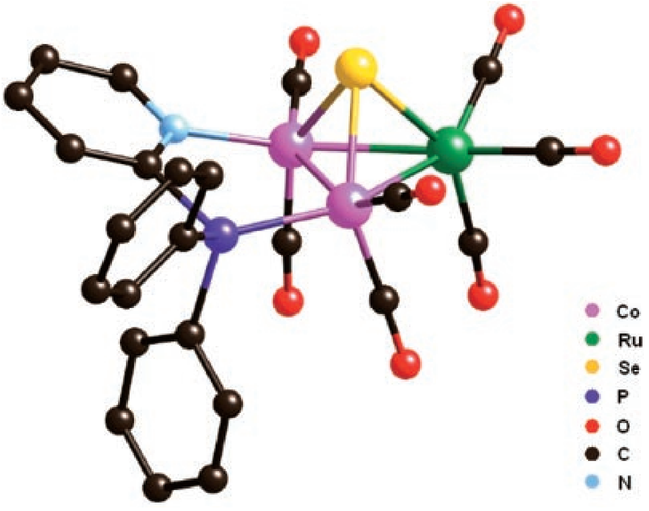


Figure 8. Perspective view of cluster $[RuCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppy})]$

The structure of $[HRuCo_3(CO)_7(\mu\text{-CO})_3(\mu\text{-dppy})]$ (Figure 9) shows a tetranuclear $RuCo_3$ core of type (*ii*) in which two carbonyl groups have been replaced by the dppy ligand bridging two cobalt atoms through the P and N atoms. Perhaps because of the steric hindrance resulting from this coordination, the hydride ligand has migrated from its original μ_3-capping position to the Ru−Co edge.

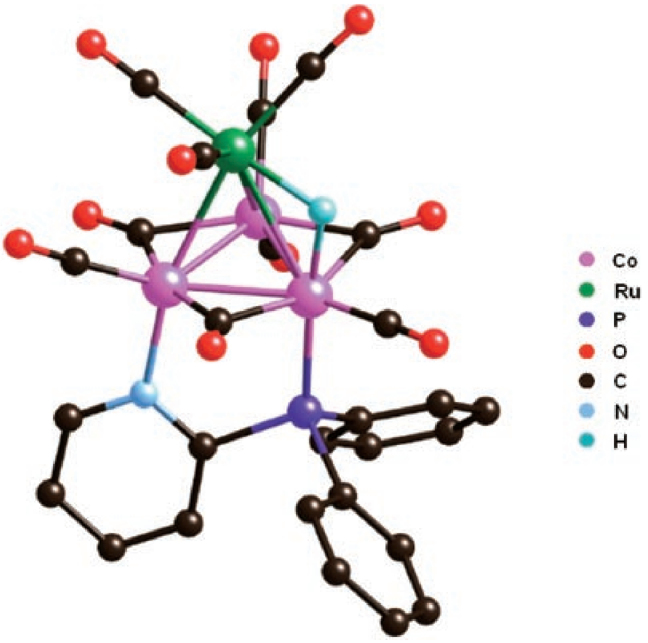


Figure 9. Perspective view of cluster $[HRuCo_3(CO)_7(\mu\text{-CO})_3(\mu\text{-dppy})]$

The linear trinuclear complex $[Pt\{Fe(CO)_3(NO)\}_2(PhCN)_2]$ was chosen for the reaction with phosphane selenides, by considering that its open geometry and the lability of the PhCN ligands could possibly result in an easy attack of the P=Se moiety to the cluster core. Actually, the reaction of the PtFe$_2$ complex with diphenyl(2-pyridyl)phosphane selenide occurs even at low temperature, affording a variety of compounds.[46] One of them was recognized as the 46-electron cluster [(CO)$_3$Fe(μ_3-Se){Pt(CO)P(2-C$_5$H$_4$N)Ph$_2$}$_2$]. It exhibits a butterfly framework consisting of two FePtSe wings sharing the common Fe−Se hinge (Figure 10). The value of the Fe−Se bond length, 2.337(1) Å, is slightly smaller than the average one, 2.37 Å, found in several clusters with a *nido*-Fe$_3$Se$_2$ core.[27] The two Pt atoms are definitely non-bonded since the Pt···Pt separation is rather large at 3.167(9) Å. By considering the two Fe−Pt bonds, the coordination about the Pt atoms is almost square-planar, with the CO and phosphane ligands being *trans* to the selenium and iron atoms, respectively.

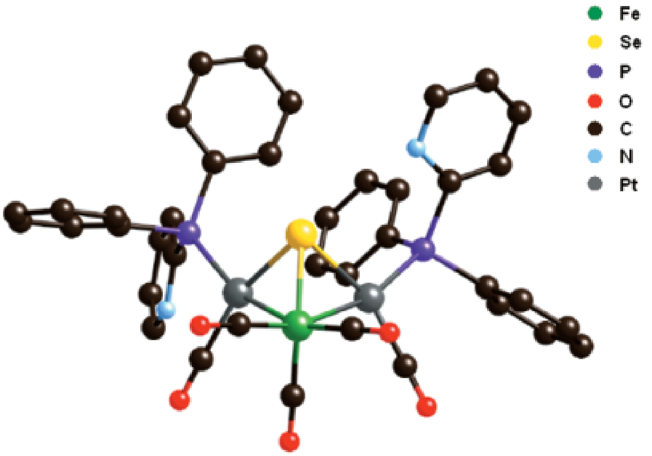
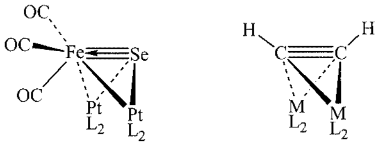


Figure 10. Perspective view of cluster [(CO)$_3$Fe(μ_3-Se){Pt(CO)P(2-C$_5$H$_4$N)Ph$_2$}$_2$]

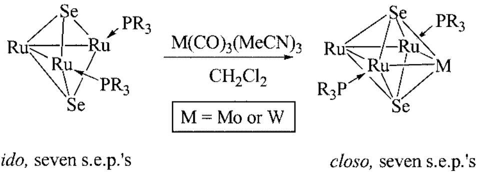
There are only a few known examples of the cluster typology found in [(CO)$_3$Fe(μ_3-Se){Pt(CO)P(2-C$_5$H$_4$N)-Ph$_2$}$_2$]. The structure can be described also as a (CO)$_3$-Fe≡Se group (a legitimate, but unknown, 18-electron species) stabilized by the double bridging interaction with two PtL$_2$ fragments, a system analogous to the well-understood L$_2$M(μ-acetylene)ML$_2$ systems, as shown in Scheme 11.



Scheme 11

The chemical bonding in this cluster, and in similar systems, has been analysed through density functional theory (DFT) and qualitative MO approaches, considering the (CO)$_3$Fe≡X unit as being equivalent to RC≡CR molecules by isolobal analogy.[46]

The second approach for the synthesis of phosphane-substituted, selenido−mixed-metal clusters consists of the reaction of preformed selenido species with organometallic fragments. This approach was chosen by considering the availability of workable amounts of complexes [Ru$_3$(μ_3-Se)$_2$(CO)$_{9-n}$L$_n$] (n = 1 or 2; L = tertiary phosphane). Compounds of this kind are open-triangular, *nido* clusters with 7 skeletal electron pairs. As a consequence, they could be prone to add a zero-s.e.p. fragment, such as M(CO)$_3$ (M = Mo or W), giving the hypothetical *closo* clusters [MRu$_3$(μ_4-Se)$_2$(CO)$_{12-n}$L$_n$]. The reactions of various [Ru$_3$(μ_3-Se)$_2$(CO)$_7$(L)$_2$] clusters with W(CO)$_3$(CH$_3$CN)$_3$ afford the dimetallic *closo* clusters [WRu$_3$(μ_4-Se)$_2$(μ-CO)$_4$(CO)$_6$L$_2$],[36] as shown in Scheme 12.



Scheme 12

In their crystal structures, most of these clusters lie on a crystallographic centre, so a disorder exists that involves the mutually opposite Ru and M (M = W or Mo) atoms of the *closo* core of the cluster, resulting in a disordered Ru$_3$M(μ_4-Se)$_2$ cluster core. This disorder caused us to formulate these clusters erroneously in a previous note as Ru$_2$W$_2$Se$_2$ electron-deficient species.[47] These complexes belong to the family of diselenide tetranuclear *closo* clusters. They could be described as distorted octahedra in which the three ruthenium atoms and the M atom lie on the basal plane and two selenium atoms at the apices. Two phosphane ligands coordinate the *trans* ruthenium atoms through the phosphorus atoms. Four carbonyl groups bridge the Ru−Ru and Ru−M edges asymmetrically. The crystal structure of compound [Ru$_3$M(μ_4-Se)$_2$(μ-CO)$_4$(CO)$_6$(t4mpp)$_2$] [t4mpp = tris(*p*-methoxyphenyl)phosphane] is reported in Figure 11.

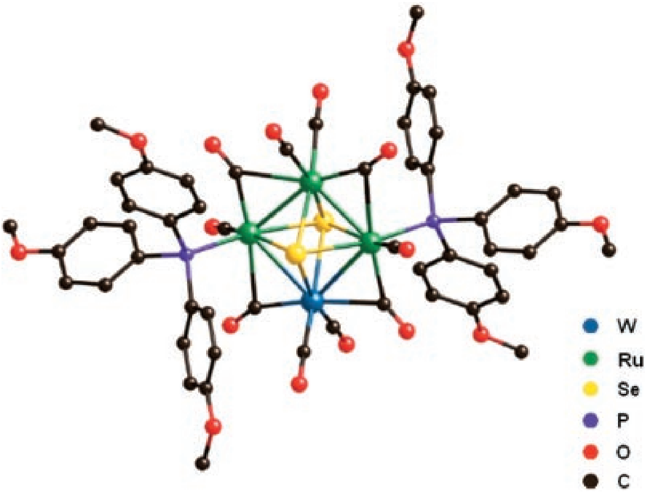
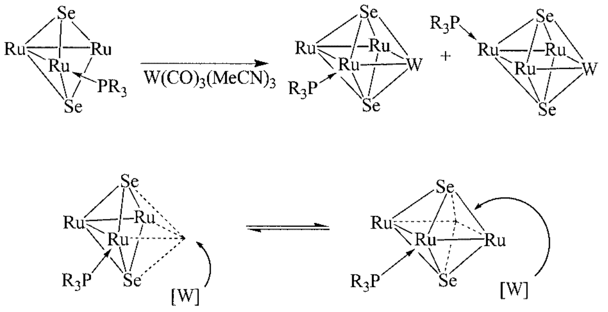


Figure 11. Perspective view of cluster [Ru$_3$M(μ_4-Se)$_2$(μ-CO)$_4$-(CO)$_6$(t4mpp)$_2$]

When the starting reagent is the monosubstituted $[Ru_3(\mu_3\text{-}Se)_2(CO)_8L]$ (L = tertiary phosphane) the reaction product is the expected dimetallic *closo* cluster $[WRu_3(\mu_4\text{-}Se)_2(\mu\text{-}CO)_4(CO)_7L]$, which was fully characterized in solution as well as in the solid state. Two isomers were obtained depending on whether the position of the tertiary phosphane on the ruthenium atom is *cis* or *trans* to the tungsten atom (see Scheme 13).



Scheme 13

A possible explanation for the synthesis of the two isomers is derived from the fluxional behaviour of the $Ru_3(\mu_3\text{-}Se)_2$ core clusters: when the Ru−Ru bond is localized on the pyramid edge, the $W(CO)_3$ fragment can fit in the *cis* position with regard to the phosphane ligand; when the Ru−Ru bond is localized on the basal plane, the unique position in which the fragment fits is the *trans* one (see Scheme 13).

In the case of the reaction between $W(CO)_3(MeCN)_3$ and $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dpbz)_2]$ (dpbz = diphenylbenzylphosphane), the compound $[Ru_3(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_7(dpbz)_2W(CO)_5]$ (Figure 12) was obtained. This cluster can be considered as the product of a donor−acceptor interaction between the fragment $W(CO)_5$ and a selenido atom of $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dpbz)_2]$.

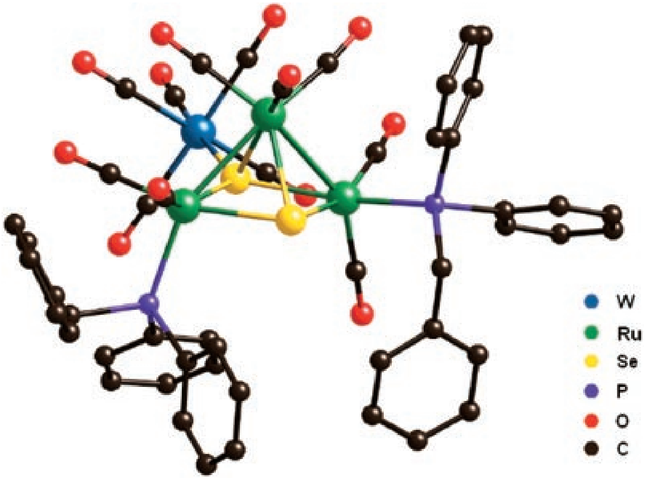
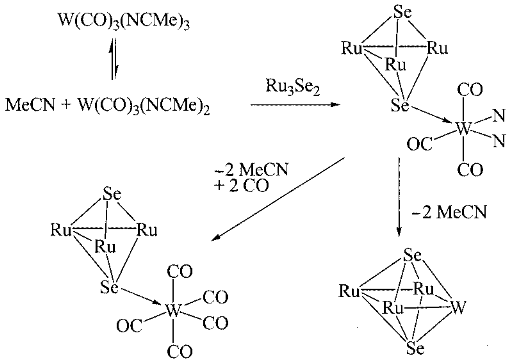


Figure 12. Perspective view of cluster $[Ru_3(\mu_3\text{-}Se)(\mu_4\text{-}Se)(O)_7(dpbz)_2W(CO)_5]$

A possible mechanism for the production of this compound involves the formation of the labile intermediate $[Ru_3(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_7(dpbz)_2W(CO)_3(CH_3CN)_2]$ (Scheme 14) that could undergo easily the substitution of two acetonitrile groups with two carbonyl groups. If the loss of the two acetonitrile groups is followed by saturation of the coordinative vacancy on the basal plane of the pyramid, the previously described *closo* cluster is obtained.



Scheme 14

Concluding Remarks

Systematic investigations on the reactions of tertiary phosphane and diphosphane selenides towards (carbonyl)iron and -ruthenium clusters have achieved the following results: (*i*) The reaction provides a simple, stepwise synthetic route to phosphane-substituted, small-nucleus selenido carbonyl clusters, through transfer of selenium atoms; (*ii*) it leads, in some cases, to the formation of new species, such as the cubane-like cage complex $[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(\mu\text{-}dppm)]$, that are not easily attainable by other routes; (*iii*) when the tertiary phosphane selenide bears heterocyclic fragments, the reaction is not only limited to the transfer of the chalcogenido atom, but proceeds with P−C and/or C−H bond cleavages, affording selenido-phosphido carbonyl compounds; (*iv*) some clusters display particular physico-chemical characteristics, such as the fluxional behaviour in solution involving ligand exchange as well as M−M bond migration; (*v*) certain compounds exhibit specific activity in cluster-growth reactions, such as the *nido* clusters with the $Ru_3(\mu_3\text{-}Se)_2$ core, which reacts with $M(CO)_3$ fragments (M = Mo or W), leading to the corresponding dimetallic *closo* octahedral species $[Ru_3M(\mu_4\text{-}Se)_2(CO)_{12-n}L_n]$ (L = tertiary phosphane, n = 1 or 2). For the synthesis of dimetallic substituted carbonyl clusters we have also investigated another strategy: treatment of different phosphane selenides with the dimetallic tetrahedral clusters $[HMCo_3(CO)_{12}]$ (M = Fe or Ru) and with the linear trinuclear complex $[Pt\{Fe(CO)_3(NO)\}_2(PhCN)_2]$ obtaining new selenido−mixed-metal clusters substituted by tertiary phosphanes.

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