I INTRODUCTION

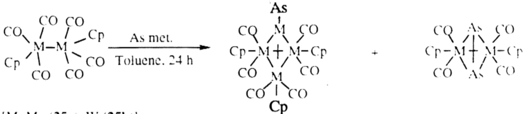
In recent years, the chemistry of organotransition metal complexes incorporating atoms or small aggregates of the main group elements as ligands, has been an active area of research, of particular interest to synthetic chemists. The intensity of interest is evident from the numerous reviews that have appeared in the last decade dealing with reactions of elements from Groups 15 and 16, as well as poly-heteroatomic molecules from these two groups.[1-12] Particular interest lies in the ability of these elements or polyatomic aggregates to link transition metal units to generate large clusters, frequently possessing unusual structures and exhibiting a variety of bonding modes[2]. Work in this laboratory has included reactions of sulphur[13], selenium[14] and phosphorus[15, 16] with $[CpCr(CO)_3]_2$. This present work will serve to develop further aspects of this area of chemistry.

1.1 A review on the syntheses and structures of transition-metal compounds containing arsenic atoms and units

Naked arsenic acting as ligands in transition-metal compounds ranging from one to eight atoms is of current research interest. These ligands can be stabilized in the coordination spheres of certain transition metal fragments. The section below gives a brief summary of reported work.

1.1.1 Compounds containing a single arsenic atom

The cluster compound $(C_5H_5)_3M_3(CO)_6As$ [M = Mo (**26a**), W (**26b**)] has been prepared from the dinuclear complexes $(C_5H_5)_2M_2(CO)_6$ (**25a**, **25b**) and metallic arsenic in a simple reaction[17] (Equation i).

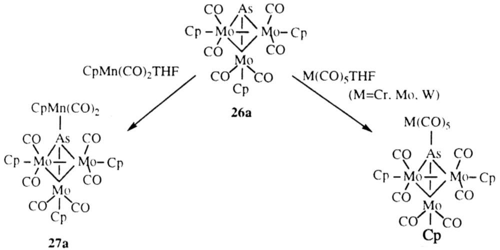


[M=Mo (**25a**); W (**25b**)]

[M=Mo (**26a**); W (**26b**)]

. . . (i)

Because the arsenic atom in these complexes utilizes only three of its five valence electrons, it provides a suitable site for electrophilic reactions. Metal fragments such as $(C_5H_5)_2Mn(CO)_2THF$ and $M(CO)_5THF$ (M = Cr, Mo, W) react readily with **26a** to yield $(C_5H_5)_3Mo_3(CO)_6AsMn(C_5H_5)(CO)_2$ (**27a**) and $(C_5H_5)_3Mo_3(CO)_6As$-$M(CO)_5$ (**27b**) (Equation ii).



26a

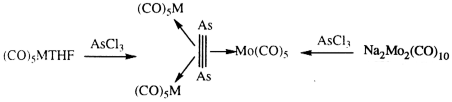
27a

27b

. . . (ii)

1.1.2 Compounds containing the diarsenic unit

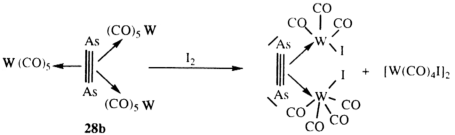
Diarsenic complexes can be synthesized by a wide range of reactions. Their structures normally contain the As_2 ligand which is a very versatile because it can act as four, six or eight-electron donor. For example, $[(CO)_5Mo]_3As_2$ (**28a**) can be obtained from the reaction of $Na_2Mo_2(CO)_{10}$ with $AsCl_3$. The star-type compound formed contains As_2 side-on coordinated as a six-electron donor [18] (Equation iii).



28a

. . . (iii)

Its tungsten analogue [$(CO)_5W]_3As_2$ (**28b**) reacts with iodine to give $[(CO)_7W_2I](\mu\text{-}I)(\mu\text{-}\eta^2\text{-}As_2)$ (**29**) containing As_2 as a side-on coodinated four-electron donor (Equation iv).

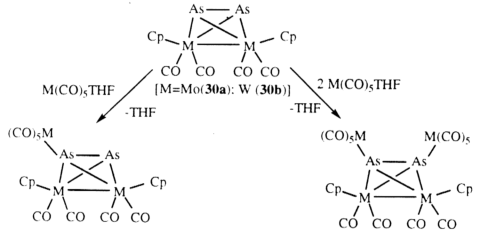


28b

29

. . . (iv)

The compounds $[Cp(CO)_2M]_2As_2$ [M = Mo (**30a**), W (**30b**)]act as six-electron donors when reacted with an equimolar of $Cr(CO)_5(THF)$ to yield $[Cp(CO)_2M]_2As_2Cr(CO)_5$ [M = Mo (**31a**), W (**31b**)] or as an eight-electron donor with two moles of $Cr(CO)_5(THF)$ to yield $[Cp(CO)_2M]_2As_2[Cr(CO)_5]_2$ [M = Mo (**32a**), W (**32b**)], respectively, by additional end-on coordination via its lone pairs[18] (Equation v).



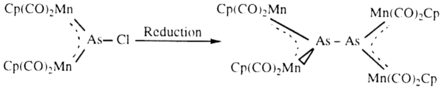
[M=Mo(**30a**): W (**30b**)]

[M=Mo(**31a**): W (**31b**)]

[M=Mo(**32a**): W (**32b**)]

. . . (v)

Another example of As as an eight-electron donor, is found in the complex, $[Cp(CO)_2Mn]_2As\text{-}As[Mn(CO)_2Cp]_2$ (**33**), from the reductive coupling of two arsinidene complexes $[Cp(CO)_2Mn]_2AsCl$ in which an As_2 ligand is coordinated to four 16-electron fragments[18] (Equation vi).

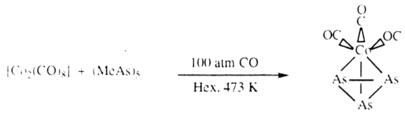


33

. . . (vi)

1.1.3 Compounds containing the *cyclo*-As_3 ligands

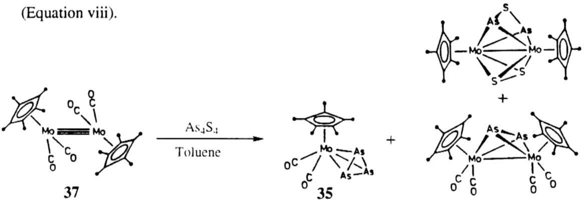
Cyclo-As_3 complexes are less common, only a few examples are known. The first cyclotriarsenic complex reported was $[Co(CO)_3(\eta^3\text{-}As_3)]$ (**34**), which was obtained from the reaction of $Co_2(CO)_8$ with *cyclo*-$(MeAs)_5$ at 473 K in hexane under high pressure at 100 atm of CO[19] (Equation vii).



34

. . . (vii)

The other two examples are $[(C_5Me_5)Mo(CO)_2(\mu^3\text{-}As_3)]$ (**35**) and the *cyclo*-triarsenic $[(triphos)(M)(As_3)Co(triphos)]X_2$ (**36**) [M = Co (**36a**), Ni (**36b**); X `triphos=1,1,1-tris(diphenylphosphinomethyl)ethane]` = BF_4, BPh_4 ,complexes. The former was isolated from the reaction of the triply bonded complex $[(C_5Me_5)Mo(CO)_2]_2$ (**37**) with As_4S_4[20] and also with yellow As_4[21] (Equation viii).



37 **35**

. . . (viii)

Complexes **36** were obtained from the reaction of a solution of yellow As_4 in THF with Co^{2+} or Ni^{2+} aquo-ions and the triphosphane in solution to give the As_3 complexes of **36**[22]. The new compounds have a triple-decker sandwich structure containing the bridging *cyclo*-triarsenic entity as an internal layer as shown in Figure 1.

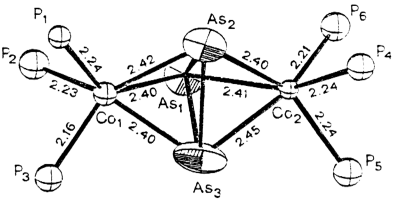


Figure 1. Structure of the $[(\text{triphos})\text{Co}(\text{As})_3\text{Co}(\text{triphos})]^{2+}$ **(36a)** dication.

Cyclo-As_3 can also form part of a polynuclear cluster. For example, in $[Co_4(\mu_3\text{-}As)_3(\mu_3,\eta^3\text{-}As_3)(PPh_3)_4]$ (**38**), synthesized from $[CoCl_2(PPh_3)_2]$ and $PhAs(SiMe_3)_2$[23], the cluster core consists of a Co_4 tetrahedron with three faces capped by As atoms and with the fourth face extended to an octahedron by an As_3 ligand (Figure 2).

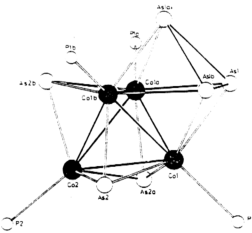


Figure 2. Structure of $[Co_4(\mu_3\text{-}As)_3(\mu_3,\ \eta^3\text{-}As_3)(PPh_3)_4]$ **(38)** (without phenyl groups).

1.1.4 Compounds containing the As_4 unit

The thermolytic reaction of *cyclo*-$(MeAs)_5$ and $[(\eta^5\text{-}MeC_5H_4)Mo(CO)_3]_2$ in toluene at 130°C in a sealed tube produces the first structurally characterized example of a $[CpMo(CO)]_2(E_2)_2$ complex (E = P, As, or ≡CR), $[(\eta^5\text{-}MeC_5H_4)Mo(CO)]_2(\mu_2,\eta^2\text{-}As_2)_2$ (**39**), which contains extremely short As-As bonds of 2.279(2) and 2.300(2) Å and an Mo-Mo bond of 2.950(1) Å; the two, four-electron donating As_2 ligands are bonded side-on to form a plane perpendicular to the Mo-Mo bond and the two CO and two $(\eta^5\text{-}MeC_5H_4)$ groups are cis[24] (Figure 3).

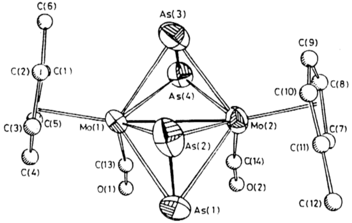


Figure 3. Molecular structure of $[(\eta^5\text{-}MeC_5H_4)Mo(CO)]_2(\mu_2,\eta^2\text{-}As_2)_2$ (**39**).

The photolysis of $[Cp^*Nb(CO)_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[25] with yellow arsenic gives the following complexes as shown in Equation (ix).

$$[Cp^*Nb(CO)_4] \xrightarrow{As_4,\ h\nu} \underset{\mathbf{40a}}{[Cp^*Nb(CO)_2(\eta^4\text{-}As_4)]} + \underset{\mathbf{40b}}{[\{Cp^*Nb(CO)\}_2(As_2)_2]}$$

. . . (ix)

The structure of [Cp*Nb(CO)$_2$(η^4-As$_4$)] reveals a planar *cyclo*-As$_4$ (tetraarsacyclobutadiene) ligand (Figure 4). This is the first example of coordinative stabilization of tetraarsacyclobutadiene~~s~~ via a 14-electrons fragment, Cp*Nb(CO)$_2$.

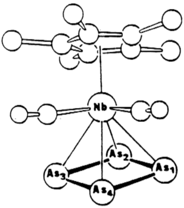


Figure 4. Structure of [η^5-C$_5$Me$_5$)(CO)$_2$Nb(η^4-As$_4$)] **(40a)**.

1.1.5 Compounds containing the *cyclo*-As$_5$ ligands

Complex (CpMo)$_2$[μ-(η^4-As$_5$)] **(41)** is the first transition-metal complex containing a ring of five unsubstituted arsenic atoms in a triple-decker sandwich structure to be isolated and structurally characterised[26] (refer to Figure 5).

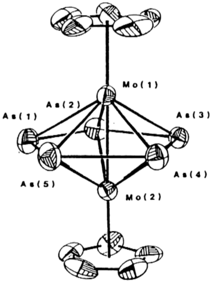


Figure 5. Molecular structure of (CpMo)$_2$[μ-(η^4-As$_5$)] **(41)**.

The anion *cyclo*-$As_5^{\ominus}$ (**42**)[27] (Figure 6) prepared from yellow arsenic As_4, is to date the largest known 6π five-membered ring ligand, and is suitable for constructing the sandwich complexes.

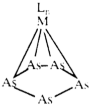


Figure 6. *Cyclo*-$As_5^{\ominus}$ **ligand (42)**.

(ML_n = Fe(η^5-C_5Me_5) (**42a**)[27a], Fe(η^5-C_5Me_4Et) (**42b**)[27a], Ru(η^5-C_5Me_5) (**42c**)[27b], Ru(η^5-C_5Me_4Et) (**42d**)27[b])

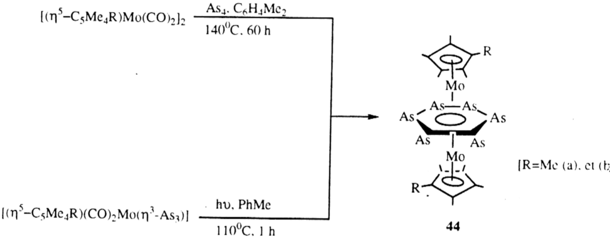
These metallocenes **42**, with a *cyclo*-As_5 deck, are generally both thermally and air-stable. They are typical nido compounds (n + 2 = 8 SEP) with a pentagonal pyrimidal core. The presence of lone pair electrons in the arsenic atoms can be utilized for further coordination.

The decamethylferrocene stacking reaction, discovered by Rybinskaya *et al.* for the synthesis of the 30 VE triple-decker sandwich complex $[(C_5H_5)Fe(C_5Me_5)$-$Fe(C_5Me_5)]PF_6$[28] can be applied to **42a**. In the stacking reaction, **42a** forms the triple-decker sandwich cation $[(\eta^5\text{-}C_5H_5)Fe(\mu,\eta^5\text{-}As_5)Fe(\eta^5\text{-}C_5Me_5)]PF_6$ (**43**) with 30 valence electrons[27a] (Equation x).

$$\mathbf{42a} \xrightarrow[\text{- } C_6H_6]{[CpFe(C_6H_6)]PF_6,\ h\nu} \underset{\mathbf{43}}{[(C_5H_5)Fe(As_5)Fe(C_5Me_5)]PF_6} \qquad \ldots (x)$$

1.1.6 Compounds containing the *cyclo*-As_6 ligands

The molecule *cyclo*-As_6 (hexaarsabenzene), isoelectronic with benzene was first coordinatively stabilized in 1989[29] as the central deck of the triple-decker sandwich complex (**44**) which is synthesized from the thermolysis of As_4 with $[(\eta^5\text{-}C_5Me_4R)Mo(CO)_2]_2$ or the photolysis of $[(\eta^5\text{-}C_5Me_4R)(CO)_2Mo(\eta^3\text{-}As_3)]$[29] (Equation xi).



. . . (xi)

The crystal structure analysis of **44** shows that both five-membered rings and the As_6-ring are planar and parallel (Figure 7). In contrast to the As_5-middle deck distorted by Jahn-Teller effects[30] in the 27-valence electron (VE) triple-decker complex **41**[26], a regular arsenic hexagon is found in the 28 VE triple-decker **44**.

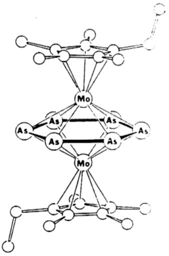


Figure 7. Crystal structure of $[(\eta^5\text{-}C_5Me_4Et)Mo(\mu, \eta^6\text{-}As_6)Mo(\eta^5\text{-}C_5Me_4Et)$ (**44**).

1.1.7 Compound containing the As_7 ligand

The synthesis of the anion $[As_7Cr(CO)_3]^{3\ominus}$ (**45**) can be achieved *via* the reaction of $[Cr(CO)_3(\eta^6\text{-mes})]$ (mes = 1, 3, 5-$Me_3C_6H_3$) with ethylenediamine extracts of Rb_3As_7 in the presence of three equivalents of 4, 7, 13, 16, 21, 24 hexaoxa-1, 10-diazabicyclo-[8.8.8]hexacosane (crypt)[31] (Equation xii).

$$[Cr(CO)_3(\eta^6\text{-mes})] + Rb_3As_7 + 3\ \text{crypt} \xrightarrow{\text{en / toluene}} \underset{\mathbf{45}}{[As_7Cr(CO)_3][(Rb.crypt)_3].\ 0.5\ \text{toluene}} + \text{Mes.} \qquad \text{. . . (xii)}$$

The structure of **45** (Figure 8) contains an opened As cage that is bound in an η^4-fashion to the $Cr(CO)_3$ fragment. The formation of **45** represents the conversion of a nortricyclic $As_7{}^{3\ominus}$ cluster into a norbornadiene-like As_7 fragment at a transition-metal centre.

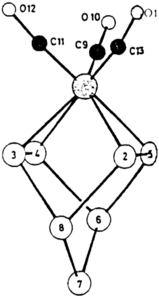


Figure 8. Ball-and-stick Chem-X representation of **45**.

1.1.8 Compound containing the *cyclo*-As_8 ligands

Recently, the reaction of tetracarbonylniobium with in excess yellow arsenic by Scherer *et al* results in formation of the binuclear niobium complex $[(Cp''Nb)_2(\mu, \eta^{4:4}\text{-}As_8)]$ (**46**) ($Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$)[32] (Equation xiii). Complex **46** can react with the metal fragment, $[Cr(CO)_5(THF)]$ to give **47**.

$$\begin{tikzcd}[(Cp''Nb(CO)_4] \arrow[r, "As_4\text{, decalin}", "170°C\text{, 2 h}"'] & {[(Cp''Nb)_3As_6] + \underset{\textbf{46}}{[(Cp''Nb)_2(\mu, \eta^{4:4}\text{-}As_8)]}} \arrow[d, "{[Cr(CO)_5(THF)]}", "THF\text{, }20°C\text{, 1.5 h}"'] \\ & \underset{\textbf{47}}{[(Cp''Nb)_2\{As_8Cr(CO)_5\}]}\end{tikzcd}$$

. . . (xiii)

Structural analyses showed that **46** (Figure 9) and **47** (Figure 10) formed a puckered, strongly distorted eight-membered As_8 ring. Such a coordination geometry has not been observed for cyclooctatetraene complexes[33]. The distortion observed is possibly due to two ten-valence electron Cp"Nb fragments.

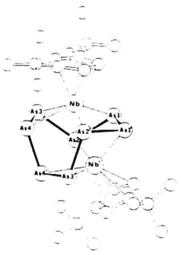


Figure 9. Molecular structure of $[(Cp''Nb)_2(\mu, \eta^{4:4}\text{-}As_8)]$ (**46**).

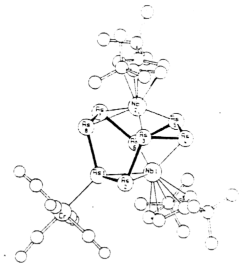
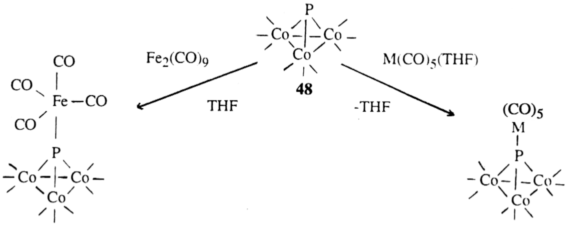


Figure 10. Molecular structure of $[(Cp''Nb)_2\{As_8Cr(CO)_5\}]$ (**47**).

1.1.9 Reactivity of coordinated Phosphorus or Arsenic atoms and units

Ligated unsubstituted pnicogen atoms (*eg*. phosphorus and arsenic) possess non-bonding electrons which are available for further, terminal or bridging, interactions with transition-metal-ligand units or electrophilic organic reagents. Thus compounds containing these naked pnicogen atoms or units have been found capable of acting as starting materials for numerous derivatives. For example, the monophosphido trimetallatetrahedranes $[\{Co(CO)_3\}_3 (\mu\text{-}P)]$ (**48**) can coordinate to metal-ligand units like $Fe(CO)_4$ generated *in situ* from $[Fe_2(CO)_9]$ in THF, giving $(\{Co(CO)_3\}_3P)Fe(CO)_4$[34, 35] (**49**), or $(\{Co(CO)_3\}_3P)M(CO)_5$ (**50**) with $M(CO)_5(THF)$ [M = Cr (**50a**), Mo (**50b**) or W (**50c**)][36] (Equation xiv).



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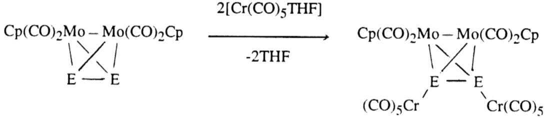
[M = Cr (**50a**), Mo (**50b**) or W (**50c**)]

. . . (xiv)

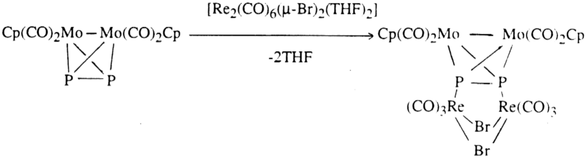
Likewise, the non-bonding electrons of the E_2 ligand in the complexes $[CpMo(CO)_2E]_2$ [E = P (**51**), As (**30a**)] can be utilized for terminal coordination as shown in **52** and **53**[18, 37] (Equation xv) to the $Cr(CO)_5$ fragments and bridging coordination as in **54**[37] to $Re_2(CO)_6(\mu\text{-}Br)_2$ fragments (Equation xvi). Here the ligands act as eight-electron donors to the transition-metal fragments.



[E = P (**51**), As (**30a**)]

[E = P (**52**), As (**53**)]

. . . (xv)



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. . . (xvi)

1.2 Reactivity of mixed Pnicogen Chalcogenides, E_4X_3 (E = P, As; X = S, Se), with transition metal complexes

Among hetero-polyatomic molecules of the main-group elements, the chalcogenides of the Group 15 elements, E_4X_3 (E = P, As; X = S, Se) (Figure 11) have featured more prominently than others in reactions with transition-metal complexes. They are able to generate a diversity of new complexes , on account of the presence of two different types of atoms in the same molecule and different chemical environments for the same type of atoms *e.g.* apical *versus* basal pnicogens. It have been observed that the E_4X_3 cage may undergo both disruptive and nondisruptive processes, depending on the nature of the metal atom, its oxidation number and its ligand environment. The following review summarises the reactivity of E_4X_3 towards transition metal complexes, an area of work extensively developed by Di Vaira and Stoppioni.[2]

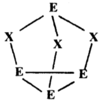
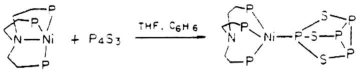


Figure 11. The atomic arrangement in E_4X_3 molecule.

1.2.1 Nondisruptive processes

Nondisruptive processes do not involve any cleavage or fragmentation of the cage molecule, therefore giving rise to transition-metal complexes containing an intact cage of E_4X_3, usually coordinated *via* its apical E atom.

Thus, the reaction of the [(np$_3$)M] (M = Ni or Pd) d^{10} metal complexes with the P_4X_3 (X = S, Se) chalcogenides afforded neutral compounds of formula [(np$_3$)M(P_4X_3)](**55**) (M = Ni, X = S or Se; M = Pd, X = S)[38, 39] (equation xvii).



. . . (xvii)

The metal in [(np$_3$)Ni(P_4S_3)].2C_6H_6 (Figure 12) is in a distorted-tetrahedral environment formed by the P atoms of the np$_3$ ligand and by the apical P atom of the cage molecule, the nitrogen of the potentially tetradentate np$_3$ ligand being uncoordinated.

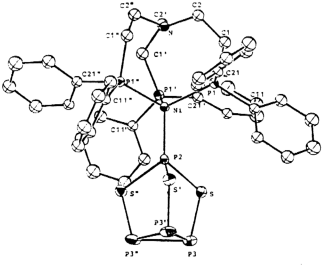


Figure 12. Perspective view of the [(np$_3$)Ni(P_4S_3)] (**55**) molecule.

A similar structure is assigned to the isomorphous P_4Se_3 adduct [(np$_3$)Ni(P_4Se_3)].2C_6H_6 and to the [(np$_3$)Pd(P_4S_3)] complex.[38] Other examples come from metal carbonyl systems, *eg*. the compounds *cis*-[(P_4S_3)$_2$Mo(CO)$_4$] (M = Cr, Mo, W), cis-$[(P_4S_3)_3Mo(CO)_3]$ (M = Cr, Mo)[40] and $[Mo(CO)_5(P_4S_3)]$ (**56**)[41] (Figure 13). **56** is prepared by refluxing molybdenum hexacarbonyl with P_4S_3 in cyclohexane.

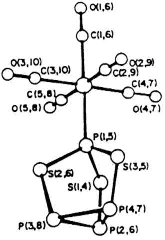


Figure 13. Structure of $Mo(CO)_5(P_4S_3)$ (**56**).

The P_4X_3 cage undergoes minor deformation upon coordination to the above mentioned metal systems. In ~~the~~ these types of complexes, the electron-rich d^{10}-ML_3 $(np_3)M$ metal moieties maybe assumed to preserve the intact cage molecules because they favoured processes in which the 18-electron configuration of the metal atom is also preserved[38]. The coordination number and the oxidation number of the metal atom remain unchanged in the process.

The d^6-ML_5 $Mo(CO)_5$ moiety has one σ-type empty orbital at an energy level suitable for interaction with the P_4S_3 unit, whereas the d^{10}-ML_3 fragment with the geometry of the $(np_3)Ni$ moiety above has one σ-orbital and one degenerate pair of π-orbitals, all occupied[42]. The P_4S_3 unit in the $(np_3)Ni$ moiety is coordinated by allowing the σ-type metal 4s and 4p contributions to the Ni-P_{ap} bond. The coordinated cage in **55** shows the P_4S_3 cage is slightly deformed at apical P atom with a slight elongation of the P_{apical}-X bonds (Figure 13) whereas molecule **56** undergoes deformation at the basal P atoms.[38, 39]

1.2.2 Disruptive processes

Disruptive processes may involve the following :

(a) Cleavage of a P-P bond of the cage molecule with insertion of a transition metal fragment

The reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with P_4S_3, afforded the compound $[\{Pt(\mu\text{-}P_4S_3)(PPh_3)\}_3]$(**57**)[43] *via* insertion of the d^9ML_3 $Pt(PPh_3)_3$ fragments into the P-P bond of the cage (Figure 14).

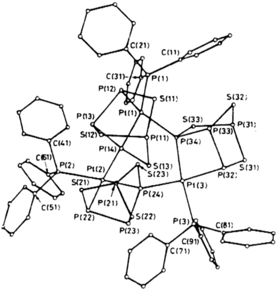


Figure 14. A view of the $[\{Pt(\mu\text{-}P_4S_3)(PPh_3)\}_3]$ (**57**) molecule.

The metal atom in each of the $Pt(\mu\text{-}P_4S_3)(PPh_3)$ units is linked to the P_4S_3 cage *via* the two "basal" P atoms. One of these P atoms is also bonded to a Pt atom of another $Pt(\mu\text{-}P_4S_3)(PPh_3)$ unit so that each of the metal atoms, which are four-coordinate, is bound to three P_4S_3 phosphorus atoms, belonging to two different cages, and to one phosphine P atom.

There are only minor changes in the bond distances within the cage after insertion except for the lengthening of the P-P bond being cleaved. Calculations based on model systems showed that the P-P bonds of a P_4S_3 cage cleave more easily than the P-S bonds, due to geometric factors. The insertion process involves an increase in the formal oxidation number of the metal atom,[44] but not in the overall electron count on going from the interacting specimen to the final product.

Further experimental evidence for an increase in the oxidation number of the metal on adduct formation has been reported in the case of the iridium compound.[45] The complex $[Ir(P_4S_3)(PPh_3)Cl(CO)]$ (**58**) is formed from the reaction of a solution of P_4S_3 in benzene with an equimolar solution of $[IrCl(CO)(PPh_3)_2]$ (Vaska's complex) at *ca.* 60°C.

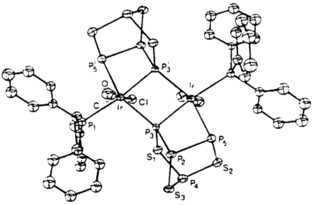


Figure 15. Crystal structure of $[Ir(\mu\text{-}P_4S_3)(PPh_3)Cl(CO)]_2$ (**58**).

X-ray structure analysis (Figure 15), showed the P_3 ring of the P_4S_3 molecule has opened, and one PPh_3 group per metal center has been displaced. The P_4S_3 group, in contrast to compounds in which it behaves as a monodentate ligand, is significantly distorted compared to the uncoordinated molecule[46]. Although the d^8 metal-ligand system present in (**58**) has a different nature, geometry and *d*-electron count with respect to those of (**57**), the two systems are isolobal.[47]

(b) Replacement of a basal P atom of the cage by a metal atom

The reaction of P_4X_3 (X = S, Se) with $[MCl(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) in the presence of triphos [triphos = 1,1,1-tris (diphenylphosphinomethyl)ethane] yields the compounds $[(triphos)M(P_3X_3).C_6H_6]$(**59**) [M = Rh; X = S, Se; M = Ir, X = S, Se].[44, 48] The structure of (triphos)Rh(P_3S_3) (Figure 16) showed the (triphos)Rh moiety in the (triphos)Rh(P_3S_3) molecule replaces one basal P atom in the P_4S_3 cage. The metal atom is coordinated to the three phosphorus atoms of the triphos ligand and to one sulphur and two phosphorus atoms of the P_3S_3 fragment in a distorted six-coordinate environment.

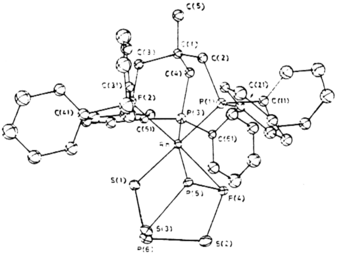


Figure 16. Perspective view of the [(triphos)Rh(P_3S_3)] (**59**) molecule.

The formation of the small cluster, mainly consisting of main group atoms, 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 (**59**) because the metal atom, which is initially in the oxidation state +1, undergoes only a moderate reduction on forming these compounds. As in the reactions involving first row transition metal cations initially in the oxidation state +2 then a greater reduction occurs which results in a more drastic fragmentation of the cage molecule. Another consideration for the formation of (**59**) is that it indicates 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 three-fold symmetry[42], is provided by its triangular P_3 base of the cage, which has similar symmetry.

This is also in line with the well-documented ability of some d^9-ML_3 units to symmetrically link to cyclic P_3 or As_3 groups [19, 49] or the preference of formally d^8-ML_3 units for the P_2S or isoelectronic heterocyclic groups,[51] and the geometry of overlap, as suggested by the MO picture for cage compounds of geometry similar to that of the present ones.[50] However, the interaction of a d^8(triphos)M (M = Rh, Ir) system with the intact P_4S_3 molecule does not seem to provide a stable electronic configuration at the metal atom, so that further disruptive steps may be anticipated. Actually, the atom of the formally d^9(triphos)M fragment in each of the present compounds reaches the 18e configuration by borrowing 3e from the P_3X_3 framework, as the displaced P atom would be considered to do in the original cage molecule.

Bond distances with the coordinated P_3X_3 fragments and those of the parent P_4X_3 molecules do not differ considerably except for a shortening of the remaining P_{bas}-P_{bas} bond in the fragment and the P_{ap}-X bond formed by the chalcogen atom bound to the metal.

(c) Extensive fragmentation of the E_4X_3 cage

The reactions of hydrated Co(II) salts with E_4X_3 molecules in the presence of a triphos ligand yielded a series of complexes of formula [(triphos)Co(E_2X)]$^+$(**60**)[51-54] 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 the monometal complex [(triphos)Co(P_3)] to form the pseudo-tetrahedral clusters CoE_2X (Figure 17).

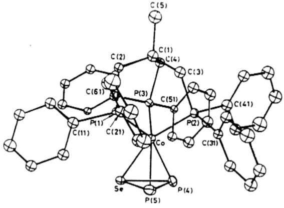


Figure 17. Perspective view of the [(triphos)CoP_2Se]$^+$ (**60**) cation.

In another example, the reaction of Ni(BF_4)$_2$·6H_2O with P_4S_3 in the presence of a triphos ligand yielded the complex [(triphos)Ni(η^3-P_3]BF_4·C_2H_5OH (**61**), isoelectronic with the cobalt cations, **60**[55, 56] (Figure 18).

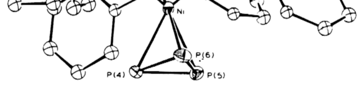


Figure 18. Molecular structure of [(triphos)Ni(P_3)]$^+$ (**61**) cation.

The metal atom in the complex cation is coordinated to the three P atoms of the phosphine ligand and to the atoms of the P_2S or P_3 unit in a distorted six-coordinate environment similar to that of the mononuclear cyclic triphosphorus complexes. By extension of considerations applied to cyclic triphosphorus complexes, the P_2S or P_3 unit is considered to act as a 4-electron donor, so that the metal atom reaches the 18-electron configuration.

The extrusion of the small triatomic fragments from the P_4X_3 cage molecules in the above processes appears to be related to the presence among the reactant of the metal atoms in high oxidation state. In the course of their interaction with the P_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.[44] This view is based on comparisons between the processes leading to compounds of the types $[(np_3)M(P_4X_3)]$ (M = Ni, X = S or Se; M = Pd, X = S), $[(triphos)M(P_3X_3)]$, $[(triphos)Co(P_2X)]^+$ and $[(triphos)Ni(P_3)]^+$, 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 do not apply to heavier transition metals with carbonyl or cyclopentadienyl ligands. On the other hand, the possibility of obtaining either P_2X or P_3 fragments from P_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 tha formation of stable compounds.

The reaction of $Cp^*_2Mo(CO)_4(Mo{\equiv}Mo)$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[57] with P_4X_3 in boiling toluene gives the following complexes as shown in Equation (xviii).

$$Cp^*_2Mo(CO)_4(\mathit{Mo{\equiv}Mo}) \; + \; P_4S_3$$

$$\Big\downarrow \begin{array}{l}\text{Toluene}\\ \text{Reflux}\end{array}$$

$$\underset{\mathbf{62}}{Cp^*Mo(CO)_2P_3} + \underset{\mathbf{63}}{Cp^*_2Mo_2(CO)_4P_2} + \underset{\mathbf{64}}{Cp^*_2Mo_2P_2S_3} + \underset{\mathbf{65}}{Cp^*_2Mo_2P_4S}$$

. . . (xviii)

The X-ray diffraction analysis of complexes (**64**) (Figure 19) and (**65**) (Figure 20) with their corresponding $Cr(CO)_5$ monoadducts are shown below.

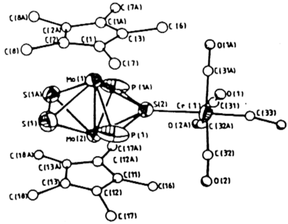


Figure 19. Molecular structure of $(C_5Me_5)_2Mo_2P_2S_3{\cdot}Cr(CO)_5$ (**64**).

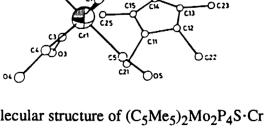


Figure 20. Molecular structure of $(C_5Me_5)_2Mo_2P_4S{\cdot}Cr(CO)_5$ (**65**).

The structure of (**65**) showed that the η^2-PS and η^3-P_3 ligands lie in a plane perpendicular to the Mo-Mo axis which is bisecting. However, (**64**) is found to have a similar geometry which contains an η^2-S_2 and an η^3-P_2S ligand.

It is noted that a variety of fragment derivatives such as bridging diatomic P_2 or S_2 units, triatomic P_3 unit and penta-atomic P_4S or P_2S_3 moieties obtained above differed very much compared from the fragments stabilized by the already mentioned (triphos)M systems.

1.3 Reactions of As_4S_4 with transition-metal complexes

The reactivity of realgar, As_4S_4, towards some of the transition metal complexes are discussed in the following.

The reaction of As_4S_4 with $[\{MCl(cod)\}_2]$ (M = Rh or Ir) in the presence of the ligand triphos yields compounds of formula $[(triphos)M(\eta^3\text{-}As_3S_3)]\cdot C_6H_6$ (**66**)[58] which is isomorphous to the $[(triphos)Rh(\eta^3\text{-}P_3X_3)]\cdot C_6H_6$ (X = S, Se)[48] derivatives.

66 contain the new As_3S_3 unit, which is trihapto bonded to the metal atom through one sulfur and two arsenic atoms. This coordinated As_3S_3 fragment is similar to the P_3X_3 fragments which are present in compounds **59**. But in the reactions with $M(BF_4)_2\cdot 6H_2O$ (M = Co or Ni)[53] in the presence of triphos, the As_4S_4 molecule undergoes more drastic rearrangement of the cage to yield $[(triphos)M(\eta^3\text{-}As_2S)]$-$BF_4\cdot C_2H_5OH$ or the *cyclo*-As_3 sandwich compound $[(triphos)Ni(\mu, \eta^3\text{-}As_3)]BF_4Ni$-$(triphos)(BF_4)_2$. The As_2S fragment are similar to those already described in **59**. These findings showed that the As_4S_4 molecule gives different fragments in the presence of various (triphos)M moieties, depending on the nature of the metal atom and its oxidation state in the parent compound which is reminiscent of the E_4X_3 cage molecules described above.

Similar fragmentation of As_4S_4 are observed in its reactions with $[Cp^*M(CO)_2]_2$ [M = Mo (refer to Equation viii)[20], Fe and Co (Equation xix)[59]] systems.

$$[(C_5Me_5)_2Fe_2(CO)_4] + As_4S_4 \xrightarrow[115°C]{toluene} [(C_5Me_5)_2Fe_2As_2S_2] + [(C_5Me_5)_2Fe_2As_2S_3]$$

$$[(C_5Me_5)_2Co_2(CO)_2] + As_4S_4 \xrightarrow[80°C]{toluene} [(C_5Me_5)_2(CO)Co_2As_2S_2] + [(C_5Me_5)_3Co_3As_2S_4]$$

$$[C_5Me_5Co(CO)_2] + As_4S_4 \xrightarrow[h\nu]{THF} \underset{\textbf{67}}{[(C_5Me_5)_2Co_2As_2S_3]} \qquad \ldots (xix)$$

An X-ray structure analysis[59] of **67** (Figure 21) revealed that in this complex a novel As_2S_3 ligand is present as a 4-electron donor with two *cis*-arranged η^2-bonded AsS units that are bridged by a S atom. This results in a "basket" with a C_2 axis through S (2) and the midpoint of the Co_2S_2 square. The structure differs from the sulfur-arsenic chains of the As_2S_3 layer lattice primarily in the all-*cis* geometry that is forced upon the molecule by the two C_5Me_5Co units.

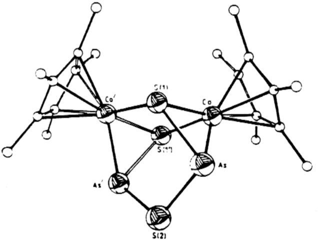


Figure 21. Molecular structure of $[(C_5Me_5)_2Co_2As_2S_3)]$ (**67**).

Recently, the reaction $[\{Cp^xCo(CO)\}_2]$ ($Cp^x = \eta^5\text{-}C_5Me_4Et$)[60] with As_4S_4 affords the following complexes (Equation xx).

$$[\{Cp^xCo(CO)\}_2] + As_4S_4 \xrightarrow[80°C]{\text{toluene}} \underset{\mathbf{68}}{[Cp^x{}_2Co_2(CO)As_2S_2]} + [Cp^x{}_2Co_2As_2S_3]$$

$$+ \underset{\mathbf{69}}{[Cp^x{}_3Co_3As_2S_4]} + [Cp^x{}_3Co_3As_4S_2]$$

. . . (xx)

The reaction has yielded two bi- and trinuclear Cp'Co complexes with AsS and As_2S_3 ligands in new modes of coordination. An important feature in the crystal of structure of **68** is the two metal Co centers *syn* bridged by the two η^1: η^2-AsS ligands (Figure 22). The crystal structure of **69** possesses a $Co_3As_2S_4$ cage, in which one μ_3-As_2S_3 ligand form the main constituents of a distorted cube (Figure 23).

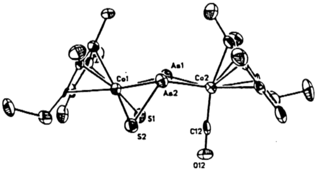


Figure 22. Crystal structure of $[Cp^x{}_2Co_2(CO)As_2S_2]$ (**68**).

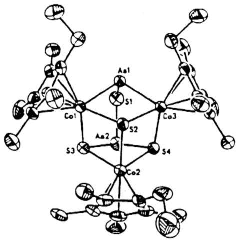


Figure 23. Crystal structure of $[Cp^{x}{}_3Co_3As_2S_4]$ (**69**).

Although the modes of bonding in complexes obtained from the $[Cp^*M(CO)_2]_2$ and (triphos)M systems are different, there are parallels noted in the similarities of related bridging groups of the $[Cp^*M(CO)_2]_2$ reactions with P_4S_3 and As_4S_4. Reactions with $[Cp^*M(CO)_2]_2$ are easier than the (triphos)M systems because smaller fragments like *cyclo*-As_3 and P_3 units are extruded in the reactions of the former with P_4S_3 or As_4S_4 which are stabilized by interaction with $Cp^*M(CO)_2$ fragments in the mononuclear compounds.[20, 57]

1.5 OBJECTIVES

This laboratory has been involved in the investigations of the reactivity of the Cr-Cr bonded $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) dimer and its Cr≡Cr bonded congener $[CpCr(CO)_2]_2$ towards the non-metal elements.[17, 18] Having successfully developed in depth the reactivity of the highly reactive $[CpCr(CO)_3]_2$ dimer with elemental P_4, this project was aimed at a comparative study with elemental gray arsenic. This will also serve to complement similar studies on the analogous complexes $[CpM(CO)_3]_2$ (M = Mo, W)[17] and $[(C_5Me_5)Mo(CO)_2]_2$.[21] On completion of this, the study was extended to reactions with the mixed pnicogen chalcogenides P_4X_3 (X = S, Se) and As_4S_4. The results are expected to provide valuable comparisons to earlier investigations with the pnicogens and the chalcogens.[13-16]