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Synthesis and reactivity of small mixed clusters formed by transition metals and main group elements

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CONTENTS

A. INTRODUCTION

In 1978, Sacconi and his co-workers reported the first fully characterized cyclotriphosphorus derivatives: the neutral monometal complex [(triphos)Co(P_3)] (**1**) [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] and the dimetal [(triphos)-Ni(P_3)Ni(triphos)]$(BPh_4)_2$ (**2**) [1]. These were obtained in mild conditions, by reacting the appropriate, hydrated, metal salts and white phosphorus in THF–butanol solution. The triangular P_3 group in **1** was trihapto-bonded to the Co atom with which it formed a pseudo-tetrahedral unit (Fig. 1); the same P_3 group was sandwiched between the two metal atoms in **2** (Fig. 2).

The ligand triphos, which had already been extensively used by Sacconi's group as a suitable ligand to form metal complexes with coligands of various types, was considered to play a major role in the formation of **1** and **2**, as well as of numerous related compounds which were subsequently synthesized, as it was capable of imposing the appropriate lobality on the metal-based orbitals to match the bonding requirements of the triangular P_3 unit provided a suitable overall electron count was

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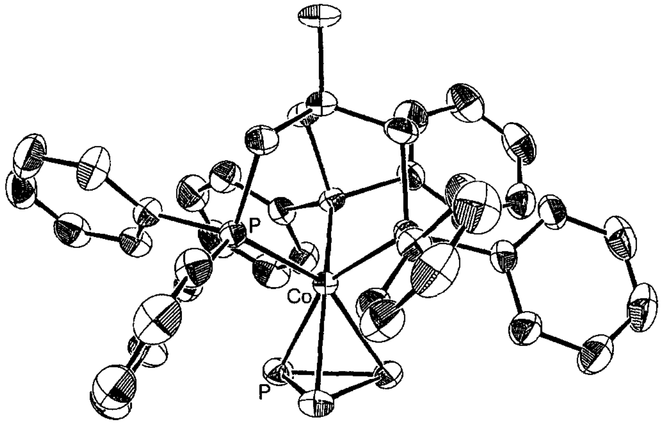

Fig. 1. Structure of the [(triphos)Co(P_3)] molecule (1), which possesses threefold symmetry.

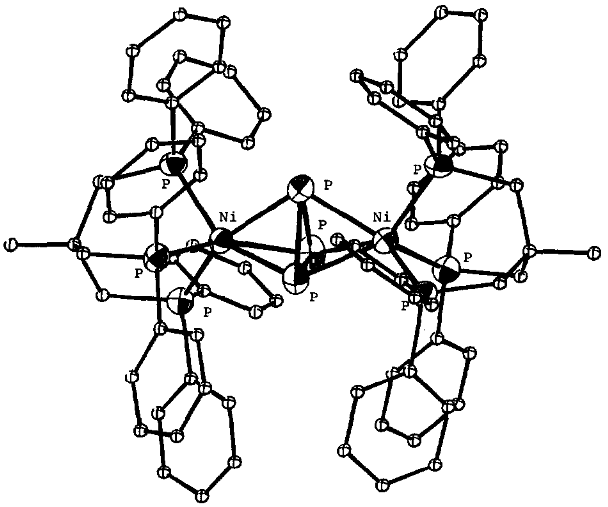

Fig. 2. A view of the [(triphos)Ni(P_3)Ni(triphos)]$^{2+}$ cation, representative of compounds of group 2.

also attained. Moreover, the triphos ligand was able to shield, with its phenyl groups, the site occupied by the co-ligand, thus limiting further reactions at that site.

Several other monometal P_3 derivatives related to **1**, as well as dimetal derivatives related to **2**, were later obtained [2–9], the dimetal compounds being both homo- and heteroatomic with valence electron numbers in the range 30–34. Sandwich compounds of higher atomicity than that of **2** were also reported, where [(triphos)-Co(P_3)] or related species acted as electron donors toward Lewis acids [10,11]. An adduct of the intact P_4 tetrahedral molecule was also obtained using the potentially tetradentate tripod ligand np$_3$ [np$_3$ = tris(2-diphenylphosphinoethyl)amine] [12]. Finally, as the reactivity of the As_4 molecule was investigated, dimetal compounds of type **2** containing the triangular As_3 unit were synthesized [13]. The same unit had been previously obtained under more drastic reaction conditions and was stabilized by carbonyl coligands in the monometal compound $[(CO)_3Co(As_3)]$ [14].

The results obtained in this field prior to 1982 were reviewed [15] and such research trends, consisting of investigations on the reactivity of properly chosen metal–ligand systems toward small molecules of the Group V elements or their chalcogenides, were pursued by various workers. Typical results of these studies were the isolation of small clusters formed by transition metals and unsubstituted main group elements, which generally could also be viewed as small main group molecular fragments stabilized through their interaction with the transition metal–ligand systems employed. Here we report mainly on the results obtained by us and our coworkers in this field. The important achievements of other authors in strictly related fields will also be briefly mentioned, although we do not aim at completeness in this latter respect.

A class of small molecules which appeared to be suitable for this type of investigation was provided by the "cage molecules" of the phosphorus or arsenic chalcogenides with general formula E_4X_3 (Fig. 3). These possess several unsubstituted atoms in different environments and homoatomic as well as heteroatomic bonds, which may provide suitable points for attack by metal–ligand systems with the appropriate bonding requirements.

B. ADDUCTS OF THE INTACT E_4X_3 CAGE MOLECULES

The reactions of the $[(np_3)M]$ ($M = Ni$ or Pd) d^{10} metal complexes with the P_4X_3 ($X = S$ or Se) chalcogenides afforded the neutral compounds of formula $[(np_3)M(P_4X_3)]$ (**3**) ($M = Ni$, $X = S$ or Se; $M = Pd$, $X = S$) [16,17]. The metal atom in these (Fig. 4) is four-coordinated in a pseudo-tetrahedral environment formed by the phosphorus atoms of the tripod ligand and by the apical P atom of the cage molecule, the nitrogen atom of the potentially tetradentate np_3 ligand being uncoordinated. The overall arrangement parallels that already found for the P_4 adducts $[(np_3)M(P_4)]$ ($M = Ni$ [12], Pd [4]). The flexibility of the np_3 ligand and the d^{10} electronic configuration of the metal atom were considered to be determinant to the formation of these complexes as a smooth reaction path could be envisaged with the P atom

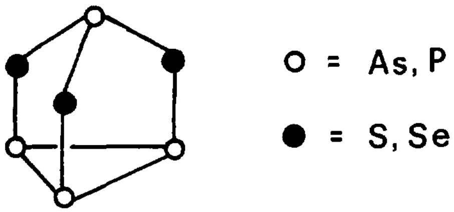

Fig. 3. The atomic arrangement in a E_4X_3 molecule.

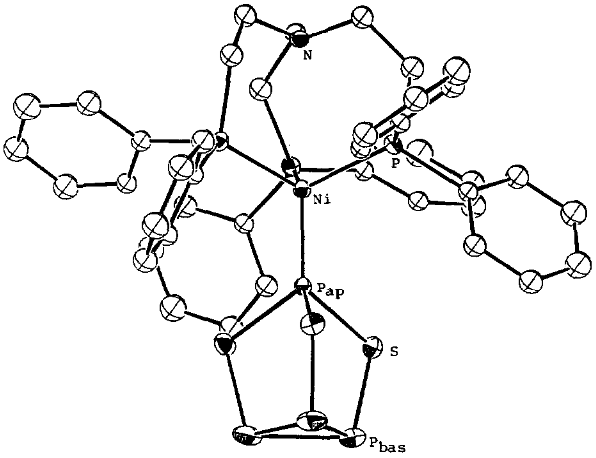

Fig. 4. Structure of the $[(np_3)Ni(P_4S_3)]$ molecule (3), having threefold symmetry: P_{ap} = phosphorus atom in the apical position of the P_4S_3 cage, P_{bas} = phosphorus atom(s) in basal position(s).

of the cage molecule entering into the coordination sphere on the opposite side of the leaving np_3 N atom, the removal of the latter donor atom being allowed by a corresponding shift of the whole np_3 ligand along the threefold axis of the complex [16]. It is noteworthy that a P_4S_3 adduct had previously been obtained, but in combination with a metal carbonyl system, in the compound $[(CO)_5Mo(P_4S_3)]$ [18]. This result and the already mentioned stabilization of the As_3 group by the $(CO)_3Co$ fragment [14], point to similar bonding propensities of the carbonyl or phosphine metal fragments of proper lobality toward soft co-ligands such as these cage molecules or their fragments, although the role played by the shielding phenyl groups in compounds **3** should not be ignored. According to fragment analysis considerations [19], the bonding of the P_4X_3 molecules to the $(CO)_5Mo$ or $(np_3)M$ (M = Ni, Pd) systems should be essentially of the σ type [16].

The P_4S_3 or P_4Se_3 molecules undergo only small deformations upon coordination, consisting of a 2–3° decrease in the values of the angles at the apical P atom and a 0.03 Å elongation of the P_{ap}–X bonds in compounds **3** [16,17], whereas a slightly different pattern of deformations, mainly involving the environment of the basal P atoms of the cage, was detected for the P_4S_3 adduct of the $(CO)_5Mo$ system [18].

C. INSERTION INTO ONE BOND OF THE CAGE MOLECULE

The reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with P_4S_3 yielded the trinuclear platinum complex $[\{Pt(P_4S_3)(PPh_3)\}_3]$ (**4**) (Fig. 5) in which insertion of a LL'Pt system into a P–P bond of the cage occurs [20]. One of the P atoms of such a bond, which opens in **4** to 3.03 Å, bridges between two metal atoms, leading to polymerization and

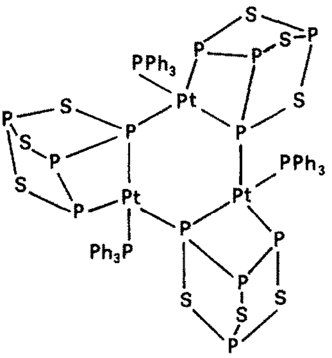

Fig. 5. Schematic representation of bonding in the $[\{Pt(P_4S_3)(PPh_3)\}_3]$ trimer (**4**).

contributing with the residual phosphine from the parent metal derivative to form the d^{10} LL′Pt metal–ligand system in **4**. Except for the lengthening of the P—P bond being cleaved, there are only minor changes in bond distances within the cage molecule caused by the insertion. The process of insertion could be rationalized [20] in terms of simple MO calculations at the extended Hückel level along the lines of those previously developed for insertions into edges of cyclopropenium ions [21,22]. The main interaction, occurring between the metal-based HOMO on the LL′Pt fragment and an empty orbital on the cage having antibonding P—P character, increases in the course of the insertion process, strongly favouring P—P bond cleavage. In agreement with experiment, calculations on model systems suggest that the P—P bonds of a P_4S_3 cage should be cleaved more easily than the P—S bonds, essentially due to geometric factors, by the above sort of mechanism. Such a process eventually leads to an increase in the formal oxidation number of the metal atom [20]. This situation should be compared with that of the smooth process of simple cage addition described in the previous section, in the course of which no change in the oxidation number of the metal atom takes place. It should also be contrasted with the processes of more or less profound attack and disruption of the cage molecules, to be described in the following sections. These processes are generally triggered by metal atoms having positive oxidation states in their parent compounds and are accompanied by metal reduction in the course of the reaction.

IR evidence for an increase in the oxidation number of the metal atom in the formation of a compound similar to **4** had been obtained [23] for the reaction of $[IrCl(CO)(PPh_3)_2]$ and P_4S_3 yielding the $[\{IrCl(CO)(P_4S_3)(PPh_3)\}_2]$ dimer (**5**) (Fig. 6). Although the d^8 metal–ligand system present in **5** has a different nature, geometry, and d-electron count with respect to those of **4**, the two systems are, however, isolobal [21].

The η^2-P_4 complex $[RhCl(P_4)(PPh_3)_2]$, which was obtained in 1971 from $[RhCl(PPh_3)_3]$ and P_4 [24] and which was fully characterized twelve years later [25], should also be mentioned in this context (Fig. 7). Although its planar L_3M-

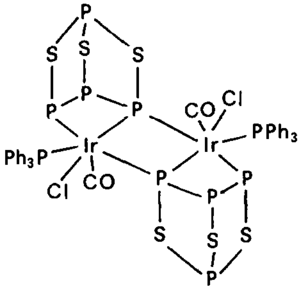

Fig. 6. Schematic representation of bonding in the [{IrCl(CO)(P_4S_3)(PPh_3)}$_2$] dimer (**5**).

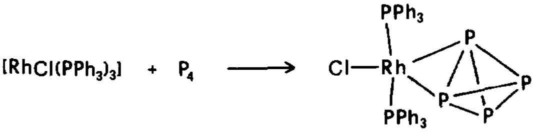

Fig. 7. Schematic representation of bonding in the [RhCl(P_4)(PPh_3)$_2$] molecule.

type d^8 system available for interaction with P_4 differs somewhat from the two metal–ligand fragments present in **4** and **5**, its geometrical preferences and mode of interaction may be rationalized along similar lines [21] and fit into the same scheme of oxidative addition.

D. REPLACEMENT OF ONE ATOM IN THE CAGE MOLECULE

When the P_4X_3 (X = S, Se) cage molecules react with the [MCl(cod)]$_2$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) species in the presence of the ligand triphos, neutral compounds of formula [(triphos)M(P_3X_3)] (**6**) are obtained [26,27] in which one basal P atom of the cage is replaced by the metal atom (Fig. 8). The small cluster, mainly consisting of main group atoms, which is obtained is considered to represent one of the early steps in the process of attack of these cage molecules by (triphos)M systems. The process of attack probably halts at such a stage in the formation of compounds **6** because the metal atom, which is initially in the oxidation state + 1, undergoes only a moderate reduction on forming these compounds. If a greater reduction occurs, as in the reactions involving first row transition metal cations initially in the oxidation state + 2 (see the next section), then a more drastic fragmentation of the cage molecule takes place. The formation of compounds **6** was also considered [27] as an indication that a suitable point for attack of the E_4X_3 cage molecules by the (triphos)M moieties, which are of the L_3M type with threefold symmetry [19], is provided by the base of the cage, which has similar symmetry. However, no stable electronic configuration is reached by interaction of the MOs of a d^8 (triphos)M(I) fragment, such as those apparently provided by the above [MCl(cod)]$_2$ and triphos reactants, with the P_{bas} combinations of the intact P_4X_3

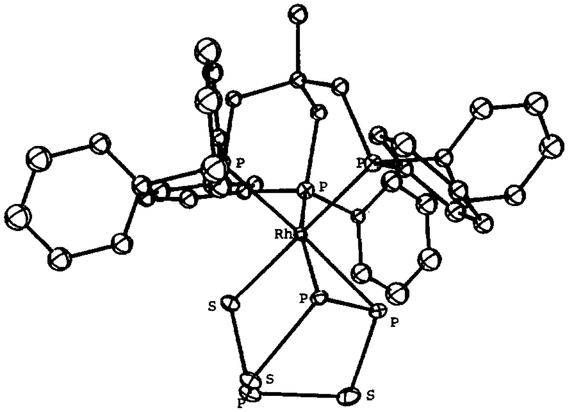

Fig. 8. A view of the structure of the [(triphos)Rh(P_3S_3)] molecule belonging to group **6** compounds.

molecule, so that partial cleavage of the latter is anticipated. It should also be noted in this connection that, on the basis of extended Hückel calculations, there appears to be differences in the mode of interaction with the cage by the d^{10} L_2M systems considered in Sect. C and the present d^8 L_3M systems. While in the former case electron density is transferred to the LUMO of the cage, in the latter the trend appears to be reversed for several interaction geometries considered. The electron density shift toward the d^8 L_3M fragment is due to interaction of both bonding and slightly antibonding filled orbitals of the cage with empty orbitals of the metal system. The presence of a positive charge on the metal atom certainly favours such shift; moreover, a positive charge, causing a stabilization of the metal orbitals, favours their interaction with the lower-lying bonding, rather than the antibonding cage orbitals, thus leading to cage destabilization.

Bond distances within the coordinated P_3X_3 fragments do not differ considerably from those of the parent P_4X_3 molecules: essentially, a shortening (ca. 0.06 Å) is observed for the remaining P_{bas}–P_{bas} bond in the fragment, as well as for the P_{ap}–X bond formed by the chalcogen atom bound to the metal. Trends in the values of metal–ligand distances on going from the rhodium to the iridium P_3S_3 derivative have also been noticed [27], which match those observed for cyclo-P_3 complexes formed by second and third row transition metals (see the next section). The $^{31}P\{^1H\}$ NMR spectra of compounds **6** have been reported and assigned [27]: a high-frequency shift is observed for the P_3X_3 phosphorus atoms, that of the pair of coordinating P atoms (P_{bas} in the original cage) being particularly noticeable.

E. TRIATOMIC FRAGMENTS FROM E_4X_3 MOLECULES

The reactions of hydrated Co(II) salts with E_4X_3 molecules in presence of triphos yielded a series of complexes of formula $[(triphos)Co(E_2X)]^+$ (**7**) (E = P, As;

X = S, Se) [28–31] containing the cyclic heteroatomic E_2X units extruded from the cage molecules and coordinated to the metal atom in the same fashion as the P_3 group in **1** to form the pseudo-tetrahedral clusters CoE_2X (Fig. 9). By reaction of a nickel(II) salt and P_4S_3, the $[(triphos)Ni(P_3)]^+$ cation (**8**), isoelectronic with the cobalt cations **7**, was also obtained [5,32]. This allowed the series of the cationic P_3 derivatives $[(triphos)M(P_3)]^+$ (M = Ni, Pd, Pt) to be completed so that trends in their ^{31}P NMR and structural properties could be examined and compared with those for the corresponding neutral P_3 compounds of the Co group; both the chemical shifts and the metal–ligand distances were found to vary non-linearly (but consistently) along the two series with increasing atomic number of the metal atom [5].

The extrusion of the small triatomic fragments from the E_4X_3 cage molecules in the above processes appears to be related to the presence among the reactants of metal atoms in relatively high oxidation states. As noted above (Sect. D), in the course of their interaction with the E_4X_3 molecules, a shift of electronic charge toward predominantly metal orbitals takes place, which causes reduction of the metal and activation of the cage molecule. However, it should be stressed that this view is based on comparisons between the processes leading to compounds of the types **3**, **6**, **7**, and **8**, mostly formed by first row transition metals and phosphine ligands with threefold symmetry, so that the validity of these considerations is probably limited to the above classes of compound. They certainly do not apply to compounds of the heavier transition metals with carbonyl or cyclopentadienyl ligands, as will appear later. On the other hand, the possibility of obtaining either E_2X (**7**) or P_3 (**8**) fragments from E_4X_3 molecules, depending on the d electron count of the (triphos)M systems employed, points to the availability of alternative reaction paths controlled by specific metal moieties for the formation of stable compounds. Moreover, compounds of type **7** containing the As_2Se and As_2Te units have also been obtained from the reactions of Co(II) salts with the polymeric chalcogenides As_2Se_3 and As_2Te_3 rather than with isolated cage molecules [31]; this again points to the efficiency of the (triphos)M systems in directing the course of reactions toward specific products.

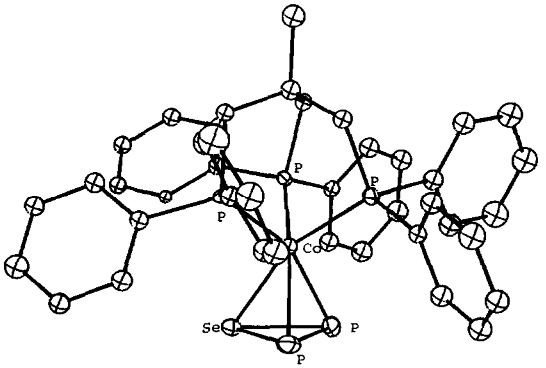

Fig. 9. Perspective view of the $[(triphos)Co(P_2Se)]^+$ cation, belonging to group 7 compounds.

Due to the low barrier to rotation of the E_2X group in compounds **7** about the molecular pseudo-threefold axis, revealed also by the ^{31}P NMR spectra [29], the E_2X groups are orientationally disordered in the structures of compounds **7**. When the E and X atoms belonged to different rows of the periodic table, the occupancies of the sites of the triatomic ring in the structure could be determined through the X-ray analyses (Fig. 9) and were found to be substantially consistent for such rings as P_2Se and As_2Te, the larger atom of the triad occupying the less hindered site in each case [29,31].

In view of the attainment of the "reaction intermediates" of type **6** containing the P_3X_3 fragments and, under different conditions, of compounds **7** containing the smaller E_2X coordinated fragments, we addressed, with the aim of achieving a deeper understanding of the cage cleavage processes, the question whether the E atoms of group V forming the E_2X triatomic units uniquely originate from the base of the E_4X_3 cage molecule or are of random (both basal and apical) parentage. To this purpose, the reactions with the "mixed" cages **9**, sketched in Fig. 10, were investigated [33]. Unfortunately, mixtures rather than substantial amounts of pure samples of such molecules are invariably obtained, so that solid solutions of [(triphos)-Co(EE′X)]BF_4 isomorphous products were also formed (Fig. 10). However, on the basis of the NMR data as well as of the structural information previously obtained about the individual members of the **7** family, we could confidently state that basal rather than apical group V atoms are extracted from **9** in the course of the reaction [33]. This conclusion may be extended to the formation of all compounds of type **7** from the E_4X_3 cages under the conditions described here and sets a connection between the "intermediates" **6** and compounds **7**. However, it should be kept in mind that this further piece of evidence for the attack of the E_4X_3 cages occurring from their triangular "basal" side, refers specifically to their interaction with systems of the triphos–metal type.

F. CLEAVAGE OF THE As_4S_4 MOLECULE AND OTHER PROCESSES

It was expected that information on the reactivity of cage molecules of types different from E_4X_3 would improve the overall knowledge about these cleavage

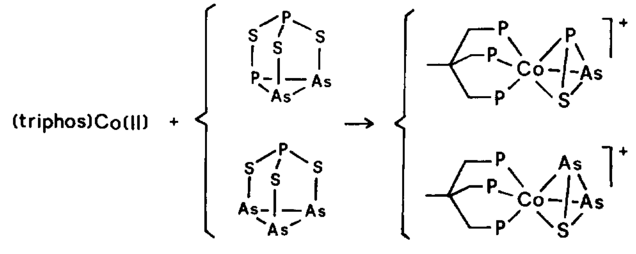

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Fig. 10. Products of the reaction on the "mixed" cages **9**.

processes. The reactions of the As_4S_4 molecule with the (triphos)M(I) moieties provided by the $[MCl(cod)]_2$ (M = Rh, Ir) species [34] allowed us to isolate the coordinated As_3X_3 fragment (Fig. 11), similar to the P_3X_3 fragments, which are present in compounds **6** [27]. The same As_4S_4 molecule, when reacted with Co(II) or Ni(II) salts in the presence of triphos [34], undergoes drastic cleavage, yielding the As_2S fragment already described [30] in connection with the compounds of class **7**, or the cyclic triarsenic unit in a sandwich compound of type **2** (Fig. 11). It should be noted that, with the exception of the As_2S unit, the formation of the other fragments from As_4S_4 involves moderate to drastic rearrangements of bonds with respect to those existing in the parent molecule. This points to the stability of the small mixed clusters of the type shown in Fig. 11, which are obtained from reactions of triphos–metal systems with both the E_4X_3 and As_4S_4 cage molecules. It also points to the ability, already noted, of the triphos–metal moieties to stabilize specific types of product.

A distinct situation, although showing similarities to that described above, is exhibited by the reactions of the $[Cp^*M(CO)_2]_2$ (M = Fe, Co, or Mo) systems with the As_4S_4 molecule under forcing conditions [35,36]. These yield a variety of dimetal derivatives with bridging diatomic As_2 or S_2 units, triatomic non-cyclic As_2S groups, and even penta-atomic As_2S_3 moieties, differing from the fragments stabilized by the (triphos)M systems (Fig. 11). Related bridging groups, in some cases differing from the former only in the substitution of P for As, were obtained by reacting $[Cp^*Mo(CO)_2]_2$ with the P_4S_3 molecule rather than As_4S_4 [37]. This points in turn to the ability of the $[Cp^*M(CO)_2]_2$ complexes to direct the course of reactions, which parallels that already noted for the (triphos)M systems, although the bonding preferences ultimately differ in the two cases. However, the systems originating from $[Cp^*M(CO)_2]_2$ appear to be more facultative than the (triphos)M systems, since cyclic As_3 and P_3 units, such as those existing in compounds of the types **1**, **2**, or **8**,

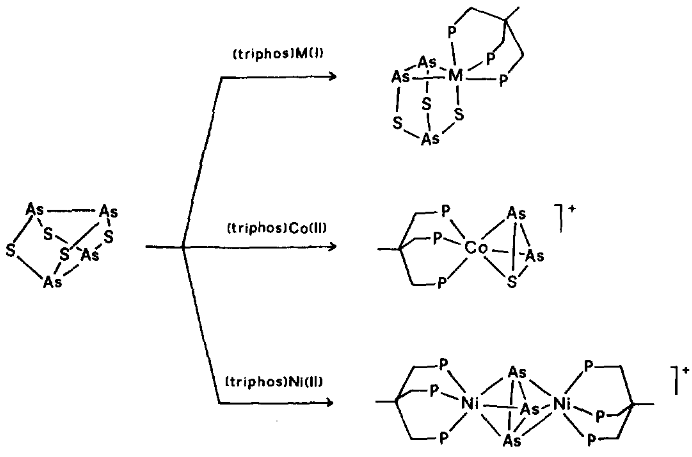

Fig. 11. Products of the reactions on the As_4S_4 molecule.

are also extruded in the reactions of $[Cp^*Mo(CO)_2]_2$ with As_4S_4 or P_4S_3 and are stabilized by interaction with the $Cp^*Mo(CO)_2$ fragment in mononuclear compounds [35,37].

A further striking example of the ability of the $[Cp^*M(CO)_2]_2$ species to form small mixed clusters by extrusion of various fragments from cage molecules is provided by the reaction of $[Cp^*Mo(CO)_2]_2$ with P_4, which produces both mono- and dimetal compounds with terminal P_3 or bridging P_2 units and even a sandwich compound with the unprecedented hexaphosphabenzene, P_6, ligand forming the inner slice [38]. It is appropriate to mention at this point that compounds containing P_4 or P_5 chains or rings have also been isolated; these and numerous other interesting results, generally obtained under different conditions from those forming the main theme of this report, have recently been reviewed [39].

Finally, when the above results are contrasted with those obtained [40] when a Co(II) salt is reacted with the same P_4 molecule in the presence of the ligand bis(diphenylphosphino)methane (dppm), the critical importance of the metal–ligand system employed in directing the course of the reaction becomes even more apparent since a six-coordinate complex is obtained containing the new ligand $Ph_2PCH_2PPh_2PPPPPPh_2CH_2PPh_2$, which is apparently formed from dppm and the P_4 molecule that has been forced to rearrange to a linear chain.

G. REACTIVITY OF COORDINATED MOLECULAR FRAGMENTS

Studies on the reactivity of the cyclic homoatomic P_3 or heteroatomic E_2X (E = P, As; X = S, Se) units η^3-coordinated to the metal to form pseudo-tetrahedral clusters have highlighted a variety of reaction modes. Some of the reactions involving the η^3-P_3 ligand have already been reviewed [15,41] and will be mentioned here only briefly. Reactions recently performed on the same system, as well as those on coordinated E_2X groups, will be described later.

Remarkably, when the reaction procedures capable of promoting P_3 or E_2X activation in the compounds of types **1**, **7**, or **8** were applied to the neutral compounds **6** containing E_3X_3 fragments as ligands, these were unaffected. Such lack of reactivity should be mostly attributed to electronic rather than steric factors as the latter could not be operative in all the cases considered. It is in line with the hypothesis (Sects. C and E) of lower reactivity of the sides or edges of a E_4X_3 molecule defined by heteroatomic E–X bonds compared with the "basal" side of the cage limited by homoatomic E–E edges: the latter part seems more prone to undergo rearrangements through which good overlaps may be established with an incoming metal unit. Actually, a coordinated E_3X_3 fragment in **6** presents only sides and edges of the mixed E/X type available for further reactions (Fig. 8), as the basal side of the original cage has already been engaged and partially transformed and its remaining P–P bond is efficiently shielded in compounds **6**.

Finally, the reactivity of the $[(np_3)M(P_4X_3)]$ (M = Ni, Pd; X = S, Se) integer cage adducts **3** to d^{10} metal systems could not be investigated due to the extreme insolubility of the compounds.

In this section, the reactivity of the pseudo-tetrahedral clusters formed by P_3 or P_2X units η^3-coordinated to a metal centre is reviewed, considering first the processes which involve addition of metal–ligand systems on the triangular face formed by main group atoms. Insertion reactions into one edge of the same triangular face will then be examined. Finally, electrophilic additions to the vertices of the pseudo-tetrahedral clusters will be briefly reviewed.

(i) Addition reactions on the triangular face formed by main group atoms

It had been proved in the course of the first studies on cyclo-triphosphorus complexes [6,15] that the trilobal (triphos)M or closely related systems [9] easily give addition reactions on the triangular P_3 face of the neutral compounds of type **1**, yielding sandwich compounds of class **2** in which the added metal–ligand system caps the face formed by main group atoms in the pseudo-tetrahedral cluster of the parent monometal compound. A partly related, but more complex, reactivity mode is exhibited by the same compounds of type **1** with respect to CuBr [10,11]. As already noted in the Introduction, multiple-decker compounds or species of more complex structure and high nuclearity are formed in which the atoms of the P_3 unit act as electron donors toward electrophilic centres.

The reactions of the cationic cobalt derivatives $[(\text{triphos})\text{Co}(E_2X)]^+$ (E = P, As; X = S, Se) **7** with a cobalt(II) salt or $[\text{RhCl(cod)}]_2$ in the presence of triphos, according to the schemes reported in Fig. 12, afforded dimetallic sandwich compounds of formula $[(\text{triphos})\text{M}(E_2X)\text{M}'(\text{triphos})]Y_2$ (**10**) (M = M′ = Co, or Rh; M = Co, M′ = Rh. Y = BPh_4, PF_6) [42,43]. Yields were high when there was no overall change in the oxidation numbers of the metal atoms involved (reaction schemes **a** and **b** in

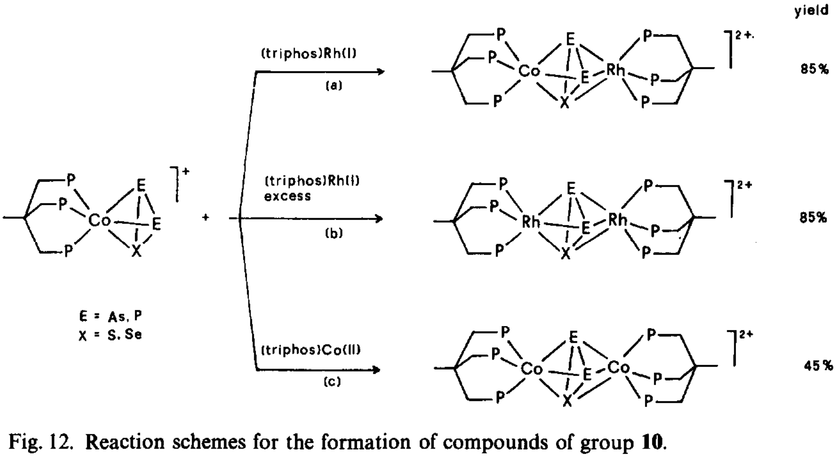

Fig. 12. Reaction schemes for the formation of compounds of group **10**.

Fig. 12), whereas lower yields characterized the processes in which partial reduction took place (scheme **c**). As exemplified in particular by reaction **b** in Fig. 12, transferability of intact E_2X units between different metal–ligand systems was attained, the general trend being that of preferential coordination of such units to 4d rather than 3d metal atoms. The structures of two compounds of type **10** were investigated by X-ray diffraction methods and revealed a notable deformation of the inner skeleton (Fig. 13) from the idealized geometry with threefold symmetry of the sandwich compounds of type **2** having a triatomic inner slice. The deformation essentially consists of a shift of the E_2X unit away from the line joining the metal centres, accompanied by cleavage of a bond in the same unit. The electronic factors at the origin of this mode of distortion, which affects dimetal compounds of both types **2** and **10** having 32 valence electrons and formed by at least one 4d (or 5d) metal atom, have been discussed [15,42]. The distortion is more pronounced for compounds of type **10** than of type **2**, as the former contain heteroatomic inner slices: in the case of the dirhodium As_2S derivative, it could be established that the bond being cleaved is a heteroatomic S—As bond [42].

A recently reported addition process [44], partly related to those described above, combines the alkylation of the P_3 ring in **1**, according to procedures to be considered below (Sect. (iii)), with the attack of a (triphos)Co(I) system on the EtP_3 unit so formed. This leads to the $[(triphos)Co(EtP_3)Co(triphos)]^{2+}$ species, isoelectronic with **10**, which exhibits a similar type of distortion of the inner slice and is fluctional in solution.

(ii) Insertion reactions into one edge of coordinated triatomic rings

The reactions of some $[(triphos)Co(E_2X)]^+$ (E = P, X = S; E = As, X = S, Se) cations **7** with the $[(C_2H_4)M(PPh_3)_2]$ (M = Pd, Pt) complexes yielded the dimetal cations $[(triphos)Co(E_2X)M(PPh_3)_2]^+$ (**11**) [45–47] in which insertion of the d^{10} L_2M-type [21] $M(PPh_3)_2$ moiety into one bond of the E_2X ring has occurred. All cations **11** are substantially isostructural. A view of one of these is shown in Fig. 14. The edge of the E_2X ring into which insertion occurs generally lengthens considerably,

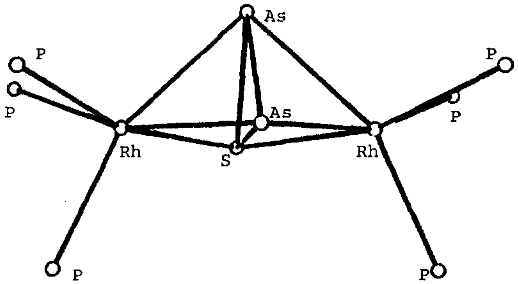

Fig. 13. Inner skeleton of the $[(triphos)Rh(As_2S)Rh(triphos)]^{2+}$ cation (group **10** compounds).

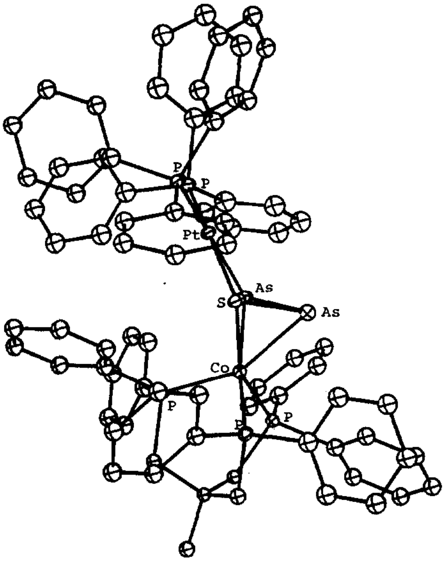

Fig. 14. Perspective view of the $[(\text{triphos})\text{Co}(\text{As}_2\text{S})\text{Pt}(\text{PPh}_3)_2]^+$ cation, representative of compounds of group **11**.

attaining a value (2.73–3.03 Å) which depends on the nature of the E_2X group and of the M atom, as discussed below. In each cation, the coordination plane about the d^{10} metal atom forms a dihedral angle close to 130° with the plane of the E_2X ring.

The mechanism of insertion may be rationalized [47] along similar lines to those proposed by Jemmis and Hoffmann for the cleaving of bonds in cyclopropenium ions [22], which have been referred to above in connection with the insertion of L_2M systems into bonds of E_4X_3 cage molecules (Sect. C). There are indications, both from ^{31}P NMR data [45,46] and from the X-ray study on the Pt derivative of the $CoAs_2S$ system [45], that the bond being cleaved in the E_2X ring is a heteroatomic E–X bond rather than the homoatomic E–E bond. However, some degree of disorder in the solid state cannot be ruled out; this might be linked to a sort of "ring-whizzing" [48] or other type of motion of the L_2M moiety over the E_2X face, which should take place in solution, according to the NMR data [47]. From the structural point of view, the elongation of the edge being cleaved in the E_2X ring increases, as would be expected, on substituting As for the smaller P atom in the ring, or Se for S (e.g. from 2.81(1) Å for $E_2X = P_2S$ to 3.03(1) Å for $E_2X = As_2S$, for **11** with M = Pt). Moreover, a greater elongation (by ca. 0.10 Å) is caused by the $Pt(PPh_3)_2$ system compared with the $Pd(PPh_3)_2$ system [47].

The insertion of the $Pt(PPh_3)_2$ system into one of the (homoatomic) bonds of the coordinated P_3 group was attained in the nickel derivative $[(\text{triphos})\text{Ni}(P_3)\text{Pt}(\text{PPh}_3)_2]\text{BPh}_4$ **12** [47] where, however, the P–P bond undergoing insertion lengthens to a smaller extent (to 2.53(1) Å) than in compounds **11**. This may be due to lower availability for bonding of the LUMO, predominantly P_3 in nature, of the (triphos)NiP$_3$ fragment in **12**, compared with the corresponding fragment orbital(s) for compounds **11**, which are essentially heterocyclic E_2X in nature. A higher degree of such an effect of energy mismatch between fragment orbitals may be responsible for the failure to perform on the neutral [(triphos)M(P$_3$)] (M = Co, Rh, Ir) derivatives of type **1** insertion reactions similar to those leading to compounds **11** or **12**.

Also, the insertion of a diphenylcarbene unit, isolobal to the previous L$_2$M systems, into one bond of the coordinated As$_2$S ring was performed by reacting [(triphos)Co(As$_2$S)]BF$_4$ with an excess of diphenyldiazomethane [49]. The resulting [(triphos)Co(As$_2$S)CPh$_2$]$^+$ cation **13**, shown in Fig. 15, contains the four-membered 3,3-diphenyl-1,2,4-thiadiarsete unit η^3-linked to the Co atom. Insertion of the CPh$_2$ unit occurs into the homoatomic As–As bond of the As$_2$S cycle in the parent compound, which lengthens from ca. 2.34 Å [30] to 2.850(3) Å. At variance with the geometry of the L$_2$M metal derivatives **11** and **12**, where the M metal environment is essentially planar, the best plane through the CPh$_2$ unit in **13** is perpendicular to the plane defined by the two As atoms and the attached C atom. This is due to the orientation of the important fragment orbital of b$_2$ symmetry, which lies in the main plane of the d^{10} L$_2$M fragment in **11** and **12**, but is normal to the best plane through the CPh$_2$ unit.

The insertion of such heavy atoms as Hg and Au, as part of metal–ligand systems, into a bond of the P$_3$ unit of a neutral compound of type **1** was also attained. The [(triphos)M(P$_3$HgR)]PF$_6$ (M = Co, Rh; R = CH$_3$, C$_6$H$_5$) compounds (**14**) were obtained by reaction of [(triphos)M(P$_3$)] and RHgCl followed by addition of TlPF$_6$ [50]. The structure of the [(triphos)Co(P$_3$HgCH$_3$)]$^+$ cation is shown in Fig. 16. The Hg atom insists on a P–P bond forming slightly different bond distances to the two

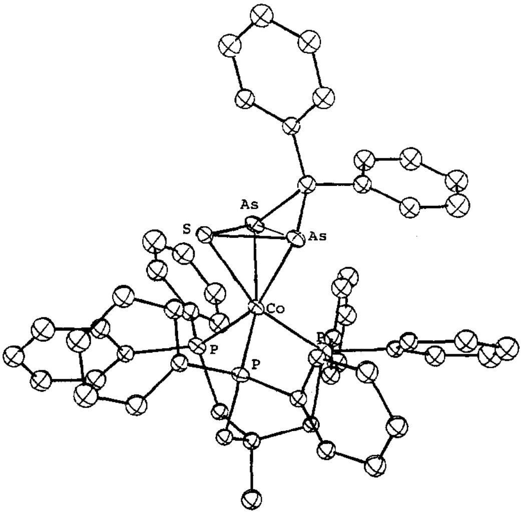

Fig. 15. Structure of the [(triphos)Co(As$_2$S)CPh$_2$]$^+$ cation (**13**).

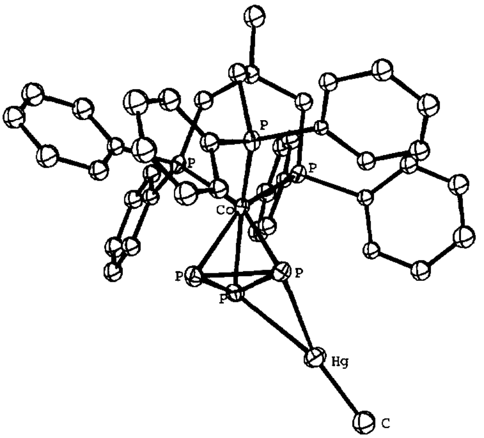

Fig. 16. Structure of the $[(\text{triphos})\text{Co}(\text{P}_3\text{HgCH}_3)]^+$ cation (**14**).

P atoms. Such a P—P bond lengthens from the 2.141(2) Å value in the parent compound to 2.293(8) Å, undergoing a definitely smaller elongation than in compounds **11–13**. However, the hinge angle between the plane of the P_3 ring and that defined by Hg and the attached P atoms is in the range of those found for the compounds **11–13**. The Co—P(P_3) bond lying opposite the $HgCH_3$ group lengthens, whereas the other two Co—P(P_3) bonds shorten with respect to their value in the parent compound, which is unique by symmetry. The smaller elongation of the P—P bond in **14** compared with **11–13** may be understood considering that the interaction in **14** essentially consists of donation from low-lying bonding, as well as from higher and slightly antibonding orbitals, all occupied, of the CoP_3 moiety to empty orbitals on the Hg atom. The donation from the slightly antibonding orbitals poses a restraint to bond lengthening. EHMO calculations do not clearly allow the ranking of possible interaction geometries according to the associated stabilities, although those with the HgR group on a P–P edge or on a vertex seem to be more likely than that with the same group capping the triangular P_3 side. This is in keeping with the mode of bonding found for **14** and its rather asymmetric fashion, as well as with the suggestion [50] that the fluxionality in solution, revealed by the ^{31}P NMR spectra, may be due to peripheral migration of the HgR group along the border of the P_3 unit rather than over its surface.

By reaction of a neutral $[(\text{triphos})\text{M}(\text{P}_3)]$ (M = Co, Rh, Ir) species **1** with $[\text{AuCl}(\text{PR}_3)]$ (R = CH_3, C_6H_5) or with dimetal Au phosphines, the trimetal derivatives $[\text{Au}\{(\text{triphos})\text{M}(\text{P}_3)\}_2]\text{PF}_6$ (**15**) were obtained [51]. In Fig. 17, the inner skeleton of the cation in one of these compounds, which are isomorphous with each other, is shown. The gold atom is sandwiched between two layers, each formed by a [(triphos)M(P_3)] species, being linked to two pairs of P atoms, one from each of the P_3 groups. Its coordination geometry is intermediate between the elongated tetrahedral

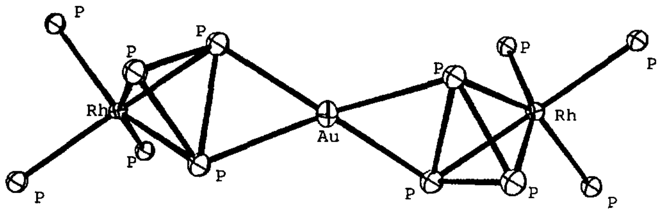

Fig. 17. Inner skeleton of the $[Au\{(triphos)Rh(P_3)\}_2]^+$ cation (**15**).

and square planar. The P—P bonds undergoing insertion lengthen to values in the range 2.30–2.37 Å, comparable with that found for **14**. Also, the trend in the $M—P(P_3)$ bond lengths corresponds to that found for **14**. The loss of all Au–P(phosphine) interactions existing in the reactant molecules, in the course of the formation of **15**, was considered to be rather unusual [51]; the complete replacement of the Au–P(phosphine) by the new $Au—P(P_3)$ bonds is certainly indicative of comparatively strong interactions between the gold atom and the P_3 groups. As in the case of compounds **14**, the ^{31}P NMR spectra of **15** are indicative of fluxional behaviour in solution.

(iii) Electrophilic additions to main group atoms at the vertices of coordinated triangular fragments

The conceivable presence of lone pair electron density on the bare main group atoms of coordinated fragments prompted attempts to perform electrophilic addition reactions on such atoms, using metal–ligand or other systems of appropriate electronic configuration and lobality. These reactions were alternative to the electrophilic additions on triangular faces already described in Sect. (i), the choice between the two types of process being essentially dictated by the nature of the frontier orbitals of the systems employed for the additions. The effective availability of the electron density on the above bare atoms, i.e. their basicity, had to be probed. It turned out that various addition reactions on individual P atoms of the cyclo-P_3 group in the neutral complexes of type **1** were feasible. On the other hand, no addition has been performed so far on single atoms of the E_2X rings in the cationic complexes **7**, presumably due to a decrease in basicity, either on the atoms of the larger E_3X_3 fragments in the neutral compounds **6**, as already discussed in the introductory part of this section.

The addition of d^6 metal carbonyl $(CO)_5Cr$ fragments, each capable of forming one σ bond, to one or two $P(P_3)$ atoms in **1**, yields the product shown in Fig. 18 [52,53]. The attack on the third $P(P_3)$ atom is probably prevented by steric hindrance. Similar reactions were later performed on the P_2 unit side-on bridging the metal

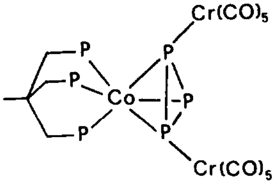

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Fig. 18. Schematic representation of bonding in the structure of the [(triphos)Co(P_3{Cr(CO)$_5$}$_2$)] adduct (**16**).

atoms in a Co_2P_2 cluster [54]. The addition of a σ acceptor on each atom of the P_3 group in **1** was obtained with the $(C_5H_5)(CO)_2Mn$ system [55], which is isolobal with, but less sterically demanding than the $(CO)_5Cr$ system. The geometry of the CoP_3 core is grossly unaffected by the additions. Moreover, as long as neutral acceptors are involved, the successive additions seem to proceed independently of each other, except for the steric effects already mentioned. These aspects, suggestive of modest perturbations of the CoP_3 frame, may be reconciled with the apparently "normal" Cr–P or Mn–P, interactions, as implied by the bond lengths in the expected range [53] and the appreciable overlap populations from EHMO calculations on model systems [15], considering that the CoP_3 orbitals mainly involved in such interactions have largely lone pair character; moreover, in spite of substantial overlaps, bonding is mainly due to donation from filled orbitals of the CoP_3 unit to an empty metal hybrid at rather high energy.

Following the isolobal analogy between d^6 $(CO)_5M$ systems and the CH_3^+ cation, methylation processes at atomic sites of the coordinated fragments were also expected to be possible. Indeed, by reacting compounds **1** with strong methylating agents, the [(triphos)M(P_3Me)]Y (M = Co, Rh, Ir; Y = BF_4, CF_3SO_3) species (**17**) were obtained (Fig. 19) [56]. Probably due to the better orbital energy match than in the case of the neutral metal adducts **16**, the strong $P-CH_3$ interaction, accompanied by a high value of the overlap population, leads to appreciable distortions in the MP_3 core of **17**. These have been rationalised in terms of frontier orbital interactions [56].

Finally, the behaviour of the CoP_3 cluster toward the simplest electrophile, H^+, was investigated by reacting the compound [(triphos)Co(P_3)] with a strong protonating agent such as CF_3SO_3H [57]. In the $[(triphos)CoP_3H]^+$ cation (**18**), which was so obtained, the position of the H atom could not be determined by X-ray analysis, although indirect but convincing evidence was obtained that, at least in the solid, the H atom should bridge between the metal and one of the P_3 phosphorus atoms, forming a three-centre bond with these atoms [57]. The compound, however, is fluxional in solution, as revealed by its NMR spectrum. The mode of bonding of H^+ in **18** differs from that of the isolobal CH_3^+ in **17**, probably due to the virtual absence of steric hindrance in the former case.

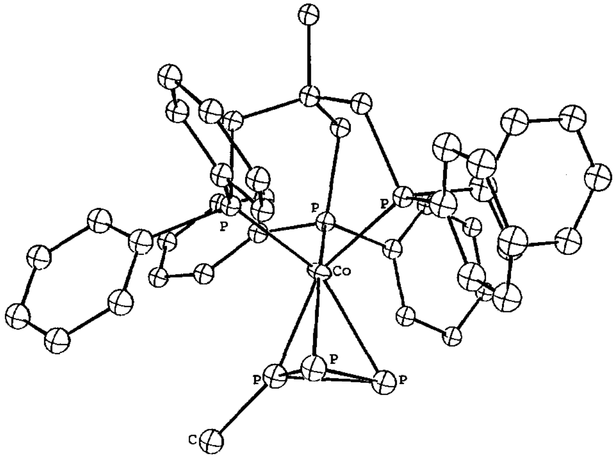

Fig. 19. A view of the $[(\text{triphos})\text{Co}(\text{P}_3\text{Me})]^+$ cation (**17**).

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