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Zero-valent Platinum Complexes and their Role in the Synthesis of Di-, Tri-, and Tetra-nuclear Metal Compounds

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Discovery of the compounds [Pt(C_2H_4)$_3$] and [Pt(C_2H_4)$_2$(PR_3)], and new procedures for preparing [Pt(C_2H_4)(PR_3)$_2$] and [Pt(cod)$_2$], have enabled these species to be used in the synthesis of many new organoplatinum compounds containing metal–metal bonds. This article summarises recent progress in this field.

Introduction

Major advances have been made in several areas of organoplatinum chemistry following the discovery of the compound [Pt(C_2H_4)$_3$] [1], and the synthesis of the complexes [Pt(C_2H_4)$_2$(PR_3)] [2]. These reagents are very reactive, the latter functioning as sources of $PtPR_3$ groups, whereas tris(ethylene)platinum behaves as a 'ligand free' source of platinum. These compounds became available through a new synthesis of [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) [1, 3], a complex with its own extensive chemistry. Moreover, the results have had a synergistic effect on the organometallic chemistry of other transition metals. For example, the preparation of [Pt_3($CNBu^t$)$_6$] [4] from [Pt(cod)$_2$] prompted work which led to the characterization of [Fe($CNBu^t$)$_5$] [5] and [Fe_2(CNEt)$_9$] [6], and the discovery of the bridged fluoroalkylidenediplatinum complex [$Pt_2\{\mu$-$C(CF_3)_2\}$(cod)$_2$] [7] initiated new chemistry of the transition metals involving alkylidene and alkylidyne ligands [8].

In this article we shall focus on one aspect of the chemistry of [Pt(C_2H_4)$_3$], [Pt(C_2H_4)$_2$(PR_3)], and [Pt(cod)$_2$], namely the employment of these species in the formation of complexes containing two to four metal atoms. At first, however, it is interesting to place the above Pt(0) complexes in the context of earlier work.

It is generally accepted that the growth of organometallic chemistry in the decade following 1952 was due to the recognition of the structure of Ferrocene [9–11]. However, organometallic chemistry would not have attained its present high level of activity without several other seminal discoveries, one of which was made in 1960. Stemming from association of the 'nickel effect' with Ziegler-Natta catalysis, the Mülheim researchers [12] prepared several zero-valent nickel complexes in which the only ligands present were unsaturated olefinic molecules. These species, which include bis(cyclo-octa-1,5-diene)nickel, (cyclododecatriene)nickel, and tris(ethylene)nickel, proved to be very reactive since the ligands are readily displaced by other molecules, hence reactions can occur easily at the metal centre. Lability of the ligands is also responsible for the high reactivity of nickel tetracarbonyl, although its toxicity, ready thermal decomposition, and volatility makes it less amenable for use as a synthetic precursor than the 'naked' nickel complexes developed by Wilke and his co-workers [12]. The latter, except for the very unstable [Ni(C_2H_4)$_3$], are all easier to manipulate in the laboratory than the carbonyl.

Since 1962 the various olefin-nickel complexes, and to a lesser extent the tetracarbonyl, have been employed as starting materials for the synthesis of a plethora of organonickel compounds, so that our knowledge of the organic chemistry of this element is the most extensive of all the transition metals except possibly iron. The wide scope of organonickel chemistry is in marked contrast with the more narrowly based organic chemistry of platinum or palladium. At first this seems surprising since organocomplexes of these metals have a long history originating from the discovery of Zeise's salt [13] over 150 years ago. However, there has been a difficulty in developing organo-platinum or -palladium chemistry arising from the absence of suitable precursors for synthetic work. Thus, unlike [Ni(CO)$_4$], the tetracarbonyls of Pd and Pt have only a fleeting existence [14, 15], and thus cannot be used as starting compounds for chemical syntheses. The absence of suitable precursors has been somewhat alleviated by the facility with which platinum or palladium in their +2 oxidation states form stable complexes having carbon-metal σ-bonds. These compounds, existing in large numbers, have mostly been prepared *via* reactions of metal complex halides with Grignard or organo-lithium reagents, or by 'oxidativeelimination' reactions of d^{10} tertiary phosphine-palladium or -platinum species [16]. Nevertheless, the absence until recently [1] of zero-valent platinum or palladium compounds with olefinic groups as the only ligands has had a major inhibiting effect on the development of the organometallic chemistry of these elements. Hence the discovery of $[Pt(cod)_2]$ by Müller and Göser [17] was a very important result since it established that for platinum such olefinic complexes were indeed capable of existence. However, the method of synthesis of $[Pt(cod)_2]$ *via* $[PtPr^{i}_{2}(cod)]$ was not practicable for exploiting the reactivity of the compound. Hence, during the course of studies on the oxidative-insertion of platinum into the cage structures of carbaboranes [18], a new synthesis of $[Pt(cod)_2]$ was successfully developed by J. L. Spencer [3], with the object of using the complex as a precursor to even more reactive Pt(0) species. Whereas excess ethylene only partially displaces the cod ligands from $[Ni(cod)_2]$, reaction of ethylene with $[Pt(cod)_2]$ affords the compound $[Pt(C_2H_4)_3]$ [19] which has the useful property of being thermally more stable than $[Ni(C_2H_4)_3]$ [12]. Moreover, by saturating solutions of $[Pt(cod)_2]$ with ethylene and adding either one or two mols of a tertiary phosphine it is possible to obtain the complexes $[Pt(C_2H_4)_2(PR_3)]$ [2], $[Pt(C_2H_4)(PR_3)_2]$ [20], or $[Pt(PR_3)_2]$ [21]. The latter species form only with bulky ligands [*e.g.* $P(cyclo\text{-}C_6H_{11})_3$ or $PBu^{t}_{2}Me$].

Before describing some reactions of these compounds which afford complexes containing metal–metal bonds, it is useful to review briefly the scope of such linkages in platinum chemistry, and to comment on the observed structures in relation to the number of valence electrons present.

Metal–metal Bonds in Platinum Chemistry

Platinum readily forms compounds having metal–metal bonds. The cluster anions $[Pt_{18}(CO)_{36}]^{2-}$ and $[Pt_{26}(CO)_{32}]^{2-}$, discovered by Chini and his coworkers [22, 23], are remarkable examples of the tendency of platinum in this respect. The mechanism of formation of these large clusters is not understood, but undoubtedly proceeds in a stepwise fashion. Studies underway in various laboratories on the synthesis and properties of species with fewer platinum atoms are also useful, because much remains to be learned about the reactivity of organic molecules at di-, or tri-, or even tetra-nuclear metal centres. The simplest systems with metal–metal bonds are dimetal complexes of which three types are known: homonuclear species with bridging ligands, homonuclear species without bridging ligands, and heteronuclear species with bridging ligands. These classes are illustrated by the compounds $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$ [24, 25], $[Pt_2Cl_4(CO)_2]^{2-}$ [26, 27], and $[PtW\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$ [20], respectively.

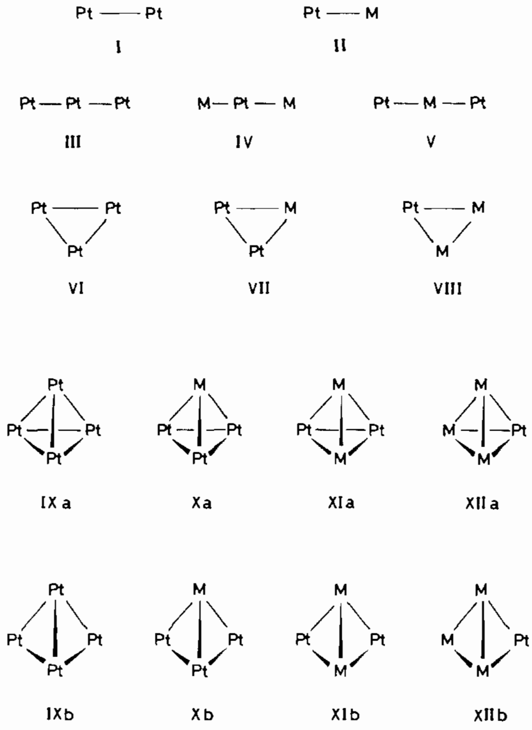


Fig. 1. Metal atom arrangements in platinum complexes containing two to four metal atoms.

With trimetallic complexes, the structural possibilities are greater, since either a metal sequence or a metal triangle can be involved, and there is the possibility of homo- or hetero-nuclear metal–metal bonds (see Fig. 1, III–VIII). As yet there appears to be no known species involving platinum and a transition metal with the back-bone structure V. It can be argued that the compound $[Pt_3(\mu_2\text{-}CF_3C_2CF_3)_2\{\mu_2\text{-}(CF_3)C_2(CF_3)(CF_3)C_2(CF_3)\}(cod)_2]$ [28] provides an example of structure III, however, one of the two Pt–Pt separations is relatively long for a bond [29]. In contrast there are several platinum-containing complexes known with the metal atom arrangement IV, which can be linear without bridging ligands as in $[Mn_2Pt(CO)_{10}L_2]$ (L = py, CNR, or CO) and $[Mo_2Pt\{C(OEt)(NHC_6H_{11})\}(CNC_6H_{11})(CO_6(\eta\text{-}C_5H_5)_2]$ [30], or bent with bridging ligands as in $[Mn_2Pt(\mu\text{-}PPh_2)_2(CO)_9]$ [31] and $[PtW_2(\mu\text{-}CC_6H_4Me)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [32]. There is also a rapidly growing number of complexes with the triangular arrangements VI–VIII, *e.g.*

VI: $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ [33–37], $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$ [33, 34], $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\}_3(CO)_3]$ [38], $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PR_3)_3]$ [36], and $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ [4].

VII: $[\mathrm{FePt_2(CO)_5\{P(OPh)_3\}_3}]$ [39], $[\mathrm{Pt_2Ru(CO)_5(PR_3)_3}]$, $[\mathrm{Pt_2Ru(CO)_4(PR_3)_4}]$ [40], and $[\mathrm{MPt_2\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2}]$ (M = Cr or W) [36].

VIII: $[\mathrm{Fe_2Pt(CO)_8(PR_3)_2}]$, $[\mathrm{Fe_2Pt(CO)_9(PR_3)}]$ [41], $[\mathrm{Fe_2Pt(CO)_8(cod)}]$ [42], $[\mathrm{PtRu_2(CO)_8(diphos)}]$ [40], $[\mathrm{PtOs_2(CO)_7(PMePh_2)_3}]$ [40], and $[\mathrm{PtRe_2(\mu\text{-}H)_2(CO)_9(PPh_3)}]$ [8, 43].

Several tetranuclear metal complexes containing platinum are known. Whereas homonuclear species are rare, the number of heteronuclear compounds reported in the literature is rapidly increasing. The core atoms usually adopt tetrahedral, distorted tetrahedral or butterfly geometries (Fig. 1). It is often difficult to decide whether a particular structure should be classed as 'tetrahedral' or 'butterfly', based on the metal–metal distances established by X-ray crystallography. As more structural studies are reported it is becoming evident that the distances between various core atoms range over a continuum of values corresponding to those which are clearly bonding to those which are so great that no direct metal–metal bonding can occur. For many molecules there appears to be a delicate balance between the *closo*-tetrahedral core and the open butterfly geometry. Indeed, the dynamic behaviour frequently observed *via* NMR spectroscopy in solution for the peripheral ligands may involve in some cases flexing of the metal cage between T_d and C_{2v} symmetries.

Tetranuclear platinum complexes were first obtained by Chatt and Chini [33] by treating the trinuclear $[\mathrm{Pt_3(CO)_3(PR_3)_4}]$ compounds with carbon monoxide. An X-ray diffraction study [44] on $[\mathrm{Pt_4(CO)_5(PMe_2Ph)_4}]$ showed that the core atoms adopt a butterfly arrangement IXb, since one Pt–Pt distance [3.543(8) Å] is clearly non-bonding. The compound $[\mathrm{Pt_4(CO)_5(AsPh_3)_3}]$ was also prepared [33] and with two fewer cluster valence electrons (see below) may be an example of a molecule having the tetrahedral core IXa.

As yet no compounds with tetrahedral or butterfly geometries have been reported containing three platinum atoms and an atom of another metal (Fig. 1, Xa or Xb) [45]. There is, however, an increasing number of complexes with the core structure $\mathrm{M_2Pt_2}$. X-ray crystallographic studies have revealed that in the following species the metal atoms adopt the butterfly geometry, with the distances between the two platinum atoms forming the wing tips of the butterfly being given in brackets:

$[\mathrm{Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2}]$ [3.206(1) Å] [46]

$[\mathrm{Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2}]$ [2.987(4) Å] [47]

$[\mathrm{Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2}]^-$ [2.966(1) Å] [42]

$[\mathrm{Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2}]$ [2.998(2) Å] [42]

The Pt–Pt separations are all greater by 0.4 Å than twice the covalent radius of platinum. However, in $[\mathrm{Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4}]$ a Pt–Pt distance of 2.790(7) Å is regarded as bonding [44], so that in the above $\mathrm{Os_2Pt_2}$, $\mathrm{Co_2Pt_2}$, and $\mathrm{Fe_2Pt_2}$ species, only with the diosmium-diplatinum complex is there unambiguous evidence from the metal atom separations of the absence of Pt–Pt bonding, although such bonding in the other complexes must be weak if it occurs [29].

The complex $[\mathrm{Mo_2Pt_2(\mu\text{-}CO)_4(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)_2}]$ may have a butterfly arrangement for the core atoms, but an X-ray crystallographic study of the related compound $[\mathrm{Mo_2Pt_2(\mu\text{-}CO)_6(PEt_3)_2(\eta\text{-}C_5H_5)_2}]$ revealed a planar arrangement of metal atoms, forming two triangles sharing a Pt–Pt edge (2.662 Å) [48].

The cluster compounds $(\mathrm{Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)})$ have molecular structures with the $\mathrm{Os_3Pt}$ geometry corresponding to XIIa [49]. These complexes react with electron pair donor ligands (see later) to give derivatives $[\mathrm{Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)L}]$ (L = $\mathrm{PR_3}$, $\mathrm{AsPh_3}$, or CO) in which the metal atoms adopt the butterfly configuration XIIb. Thus in $[\mathrm{Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2}]$ there is one Os–Pt separation [3.530(1) Å] which is substantially longer than the other two [2.848(1) and 2.717(1) Å] [50].

Application of Electron Counting Rules to Metal Clusters Containing Platinum

In many polynuclear metal complexes it is possible to relate the geometry of the core atoms to the number of skeletal electron pairs required to fill the bonding molecular orbitals of the particular cluster [51]. Thus there is a characteristic number of valence electrons associated with a given structure. Generally for triangular and tetrahederal clusters, and in contrast to the larger clusters, the 18 electron rule is followed by the individual metal atoms, and it is possible to assume that metal–metal bonds coincide with the metal–metal vectors. Most organometallic three-atom clusters have 48 valence electrons, *e.g.* $[\mathrm{Os_3(CO)_{12}}]$ or $[\mathrm{Co_3(CO)_3(\eta\text{-}C_5H_5)_3}]$, whereas four-atom clusters have 60 valence electrons, *e.g.* $[\mathrm{Ir_4(CO)_{12}}]$ or $[\mathrm{Fe_4(CO)_4(\eta\text{-}C_5H_5)_4}]$. However, the number of valence electron pairs required to hold the cluster together in a particular geometry is reduced when platinum atoms are present. Thus for triangular clusters involving platinum there are species known with 42, 44 or 46 cluster valence electrons, rather than the 48 preferred by most other metals.

42 electrons	$[\mathrm{Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3}]$, $[\mathrm{Pt_3(\mu\text{-}CO)_3(PR_3)_3}]$, $[\mathrm{Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\}_3(CO)_3}]$.
44 electrons	$[\mathrm{Pt_3(\mu\text{-}CO)_3(PR_3)_4}]$, $[\mathrm{Pt_3(CO)_6}]^{2-}$, $[\mathrm{Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2}]$.

46 electrons $[PtFe_2(CO)_8(cod)]$, $[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PBu^t_2Me)_3]$.

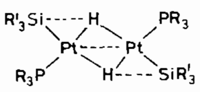
Tetranuclear clusters also show an apparent deficiency of cluster valence electrons when platinum atoms are incorporated. Tetrahedral structures, *e.g.* $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$, can exist with 58 electrons rather than 60. Moreover, the compound $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ has only 58 electrons and yet, as mentioned above, it adopts a butterfly geometry. This configuration is also shown by the several 58 electron clusters containing two platinum atoms listed earlier, *e.g.* $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$. The folded butterfly geometry corresponds to an octahedron with two adjacent vertices missing, and as such requires 7 skeletal electron pairs according to Wade's rules. However, this geometry is adopted by $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ with only 5 skeletal electron pairs.

The apparent electron deficiencies in the tri- and tetra-nuclear metal clusters containing platinum are related to the fact that in many of its mononuclear complexes platinum does not obey the 18 electron rule but follows a 16 electron bonding scheme, due to destabilization of a p orbital. Correspondingly, in polynuclear species involving platinum, for given geometries there are evidently cluster valence molecular orbitals of relatively high energy which are not filled [52]. Thus stable core structures are produced employing fewer valence electrons than expected by analogy with clusters formed by nickel [53], and by other metals, particularly those of the Fe and Co subgroups.

Formation of Metal–metal Bonds from Zero-valent Platinum Complexes

Dinuclear Metal Compounds

The largest class of platinum compounds with metal–metal bonds are the dimetal species and most have been obtained starting from the new zero-valent platinum reagents [54].



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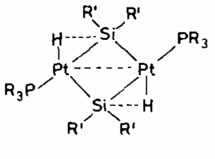

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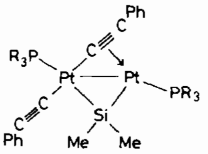

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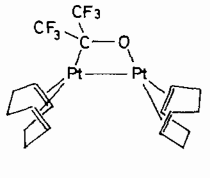

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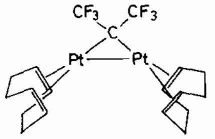

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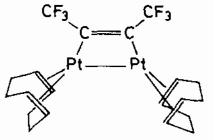


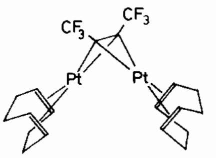
(6)

The complexes $[Pt(C_2H_4)_2(PR_3)]$ undergo oxidative-addition reactions with triorganosilanes $SiHR'_3$ to afford binuclear compounds $[Pt(\mu\text{-}H)(SiR'_3)(PR_3)]_2$ (1) [55]. An X-ray diffraction study on the compound with R = cyclo-C_6H_{11} and R' = Et revealed a Pt–Pt separation of 2.692(3) Å. The hydrido ligands were not detected, but the spectroscopic properties (IR and NMR) and chemical reactivity of the compounds have led to the proposal that the bridge bonding is multi-centre and asymmetric, involving both $Pt(\mu\text{-}H)Pt$ and $Pt(\mu\text{-}H)Si$ interactions. Thus ^1H NMR studies revealed the signal for the hydrido ligands at the unusual chemical shift of *circa* δ 3 p.p.m. Moreover, with some reagents $[P(OPh)_3$ or CO] bridge cleavage occurs with release of $HSiR'_3$. However, further diffraction studies (X-ray and neutron) are required to locate the hydrido-ligands before firmer conclusions about the nature of the bridge bonding can be drawn, and even these studies may not resolve the problem since the compounds undergo dynamic behaviour in solution. Firmer evidence for $Pt(\mu\text{-}H)Si$ interactions is found in the complexes (2), prepared by reacting $[Pt(C_2H_4)_2(PR_3)]$ with diorganosilanes SiR'_2H_2 [56]. These compounds also show in their ^1H NMR spectra hydrido ligand signals at relatively low field (*circa* δ 2 p.p.m.). Moreover, an X-ray diffraction study on $[PtH(\mu\text{-}SiMe_2)\{P(cyclo\text{-}C_6H_{11})_3\}]_2$ [Pt–Pt 2.708(1) Å] led to location of the hydrido ligands (Pt–H 1.78 Å) ***trans*** to the shorter Pt–Si bonds at a distance of 1.72 Å from the *cis* Si atom. The sum of the van der Waals radii for Si and H is 3.2 Å.

The compounds $[Pt(C_2H_4)_2(PR_3)]$ undergo an unusual oxidative reaction with $Si(C{\equiv}CPh)_2Me_2$ resulting in C–Si bond cleavage and formation of the species (3) [57]. One metal atom is formally Pt(III) and the other Pt(I). An X-ray diffraction study on (3, R = cyclo-C_6H_{11}) established a Pt–Pt distance of 2.703(1) Å, which is well within the range for a metal–metal bond [29].

Several diplatinum compounds have been isolated from reactions between fluorocarbon species and Pt(0) complexes. Hexafluoroacetone and $[Pt(cod)_2]$ react to give several products including (4) [58]. The latter has one of the shortest known metal–metal bonds [2.585(1) Å] for a diplatinum complex. Hexafluoropropene and $[Pt(cod)_2]$ undergo an interesting reaction to afford compound **(5)** [7]. The mechanism of this reaction may involve attack of $[Pt(cod)_2]$ on a mononuclear platinum-carbene intermediate in a process related to those described below.

Equimolar amounts of $[Pt(cod)_2]$ and $[Pt(\eta^2\text{-}CF_3C_2CF_3)(cod)]$ react to give the diplatinacyclobutene complex **(6)**, and traces of its isomer **(7)** [59]. Many bridged alkyne-diplatinum complexes are known [60, 61] having structures similar to **(7)**, and typical of these is **(8)**, prepared by reacting $[Pt(C_2H_4)_3]$ with $Me_3SiC{\equiv}CSiMe_3$. In compounds such as **(7)** or **(8)** it is doubtful if there is any direct metal–metal bonding. The Pt–Pt separation is probably determined by the stereochemistry associated with the bonding of the platinum atoms to the two orthogonal π orbitals of the alkyne [62]. Indeed, in $[Pt_2(\mu_2\text{-}PhC_2SiMe_3)(cod)_2]$, structurally analogous to **(7)**, the Pt–Pt distance (2.914 Å) [61] is at the limiting range for bonding [29]. Moreover, for these structures in which the alkyne is perpendicular to the Pt–Pt vector each metal atom adopts a 16 electron configuration as in **(7)** or, less commonly, a 14 electron configuration as in **(8)**.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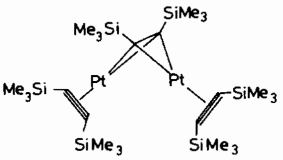
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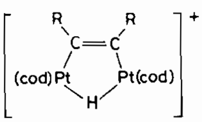
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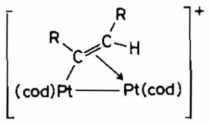
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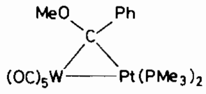
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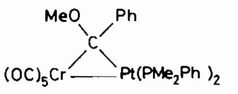
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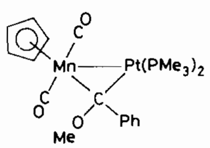
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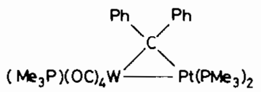
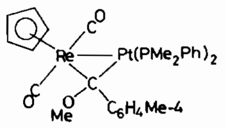

(14)

The metal–metal bonds in the complexes containing diplatinacyclobutene rings can be protonated giving initially a Pt(μ-H)Pt species **(9)** followed by an η^1, η^2-bridged vinyl cation **(10)** [59].

As mentioned earlier, complex **(5)** is thought to result from attack of $[Pt(cod)_2]$ on a mononuclear platinum-carbene or -ylide intermediate $[PtC(CF_3)_2(cod)]$. This prompted the idea [63] that Pt(0) complexes would react with mononuclear metal-carbene and -carbyne compounds in general, to afford species containing heteronuclear metal–metal bonds and bridging alkylidene or alkylidyne ligands. The carbon–metal bonds in mononuclear metal-carbene or -carbyne complexes are known to be dipolar in character and this would make them susceptible to attack by Pt(0) [64]. These ideas were confirmed by experiment, and complexes **(11)**–**(16)** are representative of many that have been synthesized by addition of the complexes $[Pt(C_2H_4)(PR_3)_2]$, generated *in situ* from $[Pt(C_2H_4)_3]$, to the appropriate metal-carbene or -carbyne complex [20, 35, 65–67].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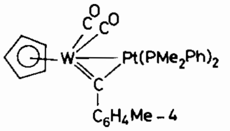
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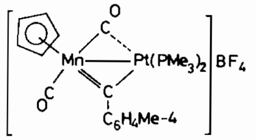
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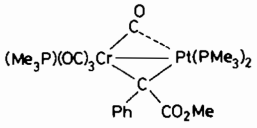
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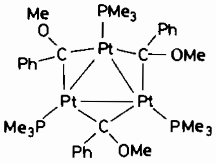
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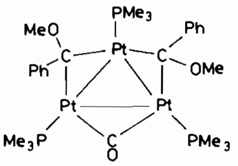
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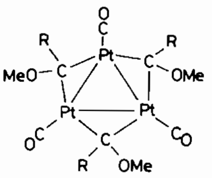
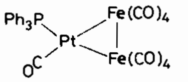

(21, R = C_6H_4Me-4)


(22)

Structural studies on the heteronuclear dimetal compounds have revealed a number of novel features. Thus in **(11)** the alkylidene ligand asymmetrically bridges the Pt–W bond, being closer to the platinum [20]. This displacement is less in the complex $[(Me_3P)(OC)_4\overline{W\{\mu\text{-}C(OMe)C_6H_4Me\}Pt}(PMe_3)_2]$, which also has a shorter metal–metal bond than **(11)**, confirming that the geometry of the dimetallacyclopropane ring systems are susceptible to the nature of the ligands on the metal atoms [66]. In **(16)** the W–μ-C distance corresponds to that expected for a W=C bond, and the two CO ligands lie back over the Pt–W bond probably reflecting some interaction of the C≡O groups with the platinum atom [65].

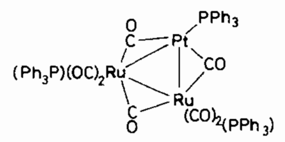
Preliminary results indicate that the various heteronuclear dimetal complexes will have an extensive chemistry. In this article only a brief indication of recent research can be given.

Compounds containing bridging C(OMe)R ligands can be converted to cationic complexes possessing bridging CR groups by treatment with $Me_3O^+BF_4^-$. The salts formed in this manner react with nucleophiles to produce a variety of products. Thus the neutral dimetal compound $[MnPt\{\mu\text{-}C(OMe)C_6H_4Me\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ reacts with $Me_3O^+BF_4^-$ to give the complex **(17)** [67]. The latter with Me_3P and $LiSC_6H_4Me$-4 affords the compounds $[MnPt\{\mu\text{-}C(PMe_3)C_6H_4Me\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]BF_4$ and $[MnPt\{\mu\text{-}C(PMe_3)C_6H_4Me\}(SC_6H_4Me)(CO)_2(PMe_3)(\eta\text{-}C_5H_5)]$, respectively [68]. The salt $[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3]BF_4$, generated from $[(Me_3P)(OC)_4\overline{Cr\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$, and $Me_3O^+BF_4^-$, undergoes a novel reaction with NaOMe to give the neutral complex **(18)**, containing a CO_2Me group [67]. Evidently, a CO group migrates from chromium to the bridging alkylidyne carbon of the salt and is attacked by OMe^-.

We referred above to the asymmetric bridging of the carbene ligands observed in some of the complexes *via* X-ray crystallographic studies. This reflects partial transfer of these ligands from chromium or tungsten to platinum. It is not surprising therefore that complete transfer of the carbene ligands from one metal centre to the other is observed under certain conditions. Thus $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_5(PMe_3)_2]$ in toluene at 80 °C decomposes to give $[Cr(CO)_5(PMe_3)]$ and the triplatinum compounds **(19)** and **(20)** [20]. Reaction of $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\}(CO)_5(cod)]$ with carbon monoxide leads to rupture of the Pt–W bond with formation of $[W(CO)_6]$ and the triplatinum complex **(21)** [38]. The latter, and **(20)**, were produced as a mixture of two isomers, separated by chromatography.

Trinuclear Metal Compounds

It was observed some years ago that the complexes $[Pt(PR_3)_4]$ or $[Pt(PhCH{:}CHPh)(PPh_3)_2]$ react with $[Fe_2(CO)_9]$, $[Ru_3(CO)_{12}]$, and $[H_2Os(CO)_4]$ to give a variety of heteronuclear trimetal complexes, *e.g.* (22)–(24) [40, 41]. Generally the yields of the trimetal species from these reactions are very low, the major products being tertiaryphosphine-substituted derivatives of iron, ruthenium, or osmium carbonyls. Because of their CO abstracting ability, discussed in the next Section, it is likely that the complexes $[Pt(C_2H_4)_2(PR_3)]$ and Fe, Ru, or Os carbonyls would afford trimetal species in high yields. Indeed the $[Pt(C_2H_4)_2(PR_3)]$ compounds react with the carbene complexes $[M\{C(OMe)Ph\}(CO)_5]$ (M = Cr or W) to afford products such as **(25)** in which both CO and C(OMe)Ph ligands have been transferred from chromium or tungsten to platinum [36].



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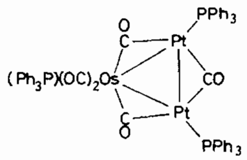

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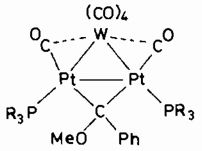

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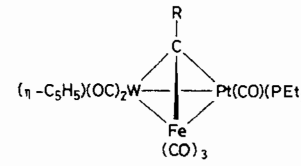
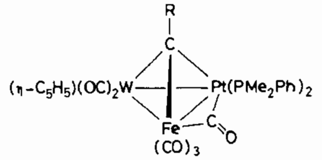
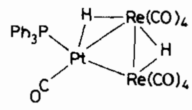


(26, R = C₆H₄Me-4)



(27, R = C₆H₄Me-4)

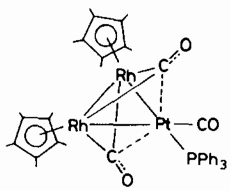


(28)

Dimetal compounds of the kind illustrated by **(16)** are unsaturated and will add another metal fragment to give trimetal species containing an alkylidyne ligand triply bridging three different transition metal atoms. Thus treatment of $[Pt(C_2H_4)_3]$ with two equivalents of PEt_3 followed by $[W{\equiv}CC_6H_4Me(CO)_2(\eta\text{-}C_5H_5)]$ yields $[PtW(\mu\text{-}CC_6H_4Me)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$, which with $[Fe_2(CO)_9]$ affords $[Fe(CO)_4(PEt_3)]$ and the cluster complex **(26)**. Similarly, treatment of **(16)** with $[Fe(CO)_5]$ gave compound **(27)** [69]. These stepwise syntheses of clusters with three different transiton elements have been carried out with reagents other than those containing platinum, illustrating how work with the Pt(0) compounds has stimulated related research. Thus the bridged alkylidyne complex $[RhW(\mu\text{-}CC_6H_4Me)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ reacts with $[Fe_2(CO)_9]$ to give $[FeRhW(\mu_3\text{-}CC_6H_4Me)(\mu_2\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ [69].

Since the reagents $[Pt(C_2H_4)(PR_3)_2]$, generated from $[Pt(C_2H_4)_3]$, readily add to M=C and M≡C bonds it was of importance to establish whether similar reactions would occur with metal–metal multiple bonds. The first success in this area was achieved with $[Re_2(\mu\text{-}H)_2(CO)_8]$, a compound containing a Re=Re bond [70]. The dirhenium species reacts with [$Pt(C_2H_4)(PPh_3)_2$] to give the 46 electron tri-metallic compound **(28)** [8, 43]. It should be noted that in the product a CO ligand is attached to platinum, having thereby displaced a PPh_3 group. This is a common feature in these cluster building reactions, and other examples will be described below. Interestingly, **(28)** is only formed in low yield from the reactionof [$Re_2(\mu\text{-}H)_2(CO)_8$] with [$Pt(C_2H_4)_2(PPh_3)$].

The compound [$Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2$], which has a Rh=Rh bond [71], reacts with [$Pt(C_2H_4)(PPh_3)_2$] to give the novel complex **(29)**, containing two asymmetrically bridging CO ligands [72]. Bis(cyclo-octa-1,5-diene)platinum and the dirhodium compound react to give a structurally similar complex [$PtRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2$].



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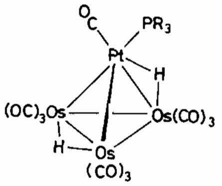

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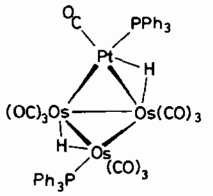

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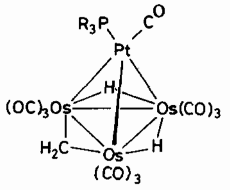

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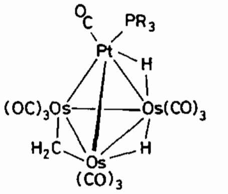

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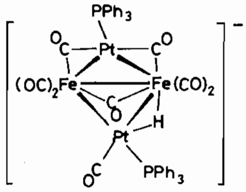


(34)

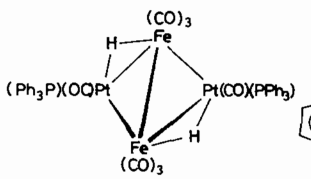
Tetranuclear Metal Compounds

The 46 electron triosmium compound [$Os_3(\mu\text{-}H)_2(CO)_{10}$], which formally contains an Os=Os bond, readily reacts with the complexes [$Pt(C_2H_4)_2(PR_3)$] (R = cyclo-C_6H_{11} or Ph) to give 58 electron *closo* tetrahedral clusters **(30)**. These compounds undergo dynamic behaviour in solution and engage in a number of interesting reactions [49, 50]. Addition of CO, PPh_3 or $AsPh_3$ affords 60 electron clusters with butterfly structures **(31)**. With carbon monoxide the reaction is reversible, providing a good example of the opening and closing of a cluster by addition or removal of an electron pair donor ligand.

Complex (**30**, R = cyclo-C_6H_{11}) reacts with CH_2N_2 to give two isomeric species **(32)** and **(33)**, the structures of which have been established by X-ray diffraction studies [73]. It is interesting that although **(32)** and **(33)** are 60 electron clusters containing platinum, they have *closo* rather than butterfly structures. The two isomers interconvert in solution in a process which involves rotation of the $Pt(CO)(PR_3)$ group about an axis perpendicular to the Os_3 plane, coupled with hydrido bridge site exchange.

The readiness with which the Pt(0) complexes, particularly [$Pt(C_2H_4)_2(PR_3)$], bond a CO ligand makes it possible to synthesize a variety of platinum-containing cluster compounds by reaction of the Pt(0) species with co-ordinatively and electronically saturated metal carbonyls. In its simplest form this reaction involves transfer of a CO ligand to a platinum atom which becomes inserted into the molecular framework. Thus [$Pt(C_2H_4)_2(PPh_3)$] reacts with the 48-electron anion [$Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$]$^-$ to give the anion [$Fe_3Pt(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(PPh_3)$]$^-$. The latter has 60 cluster valence electrons and is probably isostructural with compound **(31)** [42]. This route to cluster complexes containing platinum is well documented in the reaction of [$Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6$]$^-$ with [$Pt(C_2H_4)_2(PPh_3)$]. The product is the diiron–diplatinum anion **(34)** in which the metal framework adopts a butterfly geometry. As discussed earlier, the Pt–Pt distance [2.966(1) Å] probably represents little if any direct metal–metal bonding. Protonation of **(34)** affords **(35)** in which all the CO ligands are terminally bound [42].

Similar transfer of CO from a metal carbonyl derivative to platinum occurs in the reactions of



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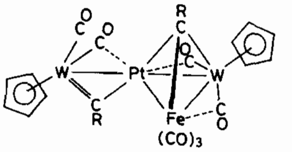

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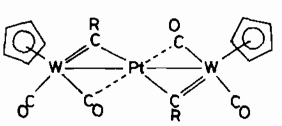
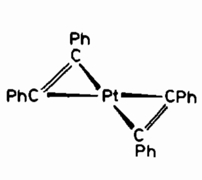


(37, R = C_6H_4Me-4)



(38)

$[H_2Os(CO)_4]$ with $[Pt(C_2H_4)_2(PR_3)]$ (R = Me, Ph or cyclo-C_6H_{11}). The products are diosmium–diplatinum compounds $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ isostructural with the diiron–diplatinum complex (**35**) [43, 46].

A novel tetranuclear metal complex (**36**) is formed by reacting (**37**) with $[Fe_2(CO)_9]$ [74]. The trimetallic precursor (**37**) can be readily prepared by treating $[W{\equiv}CC_6H_4Me(CO)_2(\eta\text{-}C_5H_5)]$ with $[Pt(C_2H_4)_3]$ [32]. This synthesis is analogous to the preparation of $[Pt(PhC_2Ph)_2]$ from PhC≡CPh and $[Pt(C_2H_4)_3]$ [75]. The structure of bis(diphenylacetylene)platinum may be represented by (**38**) which demonstrates the structural relationship with (**37**).

Conclusions

The study of organoplatinum compounds containing two, three, or four metal atoms is a thriving subject of research which embraces several areas of organometallic chemistry currently under very active study. These include the activation of small organic ligands bonded to more than one metal centre, the core geometries of small metal clusters in relation to their number of valence electrons, the properties of hetero-nuclear metal–metal bonds in comparison with their homonuclear analogues, and the mechanisms of the dynamic behaviour in solution of the peripheral ligands. Platinum can play a major rôle in contributing to our knowledge of the above topics now that reactive complexes of this metal have been discovered and can be used in synthesis.

References

1 M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 271 (1977); *idem, J. Chem. Soc., Chem. Commun.*, 3, 449 (1975).

2 N. C. Harrison, M. Murray, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1337 (1978).

3 J. L. Spencer, *Inorg. Synth., 19,* 213 (1979).

4 M. Green, J. A. K. Howard, M. Murray, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1509 (1977).

5 J.-M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1003 (1979).

6 J.-M. Bassett, G. K. Barker, J. A. K. Howard, F. G. A. Stone and W. C. Wolsey, *J. Chem. Soc., Dalton Trans.*, 219 (1981).

7 M. Green, A. Laguna, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1010 (1977).

8 T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. Mills, G. N. Pain, F. G. A. Stone and P. Woodward, Amer. Chem. Soc. Symposium Series, to be published.

9 D. Seyferth and A. Davison, *Science, 182,* 699 (1973).

10 J. S. Thayer, *Adv. Organomet. Chem., 13,* 1 (1975).

11 G. Wilkinson, *J. Organomet. Chem., 100,* 273 (1975).

12 P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel', *Academic Press, New York,* Vol. 1, 1974; Vol. 2, 1975.

13 W. C. Zeise, *Overs. K. Dan Vidensk. Selskabs. Forh.*, 13 (1825); *Pogg. Ann. Phys., 9,* 632 (1827); *21,* 497, 542 (1831).

14 E. P. Kundig, D. McIntosh, M. Moskovits and G. A. Ozin, *J. Am. Chem. Soc., 95,* 7234 (1973).

15 J. H. Darling and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1079 (1973).

16 Some of the products from the Pt(0) reagents behave as if they contain relatively inert Pt(II) d^8, others are more reactive. A combination of tertiary phosphine ligands and electrophilic organic molecules leads to products reflecting Pt(d^8) rather than Pt(d^{10}) chemistry, as for example in the complexes $[Pt(C_2F_4)(PPh_3)_2]$ (M. Green, R. B. L. Osborn, A. J. Rest and F. G. A. Stone, *J. Chem. Soc. (A),* 2525 (1968) and $[Pt\{C_2(CN)_4\}(PPh_3)_2]$ (W. H. Baddley and L. M. Venanzi, *Inorg. Chem., 5,* 33 (1966)). Consequently, these and related compounds are unreactive and have little derivative chemistry associated with them. However, there are several long known species of the type $[Pt(olefin)(PPh_3)_2]$ which have been employed in synthesis as sources of the $Pt(PPh_3)_2$ fragment, by virtue of their ready loss of olefin. Notable among these are $[Pt(C_2H_4)(PPh_3)_2]$ (C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc., 90,* 1464 (1968)) and [Pt(*trans*-PhCH: CHPh)$(PPh_3)_2$] (J. Chatt, B. L. Shaw and A. E. Williams, *J. Chem. Soc.*, 3269 (1962)). However, these compounds have somewhat limited use in synthesis because two coordination sites on the metal centre are blocked by the PPh_3 groups. Moreover, prior to the recent work described in this article it was difficult to prepare complexes $[Pt(C_2H_4)(PR_3)_2]$ with tertiary phosphines other than PPh_3.

17 J. Müller and P. Göser, *Angew. Chem. Int. Ed. Engl., 6,* 364 (1967).

18 J. L. Spencer, M. Green and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972); *J. Chem. Soc., Dalton, Trans.*, 1679 (1979).

19 It has been possible to grow crystals of $[Pt(C_2H_4)_3]$ of sufficient quality and size to enable X-ray and neutron diffraction studies to be made [J. A. K. Howard, to be published]. This work established the trigonal planar structure of the molecule, in accord with the prediction of N. Rösch and R. Hoffmann (*Inorg. Chem., 13,* 2656 (1974)). Tris(ethylene)platinum forms colourless crystals stable under an ethylene atmosphere at *circa* 20 °C. For synthetic work it is usually generated from $[Pt(cod)_2]$ *in situ* in a suitable hydrocarbon solvent. The palladium compounds $[Pd(cod)_2]$ and $[Pd(C_2H_4)_3]$ have also been prepared (ref. 1), but they are thermally very unstable.

20 T. V. Ashworth, J. A. K. Howard, M. Laguna and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1593 (1980).

21 J. Fornies, M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).

22 P. Chini, G. Longoni and V. G. Albano, *Adv. Organomet. Chem., 14,* 285 (1976).

23 P. Chini, *J. Organomet. Chem., 200,* 37 (1980).

24 M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A),* 865 (1967).

25 A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. (A),* 2772 (1969).

26 P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 2355 (1973).

27 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1516 (1975).

28 L. E. Smart, J. Browning, M. Green, A. Laguna, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1777 (1977).

29 From X-ray crystallographic data it is often difficult to decide whether or not a direct Pt–Pt bond exists in a polynuclear platinum complex. Several studies on ***diplatinum*** complexes have revealed metal–metal distances in the range 2.58–2.65 Å, in accord with the sum of the covalent radii being 2.62 Å. However, in the cluster complex $[Pt_4(CO)_5(PMe_2Ph)_4]$, discussed later in this article, there are Pt–Pt bonds in the range 2.790(7)–2.752 (6) Å. In the complex $[Pt_3(\mu_2\text{-}CF_3C_2CF_3)_2\{\mu_2\text{-}(CF_3)C_2(CF_3)(CF_3)C_2(CF_3)\}(cod)_2]$ the metal–metal separations are 2.630(3) and 2.841(2) Å. The former distance is as expected for a bond, but the latter cannot be taken as indicating the absence of Pt–Pt bonding in view of the aforementioned metal–metal distances found in $[Pt_4(CO)_5(PMe_2Ph)_4]$ and the interlayer Pt–Pt separations (3.08 Å) in $[Pt_{15}(CO)_{30}]^{2-}$ (refs. 22, 23).

30 P. Braunstein and J. Dehand, *J. Organomet. Chem.*, *81,* 123 (1974); J.-P. Barbier and P. Braunstein, *J. Chem. Res.*, (S) 412, (M) 5029 (1978); P. Braunstein, E. Keller and H. Vahrenkampf, *J. Organomet. Chem.*, *165,* 233 (1979).

31 P. Braunstein, D. Matt, O. Bars and D. Grandjean, *Angew. Chem. Int. Ed. Engl.*, *18,* 797 (1979).

32 T. V. Ashworth, M. J. Chetcuti, J. A. K. Howard, F. G. A. Stone, S. J. Wisbey and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 763 (1981).

33 J. Chatt and P. Chini, *J. Chem. Soc. (A),* 1538 (1970).

34 A. Albinati, G. Carturan and A. Musco, *Inorg. Chim. Acta, 16,* L3 (1976); A. Albinati, *ibid, 22,* L31 (1977).

35 M. Berry, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1601 (1980).

36 T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna and F. G. A. Stone, *J. Chem. Soc., Dalton Tans.*, 1615 (1980).

37 M. Berry, J. Martin-Gil, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1625 (1980).

38 J. C. Jeffery, I. Moore and F. G. A. Stone, to be published.

39 V. G. Albano, G. Ciani, M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Organomet. Chem.*, *42,* C99 (1972); V. G. Albano and C. Ciani, *ibid, 66,* 311 (1974).

40 M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1781 (1972).

41 M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1082 (1972).

42 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1134 (1981).

43 L. J. Farrugia and P. Mitrprachachon, Ph. D. Theses, Bristol University, 1979.

44 R. G. Vranka, L. F. Dahl, P. Chini and J. Chatt, *J. Am. Chem. Soc.*, *91,* 1574 (1969).

45 A pentametallic complex $[Co_2Pt_3(\mu\text{-}CO)_5(CO)_4(PPh_3)_3]$ is known having a distorted trigonal bipyramidal structure with a *hetero*-trimetallic Co_2Pt base (J.-P. Barbier, P. Braunstein, J. Fischer and L. Ricard, *Inorg. Chim. Acta, 31,* L361 (1978)).

46 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1274 (1981).

47 J. Fischer, A. Mitschler, R. Weiss, J. Dehand and J. F. Nennig, *J. Organomet. Chem.*, *91,* C37 (1975).

48 R. Bender, P. Braunstein, Y. Dusausoy and J. Protas, *J. Organomet. Chem.*, *172,* C51 (1979); P. Braunstein, J. Dehand and J. F. Nennig, *ibid.*, *92,* 117 (1975).

49 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 155 (1981).

50 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 162 (1981).

51 K. Wade, *Adv. Inorg. Chem. Radiochem.*, *18,* 1 (1976); Chapter 3 in "Transition Metal Clusters", Ed. B. F. G. Johnson, John Wiley, N. Y. C. 1980.

52 J. W. Lauher, *J. Am. Chem. Soc.*, *100,* 5305 (1978).

53 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 171 (1981).

54 Important diplatinum species prepared by methods other than employing as precursors Pt(0) complexes include the cations $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ (M. P. Brown, S. J. Cooper, R. J. Puddephatt, M. A. Thomson and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1117 (1979); A. A. Frew, L. Manojlović-Muir and K. W. Muir, *ibid,* 624 (1980)), $[Pt_2H(\mu\text{-dppm})_2(dppm)]^+$ (M. P. Brown, J. R. Fischer, L. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, M. A. Thomson and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 931 (1979)), $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ (M. P. Brown, R. J. Puddephatt, M. Rashidi and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 516 (1978)), $[Pt_2(CNMe)_6]^{2+}$ (J. R. Boehm, D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.*, *98,* 4845 (1976)), and the dianion $[Pt_2Cl_4(CO)_2]^{2-}$ (refs. 26, 27).

55 M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 801 (1978).

56 M. Auburn, M. Ciriano, J. A. K. Howard, M. Murray, N. J. Pugh, J. L. Spencer, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 659 (1980).

57 M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1749 (1979).

58 M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 278 (1977).

59 N. M. Boag, M. Green and F. G. A. Stone, *J. Chem. Soc. Chem. Commun.*, 1281 (1980).

60 N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, M. D. O. Thomas, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2182 (1980).

61 N. M. Boag, M. Green, J. A. K. Howard, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 862 (1981).

62 It is generally assumed that for a terminally bound alkyne ligand only one of the two sets of π and π^* orbitals is employed in the donor-acceptor bonding with the metal, and that the π and π^* set of orbitals orthogonal to these play only an insignificant role in the interaction of the carbon atoms with the metal (see S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, *14,* 245 (1976)). Hence in (8) it is best to regard the terminal $Me_3SiC_2SiMe_3$ groups as donating two electrons to the metal atoms rather than four.

63 T. V. Ashworth, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 42 (1979); T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna and F. G. A. Stone, *ibid.*, p. 43.

64 F. G. A. Stone, *Pure Appl. Chem.*, *30,* 551 (1972).

65 T. V. Ashworth, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1609 (1980).

66 J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 743 (1981).

67 J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 751 (1981) in press; *idem, J. Chem. Soc., Chem. Commun.*, 1170 (1979).

68 J. C. Jeffery, H. Razay, R. Navarro and F. G. A. Stone, *J. Chem. Soc. Dalton. Trans.*, in press.

69 M. Chetcuti, M. Green, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, S. J. Porter, F. G. A. Stone, A. A. Wilson and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1057 (1980).

70 M. J. Bennett, W. A. G. Graham, J. K. Hoyano and W. L. Hutcheon, *J. Am. Chem. Soc., 94,* 6232 (1972).

71 A. Nutton and P. M. Maitlis, *J. Organomet. Chem., 166,* C21 (1979).

72 N. M. Boag, M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone and P. Woodward, *J. Chem. Soc. Chem. Comm.,* 1171 (1980).

73 M. Green, D. R. Hankey, M. Murray, A. G. Orpen and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.,* in press.

74 M. Chetcuti, Ph. D. Thesis, Bristol University, 1980.

75 N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.,* 2170 (1980).