Trimetallic Units as Building Blocks in Cluster Chemistry

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1 Introduction

Over several decades cluster chemistry has produced a bewildering variety of complex structures. Fortunately, in more recent times, theoretical studies have provided useful rationalizations for the existence of such compounds and for their structural characteristics.[1–2] Particularly important for the development of cluster chemistry has been the recognition that even compounds with very complex structures can be described in terms of assemblies of 'building blocks', often clearly recognizable as molecular fragments, using the isolobal analogy.[3]

The most recurrent structural feature in cluster chemistry is the trimetallic unit M_3. A variety of metal centres, particularly those of Groups X and XI with d^{10}-electron configuration, build molecular compounds containing such units, generally held together by bridging ligands, and/or direct metal–metal bonds.

A striking property of many trimetallic fragments is their reactivity, which can, at least formally, be described in terms of Lewis acidic or basic character and, therefore, the ability to interact with conventional Lewis acids or bases to produce more complex structures. This account provides a brief summary of the chemistry of the best known M_3-fragments and of the types of larger clusters they can produce. The potential uses of such species will also be briefly mentioned.

2 Clusters of the Group X Elements containing M_3-Units

The elements of the nickel triad readily form complexes containing discrete M_3-units or, even more readily, clusters which can be considered as being made up of triangular units joined either through an M_2-edge or a single M-atom. Although the most extensive range of compounds is given by platinum (Pt_3), palladium (Pd_3) and nickel (Ni_3) also form such clusters (Figure 1).

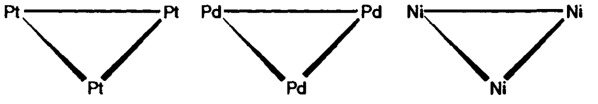
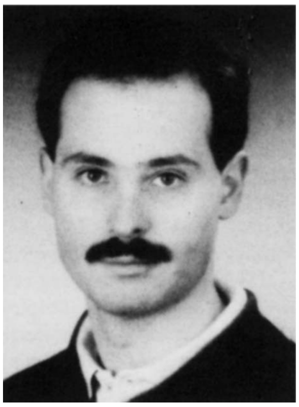


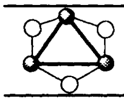
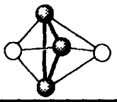
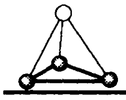
Figure 1

The most marked feature of these compounds is their readiness to form larger heterometallic clusters. The known skeletal units containing Pt_3 or Pd_3 (●) and fragments containing other metals (○) are shown in Table 1.



Daniel Imhof was educated at the Swiss Federal Institute of Technology (ETH), Zürich where he received his Dipl. S. Nat. in 1990. He is currently completing work for his Ph.D. at the ETH Zürich in the laboratory of Professor L. M. Venanzi. His fields of interest include cluster chemistry and its application in homogenous and heterogenous catalysis.

Table 1 Pt_3- and Pd_3-Heterometallic clusters

	● Pt	● Pd
	○ Ir Sn	Sn
	○ Au Hg Sn	
	Cu Ag Au ○ Zn Cd Hg Tl In	Ag

3 Platinum Compounds

The best known Pt_3-clusters, of the type $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ (*3:3:3*), are readily obtained from a variety of complexes, as can be seen in Scheme 1.

There are also many other related trimetallic clusters, with bridging ligands other than CO and terminal ligands other than PR_3. Some of these are shown in Figure 2.[4–7]

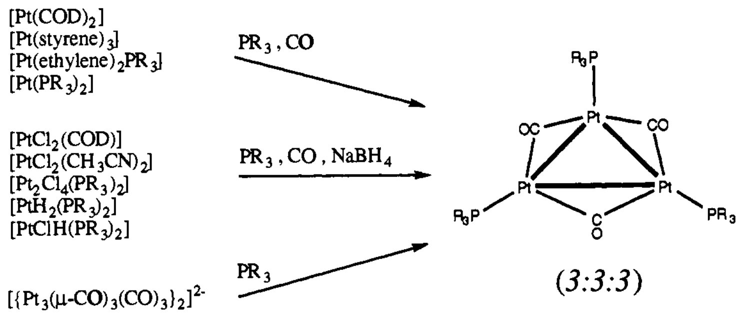
Furthermore, compounds with different Pt-to-ligand ratios are known, *viz.* $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$ (*3:3:4*),[4,8] $[Pt_4(\mu\text{-}CO)_5(PR_3)_4]$ (*4:5:4*),[9] and $[Pt_5(\mu\text{-}CO)_6(PR_3)_4]$ (*5:6:4*).[6] Their structures are shown in Figure 3.

The richest heterometallic cluster chemistry is given by compounds of the *3:3:3*-type. This arises mainly because these units can act either as Lewis bases or as Lewis acids, as can be clearly seen in the frontier orbital diagram shown in Figure 4.[1]

The HOMO, C_3-symmetric a'_1-orbital is doubly occupied and its electrons can be used to form a 'dative' bond. Furthermore the LUMO a'_2-orbital, which is also C_3-symmetric, can be used

Luigi M. Venanzi received his Dipl. Chem. from the University of Kiel in 1952. He then joined the Butterwick Research Laboratories of I.C.I. Ltd., working in J. Chatt's research group. In 1956 he was appointed I.C.I. Research Fellow at the University of Oxford where he was awarded his D.Phil. degree in 1958. He then became a Lecturer at the Inorganic Chemistry Laboratory of that University and a Fellow of Magdalen College, Oxford, positions he held until 1968 when he joined the State University of New York at Albany as Professor of Chemistry. In 1971 he became E.I. du Pont Professor and Chairman of the Chemistry Department at the University of Delaware. Professor Venanzi has been Professor of Inorganic Chemistry at the Swiss Federal Institute of Technology since 1973.

His research interests range from homogeneous catalysis to cluster chemistry, with a strong bias towards the coordination chemistry of the platinum-group metals and polydentate phosphines.



Scheme 1 Synthetic routes for *(3:3:3)*-clusters.

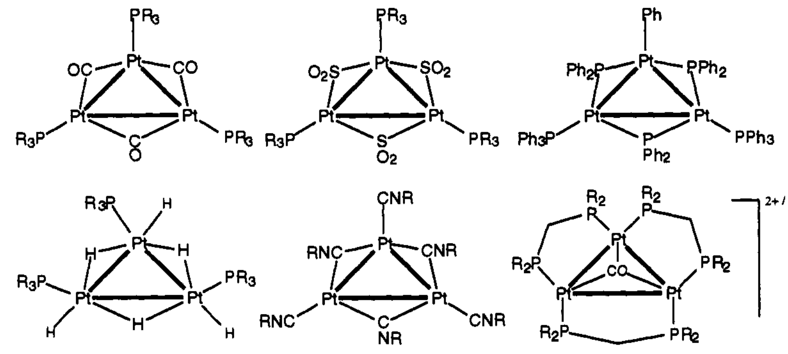
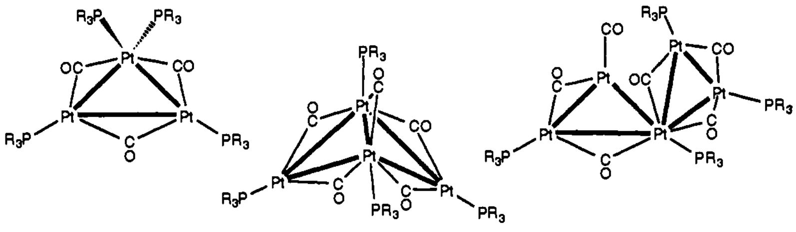


Figure 2



3:3:4 4:5:4 5:6:4

Figure 3

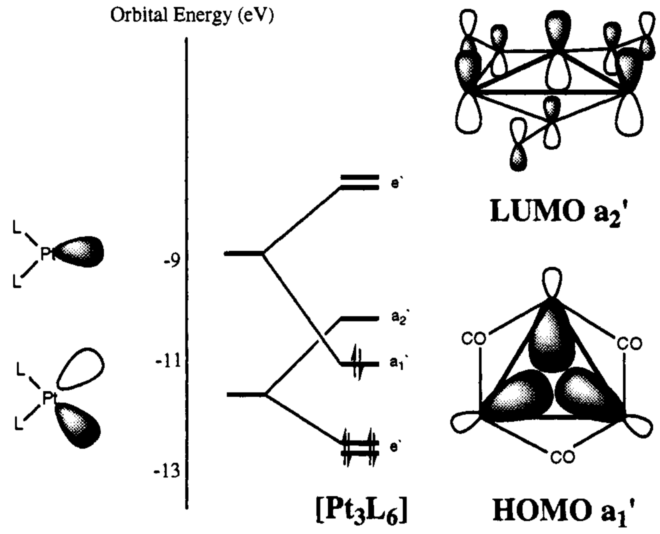


Figure 4 A simplified LCAO-MO scheme of the frontier orbitals in a cluster of the type Pt$_3$L$_6$.

as 'acceptor' orbital, imparting Lewis-acidic character to the Pt_3-unit. It should also be noted that the a-character of both orbitals renders them best suited to combine with totally symmetric acceptor or donor orbitals. The metal centres with which they can interact, either as Lewis bases or acids, are summarized in Figure 5.

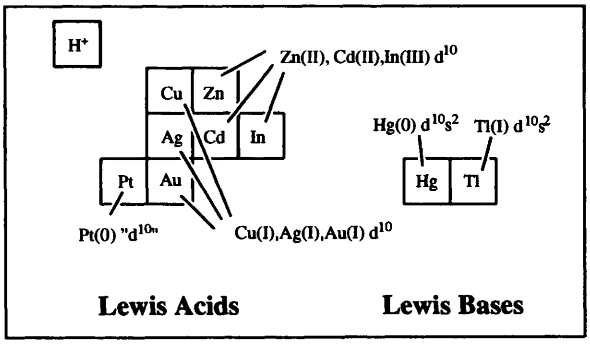
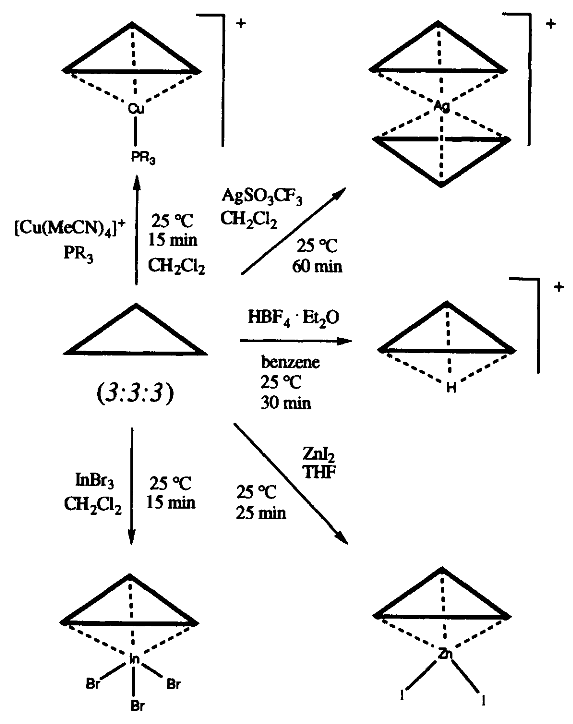


Figure 5 Metal centres forming heterometallic clusters with $[Pt_3(\mu\text{-}L)_3(L)_3]$-units.

3.1 Pt_3-Clusters as 'Electron Donors'

The *3:3:3*-complexes readily form heterometallic clusters of several types. The most common, with half-sandwich structure, has the composition $[\{3{:}3{:}3\}ML]^+$, where M is copper(I), silver(I), and gold(I) and L a ligand such as phosphine. The *3:3:3*-complexes also bind to the copper, silver, and gold monohalides, the zinc and cadmium dihalides, and the indium trihalides.[10,11] Furthermore, the cations copper(I), silver(I), gold(I), and cadmium(II) even form sandwich-type complexes of the composition $[\{3{:}3{:}3\}_2M]^+$ (Figure 6).[12]

Generally, the preparative methods for complexes of the above types are extremely simple, requiring only the addition of the appropriate reagents in stoichiometric ratios. Some specific reactions are represented in Scheme 2.

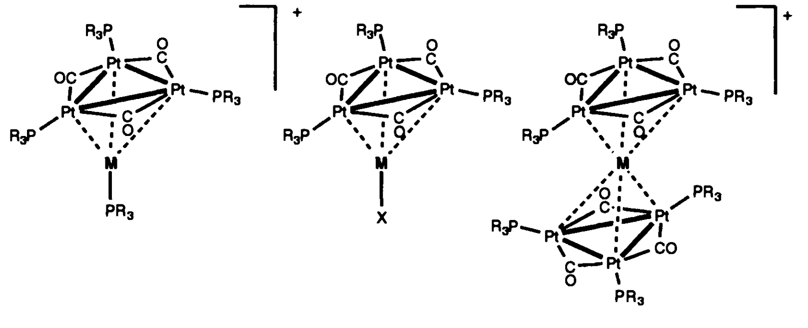


Scheme 2 Reactions of *(3:3:3)*-clusters with Lewis acids

However, phosphine ligand exchange is possible and, therefore, isomerically pure complexes of the type $[\{3{:}3{:}3\}ML]^+$ can be obtained only when phosphine equilibriation of the reagents can be prevented.[10]

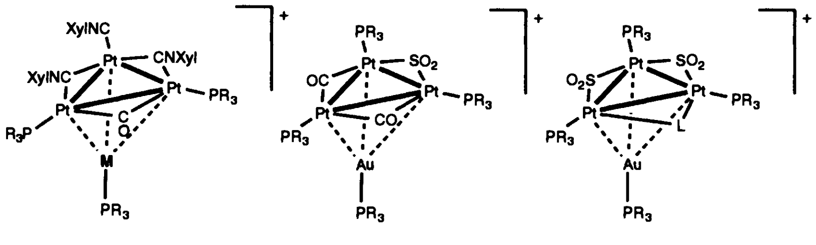
Other Pt_3-species, most notably those having SO_2- or RNC-bridging groups, can also form heterometallic clusters of half-sandwich type.[10,13,14] A representative selection of such compounds is shown in Figure 7.

As might be expected, the 'donor ability' of these triangular



M = Cu^+, Ag^+, Au^+ MX = CuX, AgX, AuX
ZnX_2, CdX_2, InX_3
M = Cu^+, Ag^+, Au^+, Cd^{2+}

Figure 6



M = Cu^+, Ag^+, Au^+ L = SO_2, CNXyl, Cl^-

Figure 7

units is affected by the nature of the bridging and terminal ligands. Preparative studies show that the tendency to form 'half-sandwich' compounds decreases in the order: $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ > $[Pt_3(\mu\text{-}SO_2)_2(\mu\text{-}CO)(PR_3)_3]$ > $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ > $[Pt_3(\mu\text{-}CNR)_2(\mu\text{-}CO)(CNR)(PR_3)_2]$ > $[Pt_3(\mu\text{-}CNR)_3(CNR)_2(PR_3)]$ > $[Pt_3(\mu\text{-}CNR)_3(CNR)_3]$.[10,13]

Even complexes of the *3:3:4*-type can form half-sandwich complexes (Figure 8).[15]

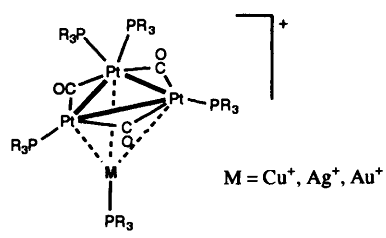
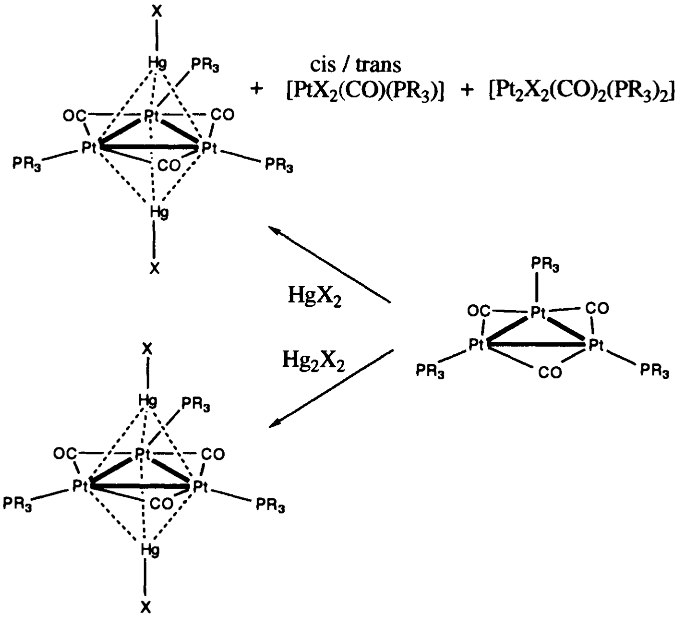


Figure 8

3.2 Electron-transfer Reactions

Particularly interesting are the redox processes which take place between the *3:3:3*-clusters with mercury(II) compounds.[16] As can be seen in Scheme 3, a platinum(0) *3:3:3*-species donates electrons to a mercury(II) halide giving a platinum(I) complex of the type $[Pt_2X_2(CO)_2(PR_3)_2]$ and a bicapped [{*3:3:3*}[HgX}$_2$] cluster containing, at least formally, mercury(I).



Scheme 3 Reactions of (*3:3:3*)-clusters with mercury halides.

Indeed, Pt_3Hg_2-clusters can be directly obtained by reacting one equivalent amount of a *3:3:3*-compound with an Hg_2X_2 salt. Furthermore, the redox potentials are such that any remaining HgX_2 will oxidize platinum(I) intermediates to platinum(II) complexes, once again with formation of 'HgX'-fragments which are stabilized as pentametallic clusters. Interestingly, in the solid state, these compounds are dimeric with a structure of the type shown in Figure 9.

These electron-transfer reactions are not limited to mercury(II) halides: they occur even with organomercury species, as indicated in Scheme 4. If one could find inexpensive clusters, which gave analogous reactions, one could use them for the detoxification of solutions containing organomercury compounds!

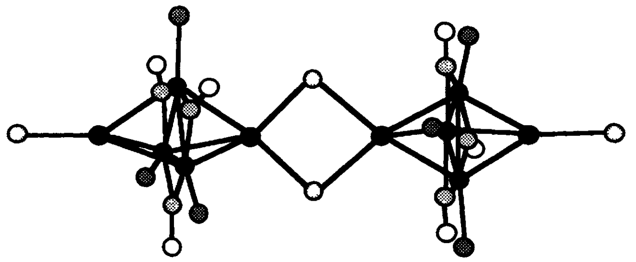
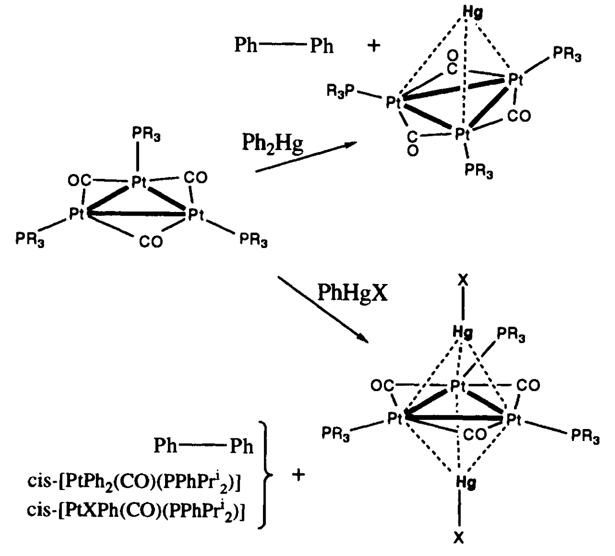


Figure 9 A schematic representation of the crystal structure of $[\{Pt_3(\mu\text{-}CO)_3(PCy_3)_3\}_2\{HgBr\}_4]$(● = Hg; ● = Pt; ○ = Br; ● = P; ○ = O; ◍ = C).



Scheme 4 Reactions of (*3:3:3*)-clusters with organomercury compounds.

3.3 Pt_3-Clusters as 'Electron Acceptors'

As mentioned earlier, the *3:3:3*-clusters can also act as 'electron acceptors'. In this context, it is noteworthy that the 'electron donors' that bind readily to the Pt_3-units are heavy B-metal atoms or ions with $d^{10}s^2$-electron configuration, *i.e.*, mercury(0) and thallium(I), as can be seen from the examples shown in Figure 10.[17,18]

An interesting feature of these compounds of the first two types is that they tend to associate in the solid state, in the case of mercury forming weak Hg—Hg bonds, and in the case of thallium, through electrostatic interactions with coordinated halides. The preparation of complexes of the above types is also remarkably simple, as shown in Scheme 5.

The mercury-containing complexes have very intense colours, ranging from blue to violet. Thus, when a solution of a *3:3:3*-cluster is exposed to traces of mercury vapour, its surface becomes blue. It appears likely that the formation of these mercury addition compounds could be used to construct a sensitive detector for mercury vapour.

Clusters in which the basic Pt_3-unit is bicapped by heterometals other than mercury are also known.[16,19] However, these appear to be exclusively formed (1) by Pt_3-fragments having SO_2-bridging units or (2) where the triangle of Pt-atoms is held together only by metal–metal bonds, as in the examples shown in Figure 11.

4 Palladium Compounds

The cluster chemistry of palladium is poor compared with that of platinum. This is likely due to the low stability of Pd—Pd bonds and the lability of the species formed. Although a variety

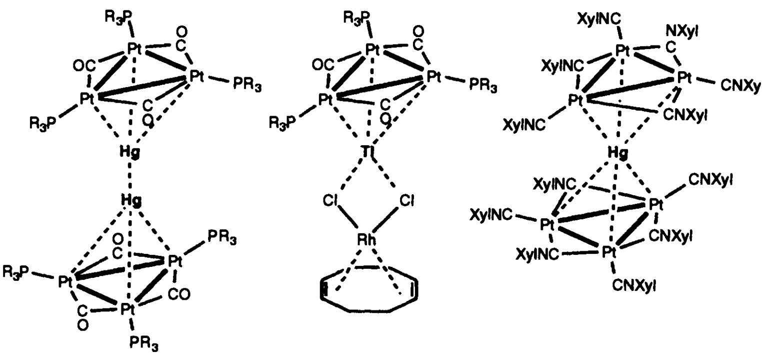
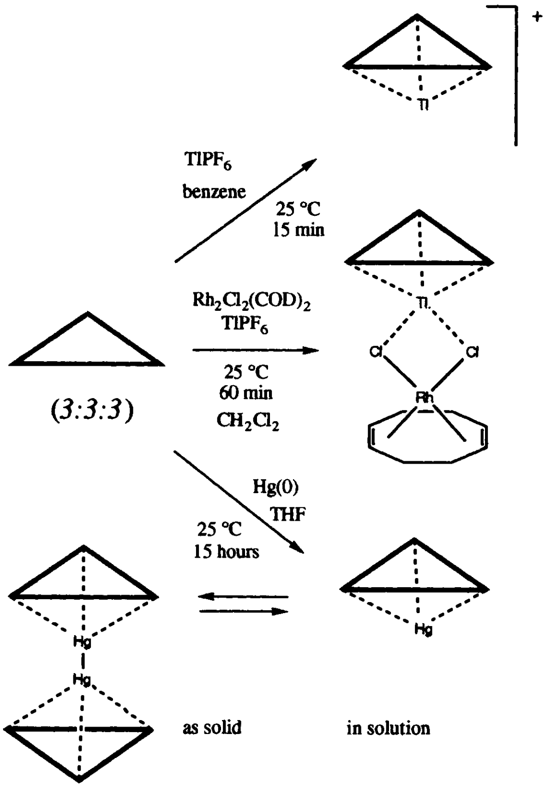


Figure 10



Scheme 5 Reactions of *(3:3:3)*-clusters with Lewis bases.

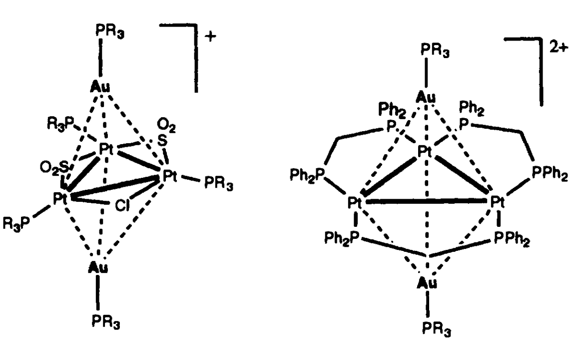


Figure 11

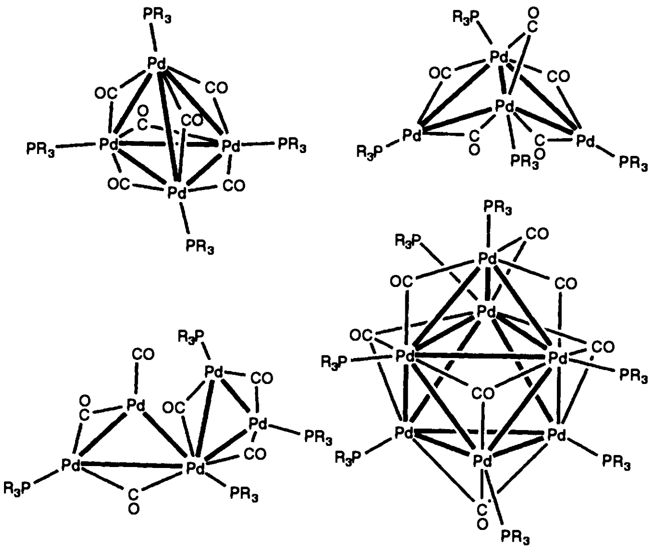
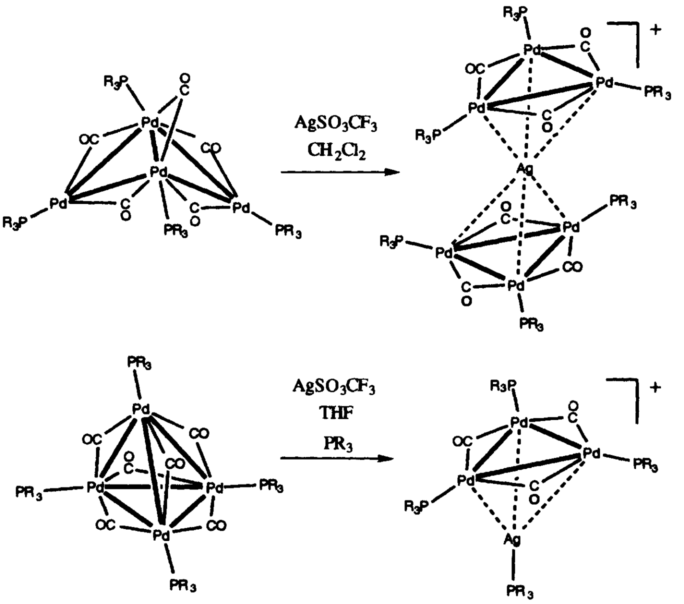


Figure 12

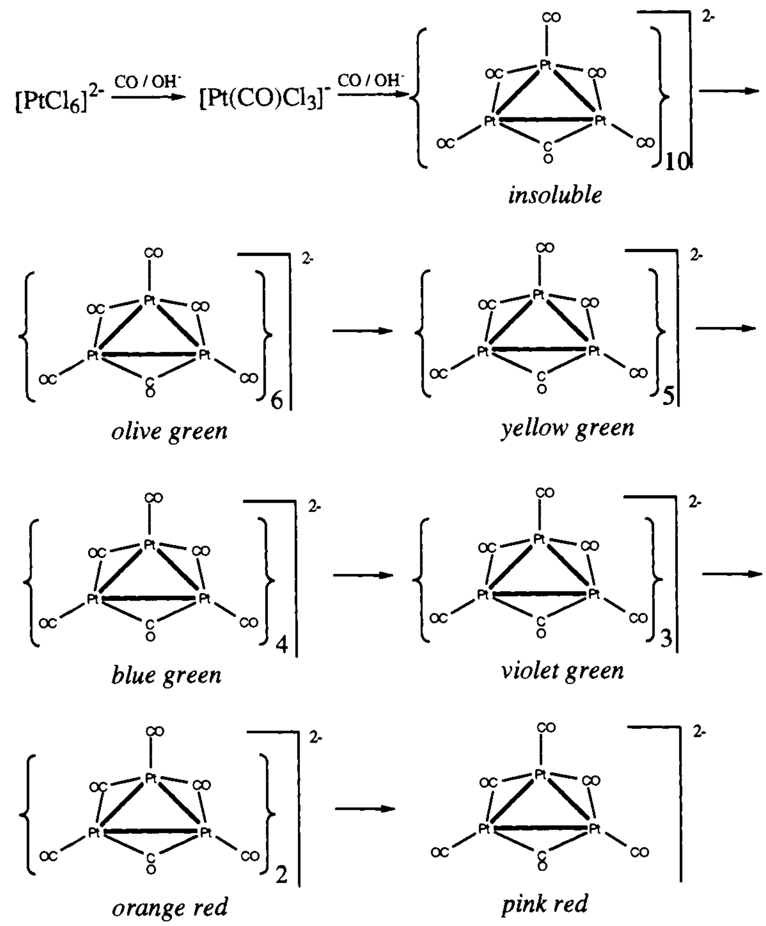


Scheme 6 Reactions of palladium clusters with silver cations.

of homometallic clusters have been identified, they are of varying nuclearities and structures, *e.g.* of the types $[Pd_4(\mu\text{-}CO)_5(PR_3)_4]$,[20] $[Pd_4(\mu\text{-}CO)_6(PR_3)_4]$,[21] $[Pd_5(\mu\text{-}CO)_6(PR_3)_4]$,[22] and $[Pd_7(\mu\text{-}CO)_7(PR_3)_7]$[23] shown in Figure 12. The composition of the isolated product appears to depend on the relative solubilities of the species present in solution as well as the electronic and steric properties of the phosphine. Furthermore, no trimetallic complexes of the type $[Pd_3(\mu\text{-}CO)_3(PR_3)_3]$ appear to be known. However, the reaction of tetrametallic clusters with silver salts has produced heterometallic species of the types shown in Scheme 6.

5 The 'Chini Clusters'

The most intriguing series containing triangular M_3-units, formed by clusters of the Group X metals, are those obtained by



Scheme 7 Reaction pathway for the formation of $[\{Pt_3(\mu\text{-}CO)_3(CO)_3\}_x]^{2-}$ clusters.

Chini and co-workers. The series of compounds given by platinum is shown in Scheme 7.[24]

A schematic representation of the crystal structures of two members of this series are shown in Figure 13.[24]

The formation of the trimetallic anion $[Pt_3(\mu\text{-}CO)_3(CO)_3]^{2-}$ can be easily rationalized in terms of the MO diagram shown in Figure 4. The two additional electrons occupy the a_2'-orbital, its high electron affinity being a consequence of the low σ-donor and high π-acceptor capacities of the terminal CO-ligands. However, this dianion can be considered as a strong Lewis base and, therefore, can associate with $[Pt_3(\mu\text{-}CO)_3(CO)_3]$ acting as a Lewis acid. Furthermore, the electron-donor capacity of the resulting hexametallic dianion remains sufficiently high to allow its association with one additional, uncharged Pt_3-unit forming a 'triple-decker' unit. Up to ten triangular fragments can be assembled through such interactions (see Scheme 7).

The Chini-type compounds also provide one of the rare examples of clusters containing triangular nickel units, *i.e.*, $[\{Ni_3(\mu\text{-}CO)_3(CO)_3\}_3]^{2-}$, which has the same basic structure as the corresponding platinum complex shown in Figure 13.[25]

6 Trimetallic Copper, Silver, and Gold Compounds

Many compounds containing M_3-fragments, where M is a coinage metal, are known. However, the basic structural units forming such species differ from those described earlier for platinum. Here, the M_3-fragments are held together by polyhydrido-complexes of the later transition elements of composition '$M'H_mL_n$' (*e.g.*, M' = Re, Ru, Os, Rh, and Ir; $m = 2$ and 3; L = tertiary phosphine and CO). The heterometallic compounds thus formed are mainly of the types $\{M_3\}\{M'H_mL_n\}_3$, $\{M_3\}\{M'H_mL_n\}_2$, and $\{M_3\}\{M'H_mL_n\}$ shown in Table 2 (M = ●, M' = ○).

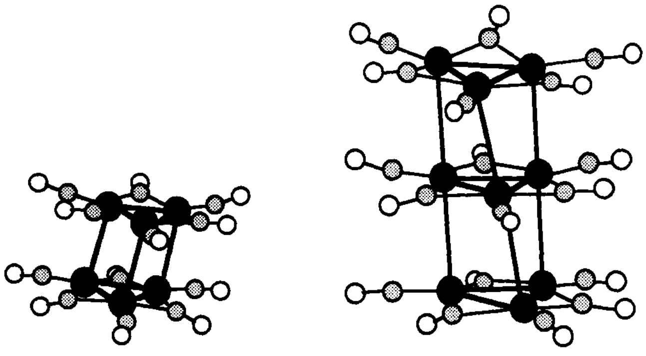
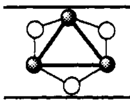
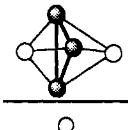
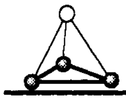
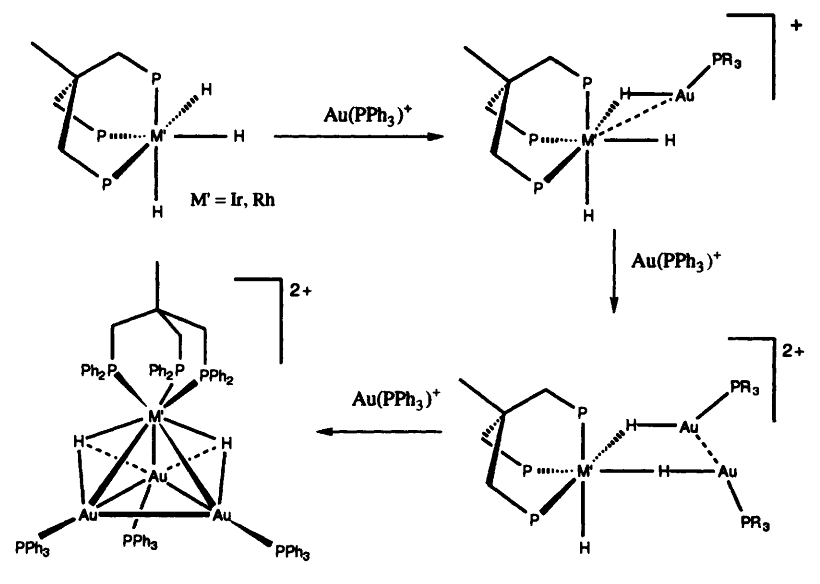


Figure 13 Schematic representations of the crystal structures of $[\{Pt_3(\mu\text{-}CO)_3(CO)_3\}_2]^{2-}$ and $[\{Pt_3(\mu\text{-}CO)_3(CO)_3\}_3]^{2-}$ (● = Pt; ◎ = C; ○ = O).

Table 2 Cu_3-, Ag_3-, and Au_3-Heterometallic clusters

		◎ Cu	◎ Ag	◎ Au
	○	Rh Ir Fe Os	Rh Ir Nb Ta	Ir Nb Ta
	○	Ir		
	○	Re		Rh Ir Ru Re V W



Scheme 8 Reaction of $M'H_3\{CH_3C(CH_2PPh_2)\}$, (M' = Rh and Ir) with one, two, and three equivalent of $Au(PPh_3)^+$.

Many polyhydrido complexes readily assemble up to three AuL^+-cations in a stepwise manner. The products obtained by successive addition of $Au(PPh_3)^+$ to the hydrido-complexes $[M'H_3\{CH_3C(CH_2PPh_2)_3\}]$ (M' = Rh and Ir) are shown in Scheme 8.[26]

It is noteworthy that the tetrametallic $M'Au_3$-cluster is formed only after deprotonation of the above hydrido-complex, *i.e.* the 'assembling unit' is the anionic species '$[M'H_2\{CH_3C(CH_2PPh_2)_3\}]^-$' containing M' in the formal oxidation state of (I).

A particularly interesting feature of clusters of this type is the strict C_3-symmetry of the metal and P-atoms, despite the fact that only two of the three $M'Au_2$-faces contain bridging hydrogen atoms, a feature confirmed by a neutron diffraction study of $[\{Au(PPh_3)\}_3H_2\{Ir\{CH_3C(CH_2PPh_2)_3\}\}][PF_6]_2$ (see Figure 14).[27] Thus, these $M'Au_3$-clusters show the hitherto unique feature of having trimetallic faces with bond distances and angles which are not affected by the presence of bridging hydrides.

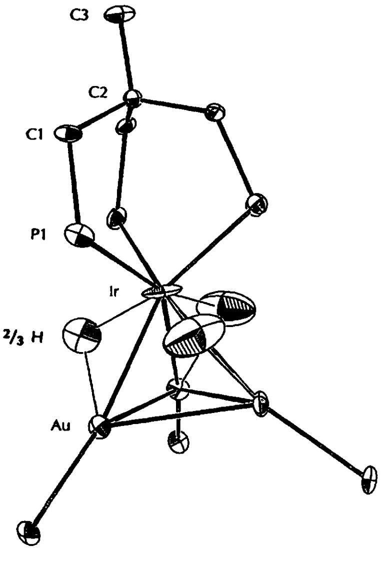


Figure 14 An ORTEP drawing of the cation $[\{Au(PPh_3)\}_3H_2\{Ir(CH_3C(CH_2PPh_2)_3)\}][PF_6]_2$ obtained by neutron diffraction. (The crystallographic C_3-axis of the cation generates three bridging hydride ligands. Each of these is to be taken as having ⅔ occupancy.) Ir–H = 1.77(4) Å; Au–H = 1.95(4) Å.

An LCAO-MO study of complexes containing $M'Au_3$-units has been carried out and the stability of clusters of this type has been correlated with the number of bridging H-atoms present.[28]

Related compounds containing vanadium,[29] tungsten,[30] rhenium, and ruthenium (M' = Re, L = PMe_2Ph, $z = 1$;[31] M' = Ru, 3L = $CH_3C(CH_2PPh_2)_3$, $z = 2$[32]), as well as rhodium[26,33] have also been reported, and one example of each type is shown in Figure 15.

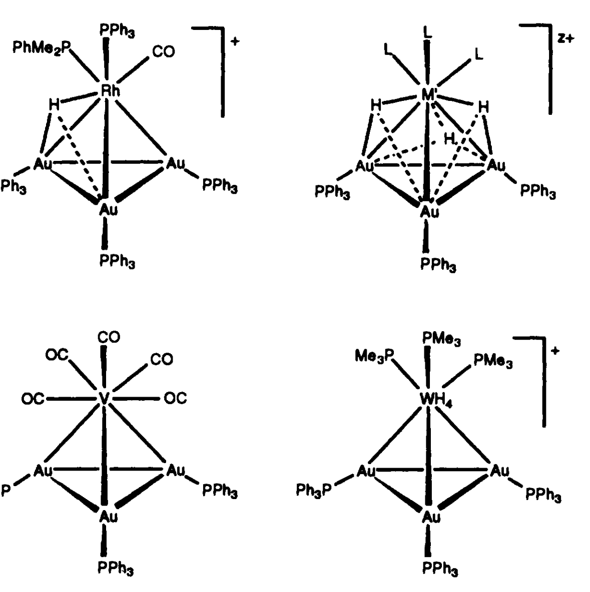
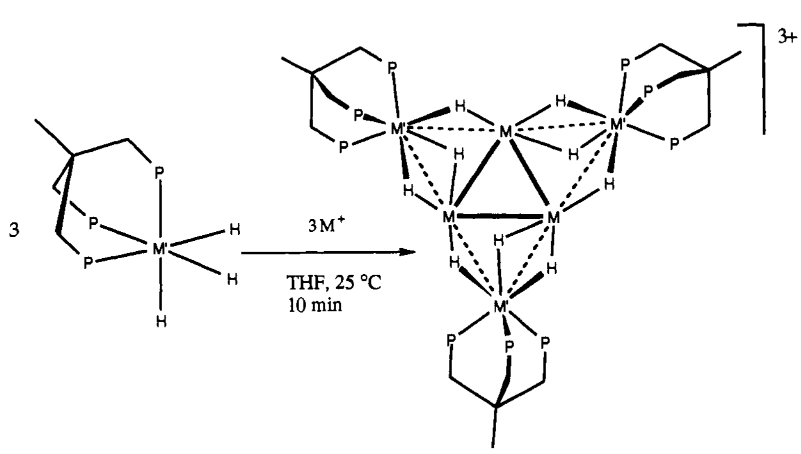


Figure 15

The assembly of Ag_3- and Cu_3-triangles requires higher metal to hydride ratios, the best combination being 1 : 1.[34] However, in these cases, the hydrides can preserve the formal oxidation state, *e.g.* (III) for rhodium and iridium.

The largest class of heterometallic hydrides has the composition $[\{M\}_3\{M'H_3L_3\}_3]^{3+}$ (M' = Rh, M = Cu^I and Ag^I; M' = Rh or Ir, M = Cu^I, Ag^I, or Au^I; L = phosphine) and can be obtained as shown in Scheme 9.

These clusters contain planar hexametallic units. The crystal structure of the rhodium–silver complex has been determined.[35] Although the hydride ligands could not be located on the Fourier map, the position of the Rh–P vectors and the Rh–Ag distances indicate that the Rh–Ag edges are alternatively singly and doubly hydrogen-bridged. However, in solution, all the hydride ligands appear as equivalent on the NMR time-scale.



Scheme 9 Planar hexametallic clusters from $M'H_3\{CH_3C(CH_2PPh_2)_3\}$ and one equivalent of M^+ (M' = Rh, M = Cu, Ag; M' = Rh and Ir, M = Cu, Ag, Au).

Although all the above compounds were obtained with platinum-metal hydrides having tripod-like tritertiary phosphines as co-ligands, these are not necessary, as shown by the formation of $[\{Cu_3\}H_9\{Os(PMe_2Ph)_3)\}_3]^{2+}$.[36]

Furthermore, one can also obtain clusters with a coinage metal-trihydride ratio of 3:2, *e.g.* $[\{Cu(MeCN\}_3H_6\{Ir(PMe_2Ph)_3\}_2]^{3+}$. Its crystal structure has been determined and a schematic representation of the cluster core is shown in Figure 16.[37]

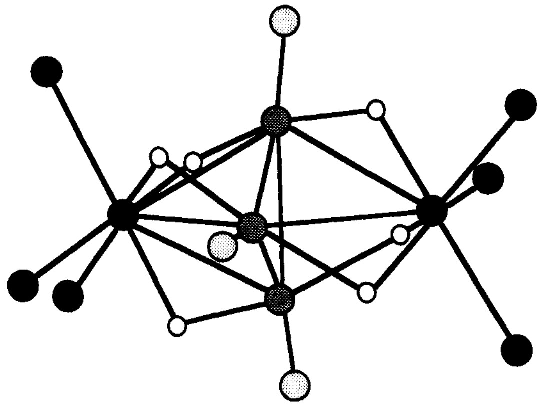
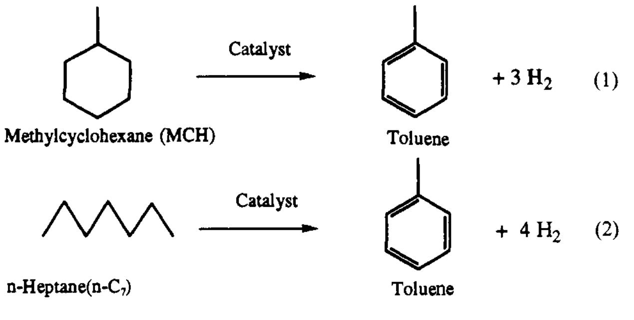


Figure 16 A schematic representation of the crystal structure of $[\{Cu_3(MeCN)_3\}H_6\{Ir(PMe_2Ph)_3\}_2]^{3+}$ (● = Ir; ● = Cu; ● = P; ◎ = N; ○ = H).

While the clusters described above provide fascinating material for theoretical studies, as well as aesthetically pleasing examples of molecular architecture, up to now, the potential for practical applications of these classes of compounds has scarcely been explored.

An exception is provided by the recent study by S. Müller and E. Newson of some homo- and heterometallic clusters as catalyst precursors for a number of heterogeneously catalysed dehydrogenation reactions (equations 1 and 2).



Different types of compounds were used, mainly $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$, $[\{Pt_3(\mu\text{-}CO)_3(PR_3)_3\}_2Ag][CF_3SO_3]$, and $[\{Pt_3(\mu\text{-}CO)_3(PR_3)_3\}_2Cu][PF_6]$. The most extensive series of tests was carried out on reaction 1. The results are summarized in Figure 17.

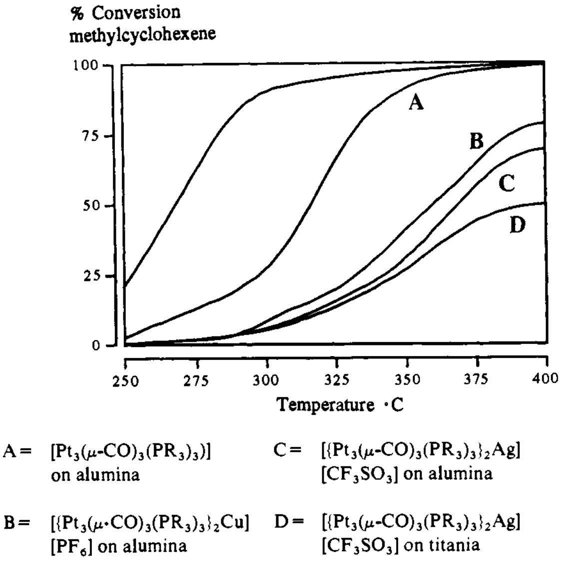


Figure 17 Platinum content: 0.8% w/w; impregnation: CH_2Cl_2 as solvent; activation: *in situ* 1 h under H_2 at 400 °C; reaction conditions: 0.05 g platinum catalyst, 30 ml H_2/min. 0.2 μl MCH or n-C_7/pulse, 2.0 bar abs.

As can be seen, the most efficient catalyst is obtained starting from a homometallic (*3:3:3*)-cluster supported on alumina. Given their preliminary nature, these results can be considered quite promising.

7 Conclusions

The d^{10}-metal centres of the Group X and XI elements are practically unique in forming a wide variety of heterometallic clusters. This versatility is likely due to the ease with which these centres form 16- and even 14-electron species, *i.e.* ML_3- and ML_2-fragments, respectively. This tendency is retained by their trimetallic clusters, which then readily add electron-rich atoms, or ions. Furthermore, filled HOMO orbitals of suitable energy are often present and can donate electrons to suitable Lewis acids, generating the rich synthetic and structural chemistry described above.

It is expected that the Lewis base/Lewis acid idea, despite its formal nature, will be useful not only in rationalizing a wealth of synthetic chemistry, but also in predicting the existence of new classes of clusters. However, it is also clear that the platinum systems discussed above are uncommon cases, as their preformed trimetallic clusters can be directly used to build up more complex molecular structures

Finally, it should not be ruled out that LCAO-MO examination of other oligometallic building blocks could lead to the discovery of new families of heterometallic clusters with features of interest for solid-state chemistry and catalysis

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