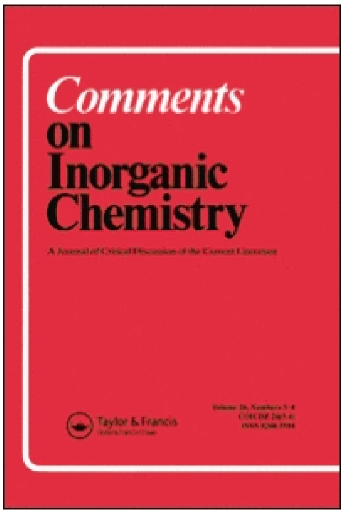

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Reactivity of Pnicogen Chalcogenides with Metal-Ligand Fragments

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Reactivity of Pnicogen Chalcogenides with Metal–Ligand Fragments

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The pnicogen chalcogenides form a large class of molecular and polymeric compounds; the molecules containing pnicogen and chalcogen atoms at the vertices of polyhedral structures exhibit several coordination sites and reactive edges and faces. The pnicogen chalcogenides interact in various ways with metal moieties: depending on the electronic properties of the metal fragments employed, compounds containing the intact cage molecules or fragments originating from their cleavage have been obtained. Different degrees of demolition of the cages have been achieved by tuning the interactions between the cages and the metal fragments through appropriate selection of the reacting species.

Key Words: *pnicogen chalcogenides, transition metal compounds, mixed clusters*

INTRODUCTION

The pnicogen chalcogenides, binary compounds formed by the elements of groups V and VI, form a remarkable class of sub-

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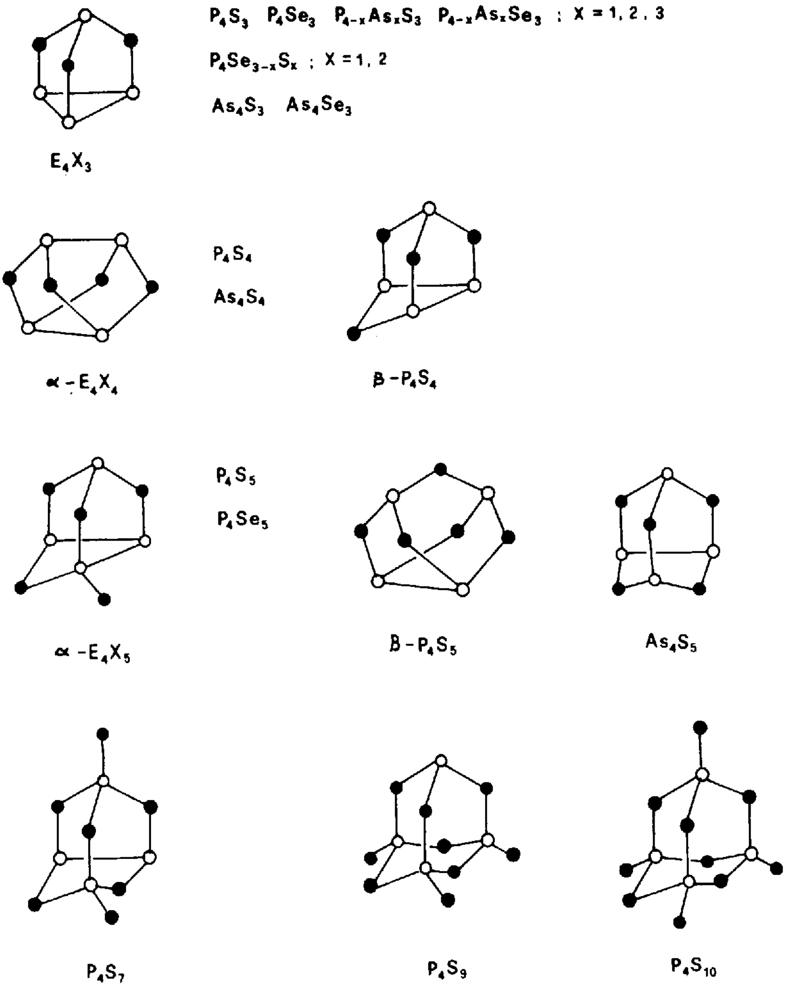
stances, which have attracted the attention of chemists for a long time due to their unusual structures and puzzling reactivity. The study of such compounds presently constitutes one of the most active areas of inorganic research, yielding numerous novel compounds, some of which are considered as suitable precursors for inorganic solid state products with peculiar electronic properties.[1] In this connection a remarkable position is occupied by thiazyl polymers $(SN)_x$ which, exhibiting metal-like superconductivity,[2] have attracted tremendous interest, which has stimulated even further the activity in this area of synthetic and structural chemistry. Tetrasulphur tetranitride, S_4N_4,[3] is the most thoroughly investigated among the latter compounds; in particular, its behavior toward metal fragments has been considered. It appears to be a valuable synthetic intermediate yielding compounds which contain: (i) the intact 8-membered heterocycle, (ii) units formed through ring contraction or fragmentation, and (iii) more complex heterocycles.[4,5]

Pnicogen chalcogenides of the heavier group V (phosphorus and arsenic) and group VI (sulphur, selenium and tellurium) elements have a remarkable chemical history and the fundamental aspects of their chemistry have been extensively investigated.[6,7] Phosphorus and arsenic form with the chalcogens a broad class of molecular or polymeric compounds: the lighter elements tend to yield molecular derivatives, whereas the heavier ones are more frequently involved in polymeric species.[7] The molecular sulphides of phosphorus and, to a lesser extent, those of arsenic form an intriguing series of cage compounds which present puzzling structural and chemical features.[8] Scheme 1 shows the molecular structures of the more representative members of the family.[9-12] Such *closo*-molecules exhibit several coordination sites differing in chemical nature and/or geometry, due to the non-bonding electron pairs located at the phosphorus, or arsenic, and at the chalcogen atoms. Furthermore, they present reactive E-E and E-X edges (Scheme 1), as well as faces of different geometries as possible reactive sites. According to such features, they may be expected to exhibit varied and interesting behavior toward metal fragments. However, such chemistry had been scarcely considered up to a few years ago, probably due to the discouraging results of the first attempts in the field.[13] In the last few years, however, considerable attention



SCHEME 1 Structure of molecular phosphorus and arsenic chalcogenides. ○ pnicogen, ● chalcogen.

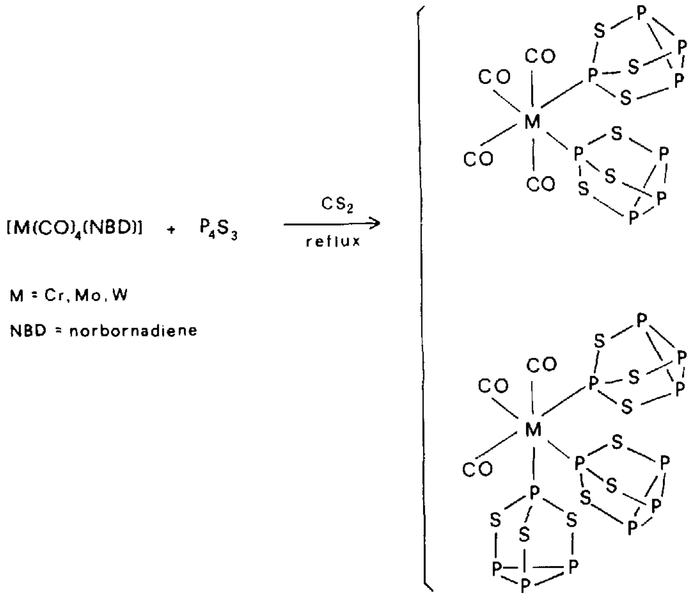
has been addressed to the chemistry of pnicogen chalcogenides, mainly due to the reactivity of the E_4X_3 cages (E = P, As; X = S, Se) toward metal fragments, and a number of interesting and unexpected reactions have been described.

The pnicogen chalcogenide cage molecules interact in various ways with metal moieties: depending on the electronic properties of the metal fragments employed, compounds containing the intact cage molecules or fragments originating from their cleavage have been obtained. Different degrees of demolition of the cages have been achieved by tuning the interactions between the cages and the metal fragments through appropriate selection of the reacting species. It is convenient for the purpose of illustration to group the compounds which have been obtained according to the progressive activation/demolition of the parent pnicogen chalcogenides. Such chemistry is far from being exploited and constitutes a continuous challenge to the chemist's imagination.

INTACT P_4X_3 MOLECULE AS A LIGAND

The electronic structure of tetraphosphorus trisulphide, P_4S_3, the most representative and stable P/S cage molecule, has been investigated.[14] It has been strengthened that both the apical and basal phosphorus atoms have good donor properties: the apical P atom is expected to exhibit a donor ability comparable to that of tertiary phosphines, whereas ligating behavior similar to that of white phosphorus, P_4, is attributed to the three phosphorus atoms of the basal P_3 cyclic unit. The donor properties of the apical phosphorus of P_4S_3 have also been tested by measuring the ionization energy of its lone pair by He I photoelectron spectroscopy.[14] The high value found allows the classification of P_4S_3 as a very weak base: the lack of reactivity toward strong alkylating reagents, such as $MeOSO_2CF_3$ or Me_3OBF_4, as well as its inability to form adducts with strong Lewis acids like BF_3 fit nicely into this picture.[15]

The first adducts of P_4S_3 with transition metal moieties were reported in 1969 by Nixon *et al.*[16] They were prepared by reacting the group VIB norbornadiene metal carbonyls, $[M(CO)_4(NBD)]$ (M = Cr, Mo, W. NBD = norbornadiene), with P_4S_3 in refluxing carbon disulphide (Scheme 2). The *cis* as well as the *facial* stereochemistry of the two series of compounds were inferred from analysis of the IR spectra in the carbonyl stretching region. ^{31}P NMR data provided unequivocal information about the nature

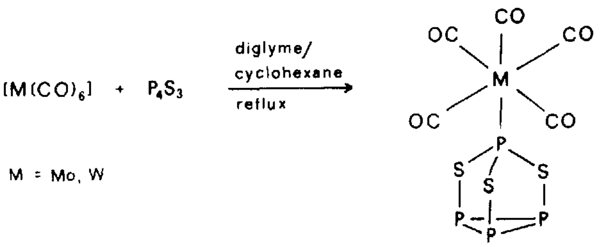


SCHEME 2

(that is, apical or basal) of the coordinating phosphorus atom. While the quartet of the apical phosphorus atom is significantly downfield shifted with respect to free P_4S_3, the doublet due to the three equivalent P basal atoms presents a very small coordination chemical shift for all compounds. Thus, it was possible to argue that the apical phosphorus atom is bound to the metal in both series of carbonyl derivatives. In the same paper also the synthesis of the nickel(0) compound $[Ni(P_4S_3)_4]$ was briefly mentioned. This was obtained by reacting P_4S_3 with nickelocene or, more conveniently, with *bis*-π-allylnickel at low temperature. The insolubility of the compound, as well as its instability, prevented a better characterization.

The reaction of copper(I) halides with P_4S_3 yields polymeric adducts of formula $[CuX(P_4S_3)]$ (X = Cl, Br, I),[17] in which P_4S_3 is considered to behave as a monodentate ligand through its apical phosphorus atom.

The first transition metal compound of P_4S_3 endowed with suf-

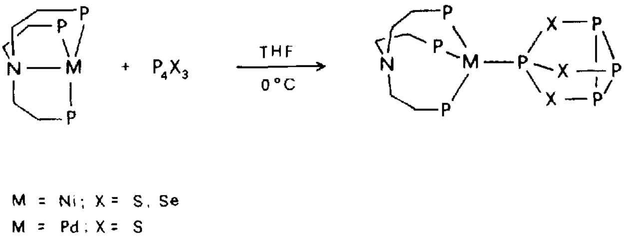


SCHEME 3

ficient stability to allow a complete X-ray characterization was reported by Cordes *et al.* in 1974.[18] The reaction of $[Mo(CO)_6]$ with P_4S_3 in a refluxing cyclohexane/diglyme mixture (Scheme 3) gives in moderate yield the compound $[Mo(CO)_5(P_4S_3)]$. Photochemical activation of the starting molybdenum hexacarbonyl considerably hastens the CO substitution.[13] The analogous tungsten derivative $[W(CO)_5(P_4S_3)]$ was obtained through the same reaction.[19]

The intact P_4S_3 cage molecule acts as monodentate ligand toward the $Mo(CO)_5$ fragment, being bound to the metal through its apical phosphorus atom.[18] The solution behavior of the molybdenum derivative, as revealed from ^{31}P NMR in various solvents, is quite puzzling as it requires the P_4S_3 molecule to act as a "quadridentate" ligand through all of its phosphorus atoms.[13]

Nickel and palladium adducts of P_4S_3[20] and P_4Se_3[21] of formula $[(np_3)M(P_4X_3)]$ (M = Ni; X = S, Se. M = Pd; X = S) were prepared by reacting the trigonal pyramidal $[(np_3)M]$ complexes [np_3 = tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$; M = Ni, Pd] with stoichiometric amounts of P_4X_3 (X = S, Se) (Scheme 4). The intact cage molecule acts as a monodentate ligand

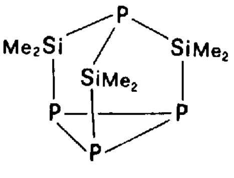


SCHEME 4

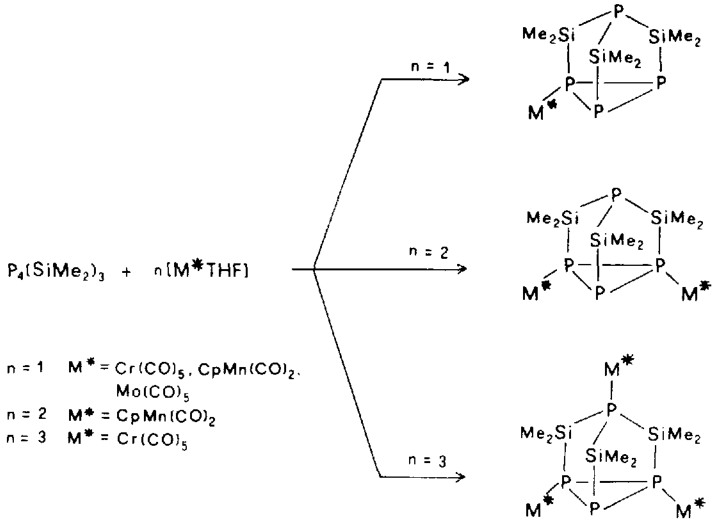
through its apical phosphorus atom. The nickel is bound in addition to the three phosphorus atoms of the np_3 ligand, but the nitrogen atom, which is bound to the metal in the parent compounds, is now uncoordinated. The easy detachment of the np_3 nitrogen, which allows the 18-electron configuration of the metal atom, existing in the parent compounds, to be preserved in the products with a modest conformational rearrangement of the tripod ligand, is of crucial importance to the formation and stability of the present adducts.[20] The coordinated P_4S_3 molecule in the molybdenum and nickel derivatives, whose X-ray structures have been determined, presents small but significant differences in bond lengths and angles from those existing in the free molecule.[22] All P–S bonds lengthen in the Mo carbonyl derivative, whereas in the nickel compound with np_3 only the P_{ap}–S distances exhibit appreciable increases. The S–P_{ap}–S angles are smaller in the latter compound than in the former or in the free molecule. Such small differences have been ascribed to the different bonding capabilities of the L_5M versus the L_3M conical fragment.[20]

Coordination through the basal phosphorus atoms of the P_4X_3 (X = S, Se) molecules has been elusive so far, although the results of theoretical calculations on model compounds do not allow the exclusion of such a possibility.[23]

In this context, it is worth stressing that the hexamethyl trisilatetraphosphanortricyclene cage molecule, $P_4(SiMe_2)_3$, which has the same skeleton as P_4X_3, the $SiMe_2$ groups replacing the sulphur atoms (Scheme 5),[24,25] is capable of interacting with metal fragments in various ways without disruption of the cage structure. The reaction of $P_4(SiMe_2)_3$ with $[Cr(CO)_5THF]$, $[CpMn(CO)_2THF]$ (Cp = cyclopentadienyl) or $[Mo(CO)_6]$ which is likely to generate $[Mo(CO)_5THF]$ in situ, in 1:1 stoichiometric ratio affords compounds in which the cage is σ bound to a transition metal moiety

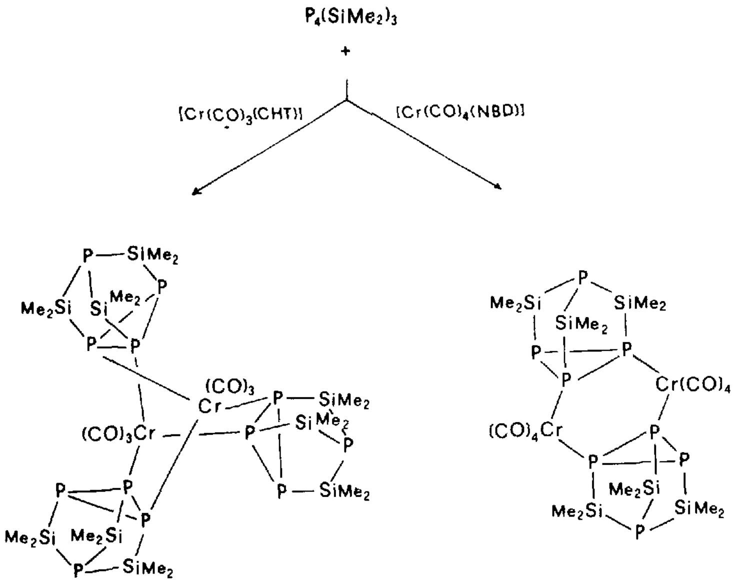


SCHEME 5



SCHEME 6

through one of the basal P atoms, (Scheme 6).[26] The formation of the monometal adduct does not extinguish the coordinating ability of the molecule. Indeed, the dimetal compound [$\{CpMn(CO)_2\}_2\{P_4(SiMe_2)_3\}$][27] (Scheme 6) is obtained by reacting the silylphosphane cage and [$CpMn(CO)_2THF$] in 1:2 stoichiometric ratio; in such a compound each manganese fragment is terminally bound to a basal phosphorus atom. Finally, the trimetal derivative [$\{Cr(CO)_5\}_3\{P_4(SiMe_2)_3\}$][28] (Scheme 6) is obtained in the presence of an excess of [$Cr(CO)_5THF$]. By reaction of $P_4(SiMe_3)_3$ with [$Cr(CO)_4(NBD)$] or [$Cr(CO)_3(CHT)$] (CHT = cycloheptatriene) complexes, which easily generate the tetracoordinated $Cr(CO)_4$ and tricoordinated $Cr(CO)_3$ metal fragments possessing two and three acceptor orbitals, respectively, polynuclear compounds were obtained in which the cage acts as a tethering unit between the metal fragments[29] (Scheme 7). The above results point to a greater versatility of $P_4(SiMe_2)_3$ toward metal fragments compared to the P_4X_3 molecules. Such behavior is probably due to the replacement of the electronegative sulphur atoms by the electron releasing $SiMe_2$ groups, which make more electron density available to the basal phosphorus atoms.



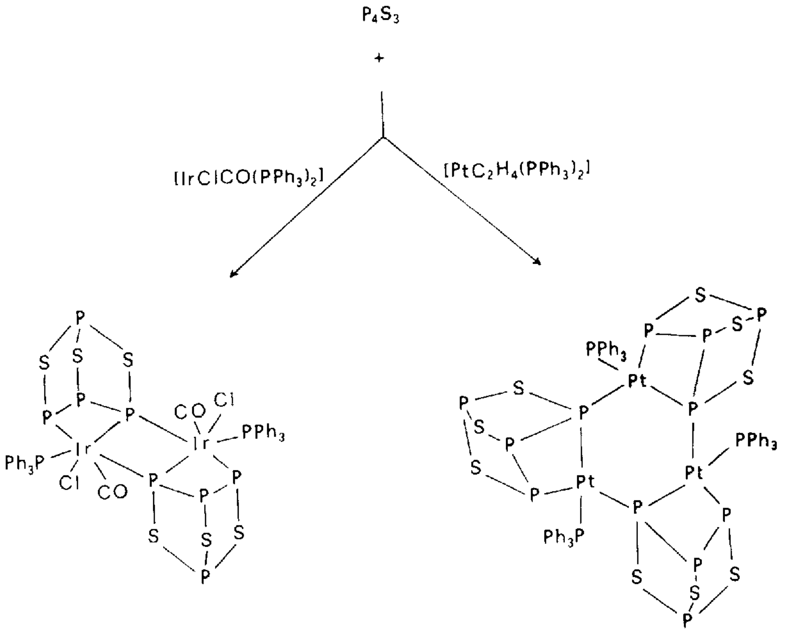
CHT = cycloheptatriene

SCHEME 7

P–P BOND ACTIVATION IN THE P_4S_3 MOLECULE

Addition of a metal fragment to a homo- or heteroatomic bond in small molecules containing unsubstituted P atoms without degradation of the molecular skeleton is an unusual process, and until recent years it had been performed only on $[MXL_2(P_4)]$ compounds (M = Rh, Ir; X = Cl, Br; L = PR_3, $AsPh_3$)[30] containing the P_4 molecule η^2-bound to the metal. Such addition, as clarified by the reaction of $[Cp^*Co(Co)]_2$ (Cp^* = pentamethylcyclopentadienyl) with P_4,[31] yields highly reactive species, which evolve to compounds containing phosphorus atom fragments[32] where the geometry of the parent molecule is lost. Such degradation cannot be avoided even if sterically hindered organic reagents are employed.[33]

Two well-defined examples of P–P bond activation on the P_4S_3



SCHEME 8

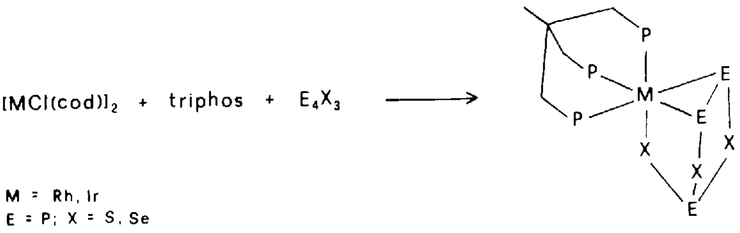
cage molecule have been recently reported. $[IrCl(CO)(PPh_3)_2]$ reacts with an equimolar amount of P_4S_3 to yield $[IrCl(CO)(PPh_3)(P_4S_3)]_2$[34] (Scheme 8) which has been characterized by X-ray analysis. A strictly related compound, $[Pt(PPh_3)(P_4S_3)]_3$, has been obtained by reacting P_4S_3 with the stoichiometric amount of $[Pt(C_2H_4)(PPh_3)_2]$[35] (Scheme 8). The two derivatives are characterized by good stability, which is probably related to their insolubility. In each of the chemically identical $Pt(\mu\text{-}P_4S_3)(PPh_3)$ units of the trinuclear platinum molecule, the metal atom is linked to two basal phosphorus atoms of the P_4S_3 cage, which lie much farther apart than in the free P_4S_3 molecule. One of these P atoms is also bonded to a second Pt atom belonging to another $Pt(\mu\text{-}P_4S_3)(PPh_3)$ unit. As a result, each one 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 in a square planar array. The formation of the trinuclear compound therefore involves loss of C_2H_4 and of one PPh_3 ligand from each molecule of the $[Pt(C_2H_4)(PPh_3)_2]$ reactant, as well as insertion of a $PtP'PPh_3$ moiety, where P′ is a phosphorus atom of a neighboring cage, into a P–P bond of the P_4S_3 molecule. Such a process is analogous to that leading to the formation of the dinuclear iridium complex, $[IrCl(CO)(PPh_3)(P_4S_3)]_2$, where a metal moiety with different geometry and d-electron count than the $PtP'PPh_3$ one, but isolobal with it, inserts into a P–P bond of the P_4S_3 cage. The insertion follows a mechanism similar to that discussed for bond cleaving in cyclopropenium ions,[36] involving changes in the formal oxidation numbers but not in the overall electron count on going from the interacting species to the final products.

TOWARD CAGE DEMOLITION

In the previous sections compounds were described containing integer P_4X_3 cage molecules, which either act as monodentate or polydentate bridging ligands or undergo insertion into one of their P–P bonds. However, P_4S_3, as well as other pnicogen/chalcogen molecular compounds, would form a richer coffer of mixed units if gradual demolition of the cage molecule could be attained. In the last few years such potentiality has been put in action and a large number of pnicogen–chalcogen fragments stabilized by transition metal moieties have been characterized.

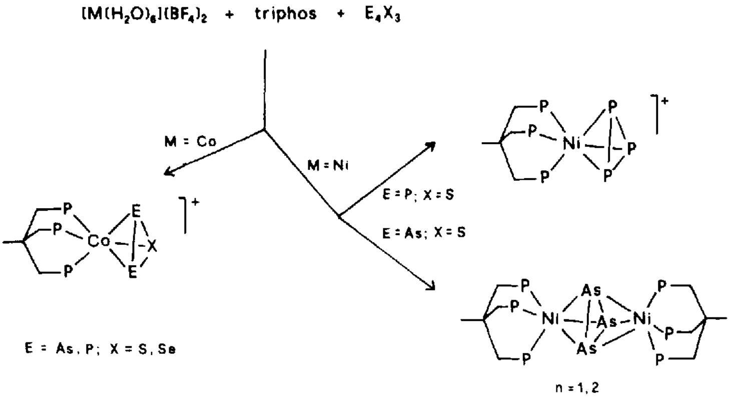
THE E_3X_3 FRAGMENTS

The reaction of $[MCl(cod)]_2$ (M = Rh, Ir; cod = 1,5-cyclo-octadiene) with E_4X_3 (E = P; X = S, Se. E = As; X = S) in the presence of triphos [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$] yields compounds of formula $[(triphos)M(E_3X_3)]$ [M = Rh, Ir. E = P; X = S, Se.[37] E = As; X = S[38]) (Scheme 9). The metal atom of the (triphos)M system in each compound replaces one pnicogen atom of the triatomic E_3 (E = P, As) side of the original E_4X_3 cage. The geometry of each coordinated E_3X_3 fragment does not deviate considerably from that of the parent E_4X_3 molecule.[39]



SCHEME 9

The rather low yields for the formation of such compounds, and the different yields when P_4S_3 or P_4Se_3 are employed, point to the existence of alternative reaction paths, so that detailed assumptions about the reaction mechanism are prevented. Nevertheless, some general comments are suggested by the nature of the above products. The fact that a basal pnicogen atom of the cage is displaced in the course of these reactions suggests that suitable directions for attack of the cage molecule by the triphos-metal systems are those pointing toward the triangular E_3 side. This is also in line with (i) the propensity of conical ML_3 fragments of suitable electron count to form a set of bonds with approximate 3-fold symmetry,[40] (ii) the well documented ability of some d^9-ML_3 units to link to cyclic P_3 or As_3 units[41,42] and (iii) the geometry of overlap, as suggested by the MO picture for cage compounds of geometry similar to that of the present ones.[43] However, the interaction of a d^8 (triphos)M(I) (M = Rh, Ir) fragment, which is considered to be present in the reaction mixture, with the triangular face of the intact E_4X_3 molecule should not lead to a stable electronic configuration at the metal atom, so that disruptive steps are expected to follow the above interaction. On the other hand, the formally d^9 metal atom in each of the final compounds may be considered to reach the 18e configuration by borrowing, in addition to the 6e from the phosphine ligand, 3e from the E_3X_3 framework, as the displaced P atom would be considered to do in the original cage molecule. In this sense, reduction of the metal atom may be considered to occur in the formation of these compounds.

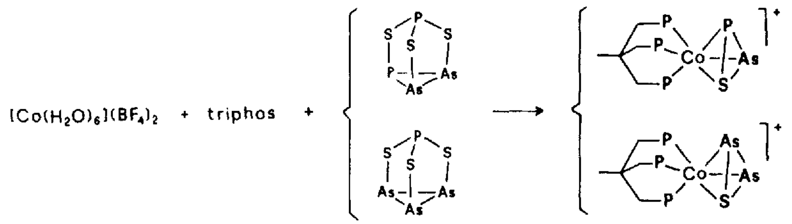


SCHEME 10

THE HETERO-E_2X (E = As, P; X = S, Se) AND THE HOMOATOMIC E_3 (E = As, P) CYCLIC FRAGMENTS

A drastic demolition of the cage molecules has been obtained in mild conditions in the presence of cobalt(II) and nickel(II) fragments.

E_4X_3 (E = As, P; X = S, Se) reacts with $Co(BF_4)_2 \cdot 6H_2O$ in the presence of triphos in an ethanol/THF mixture at ca. 40°C yielding the $[(triphos)Co(E_2X)]BF_4$ compounds (E = As,[44] P[45,46]; X = S, Se) in good yield (Scheme 10). The cobalt atom in the isostructural $[(triphos)Co(E_2X)]^+$ cations is bound to the three phosphorus atoms of the ligand and to the atoms of the heterocyclic E_2X unit, which form with the metal a pseudotetrahedral group. The reaction of the (triphos)Co(II) moiety with a mixture of phosphorus–arsenic $P_xAs_{4-x}S_3$ (x = 1, 2) sulphides having different P/As occupancies of the basal cage sites has yielded the compounds $[(triphos)Co(As_2S)]BF_4$ and $[(triphos)Co(AsPS)]BF_4$[47] in form of a solid solution (Scheme 11). The compounds contain the cyclic thiaphospharsirene, AsPS, or thiadiarsirene, As_2S, units which act as η^3 ligands toward the (triphos)Co fragment. The formation of such compounds has shown that the apical phosphorus atom of a mixed cage does not enter into the assembling of the final AsPS

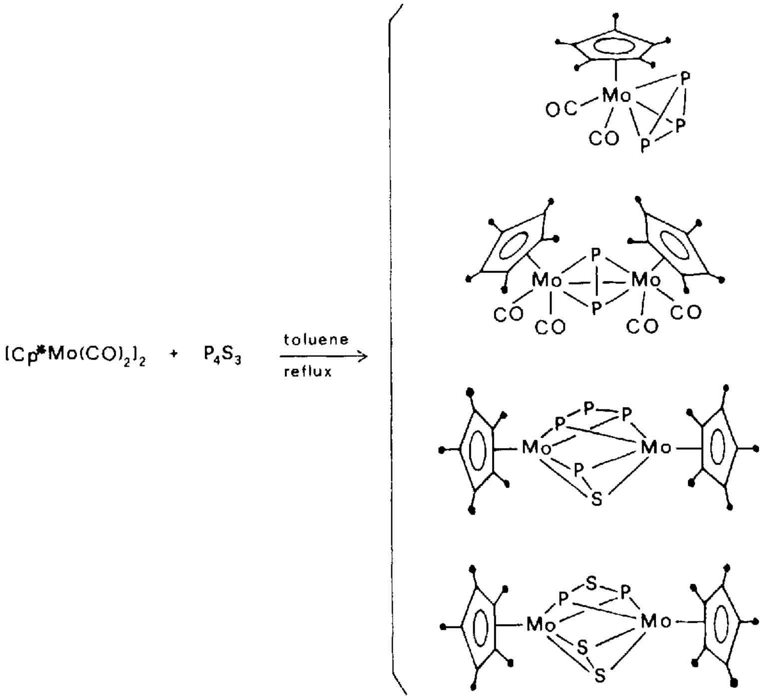


SCHEME 11

or As_2S fragments. On the assumption that cleavage of the E_4X_3 (E = As, P; X = S, Se) cages under the influence of the (triphos)Co(II) system follows a definite path, these results, showing that disruption of the cages starts at their basal sites, are consistent with the results discussed above, involving the formation of E_3X_3 fragments. Consistent with the electron count criterion already adopted for the compounds containing the E_3X_3 fragments, all of the compounds containing the heterocyclic E_2X units may be considered to be cobalt(I) derivatives, assuming that the E_2X moieties behave as neutral four electron donors.[48] Therefore, reduction of the metal atom may be considered to occur in the formation of the compounds discussed in this section. This should be related to the drastic cleavage of the cages that occurs in the reactions of the E_4X_3 or mixed-cage molecules with the (triphos)Co(II) system, where the metal atom has a higher oxidation state than in the (triphos)M(I) (M = Rh, Ir) systems mentioned in the previous section.

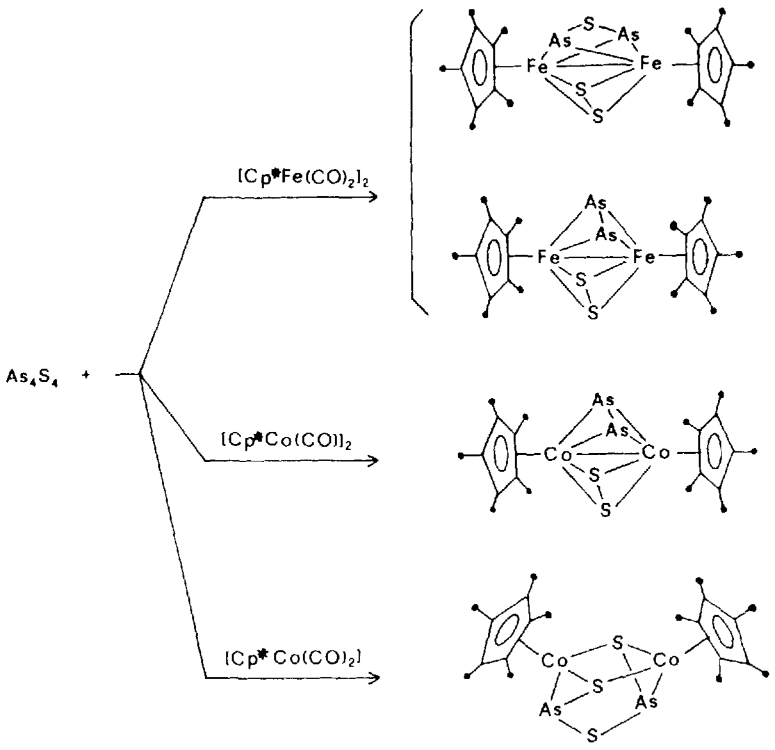
P_4S_3 in the presence of the (triphos)Ni(II) fragment yields the [(triphos)Ni(P_3)]BF_4 derivative (Scheme 10)[49] with six-coordinate nickel bound to the donor atoms of the triphos ligand and to the three phosphorus atoms of the homocyclic P_3 unit. The preference of the nickel fragment for homoatomic E_3 units, easily rationalized by the above electron count criterion, is confirmed by the reaction of (triphos)Ni(II) with As_4S_3 (Scheme 10), which yields the dimetallic [(triphos)Ni(As_3)Ni(triphos)]$(BF_4)_n$ (n = 1, 2) derivatives, containing two (triphos)Ni fragments η^3 bound to the As_3 bridging unit.[50]

The above reactions of the E_4X_3 cage molecules with Co(II) and Ni(II) in the presence of triphos lead in every case to a coordinated triatomic ring formed by one chalcogen and two pnicogen atoms or by three pnicogen atoms. This suggests that the differences in atomic orbital energies and size between P and As, or between S and Se, are overridden by other factors, probably related to the orbital symmetry requirements of the triphos-metal systems. The efficiency of the (triphos)M system in directing the course of reactions toward the formation of compounds with suitable electron counts, overriding structural differences between the chalcogenides used as reactants, is nicely illustrated by the synthesis of the [(triphos)Co(As_2X)]BF_4[51] (X = Se, Te) compounds which are isostructural to their sulphur analogues. The compounds have in fact been obtained by extruding the E_2X units from polymeric species like As_2Se_3 or As_2Te_3.



SCHEME 12

The relatively low yields for the formation in mild conditions of the compounds described in the previous sections are suggestive of the existence of alternative reactions that may occur even in the presence of stable and sterically hindering fragments, such as those provided by the tripodal tridentate (triphos) and tetradentate (np_3) ligands. Such behavior is indicative of high affinity toward the metal fragments by the pnicogen chalcogenide molecules which easily undergo cleavage. It is accordingly expected that carbonyl and cyclopentadienylcarbonyl complexes, which are capable of evolving toward fragments with different frontier orbitals than those of the metal fragments mentioned above, react with the cage molecules, especially under forcing conditions, yielding compounds



SCHEME 13

which contain numerous pnicogen–chalcogen groups with different features from those discussed above.

In keeping with these expectations, P_4S_3 reacts with the dimeric molybdenum $[Cp^*Mo(CO)_2]_2$ compound in boiling toluene to yield phosphorus or phosphorus and sulphur rich compounds[52] (Scheme 12). The phosphorus containing complexes present tetrahedral Mo_2P_2 and MoP_3 cluster arrays. The higher nuclearity clusters contain S_2, PS and the open P_2S and P_3 units saddling the two Mo atoms. The stability of compounds of this sort is indicated by the decomposition undergone by As_4S_4 in the presence of $[Cp^*Mo(CO)_2]_2$.[53] Although this is structurally different from the E_4X_3 cages, it yields the compounds $[\{Cp^*Mo(CO)_2\}_2As_2]$, $[Cp^*Mo(CO)_2As_3]$, and $[\{Cp^*Mo\}_2As_2S_3]$, which are isostructural to the phosphorus analogues.[52] It is worthwhile to note that the $Cp^*Mo(CO)_2$ fragment, having similar frontier orbitals to those of the conical CoL_3 moiety, stabilizes compounds containing the E_3 (E = As, P) cyclic unit. The reactivity of realgar, As_4S_4, has been investigated under forcing conditions also in the presence of iron and cobalt cyclopentadienyl carbonyl complexes (Scheme 13). The compounds so obtained contain two Cp^*M (M = Fe or Co) fragments, bridged by arsenic or arsenic and sulphur units, which originate from drastic demolition of the As_4S_4 cage.[53]

References

1. E. A. Davis, Endeavour **1**, 103 (1977).
2. M. Labes, P. Love and L. F. Nichols, Chem. Rev. **79**, 1 (1979).
3. *Gmelin Handbuch der Anorganischen Chemie*, Part B, Section 3 (Verlag Chemie, Weinheim, 1963). R. Adkins and A. Turner, J. Chromatogr. **110**, 202 (1975).
4. P. F. Kelly and J. D. Woollins, Polyhedron **5**, 607 (1986).
5. T. Chivers and F. Edelmann, Polyhedron **5**, 1661 (1986).
6. G. R. Burns, J. R. Rollo and R. J. H. Clark, Inorg. Chem. **25**, 1145 (1986).
7. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon Press, 1985), p. 580.
8. A. F. Wells, *Structural Inorganic Chemistry*, 4th Ed. (Oxford University Press, 1975).
9. H. G. Heal, *The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen and Phosphorus* (Academic Press, 1980), Chapter 10.
10. H. Hoffmann and M. Becke-Göhring, Topics in Phosphorus Chemistry **8**, 193 (1976).
11. A. F. Childs, "The Phosphorus Sulphides," in the Supplement to Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longman, 1971), Vol. VIII, Supplement III.

12. L. F. Fieser and M. Fieser, *Reagents in Organic Synthesis* (Wiley, continuous series from 1967).
13. J. G. Riess, "Rings, Clusters and Polymers of the Main Group Elements," ed. A. H. Cowley, *ACS Symposium Series* 232 (1983), p. 17, and references therein.
14. J. D. Head, K. A. R. Mitchell, L. Noodleman and N. L. Paddock, Can. J. Chem. **55**, 669 (1977).
15. M. R. Le Geyt, Diss. Abs. Int. B **35**, 5309 (1975).
16. R. Jefferson, H. F. Klein and J. F. Nixon, J. Chem. Soc., Chem. Commun. 536 (1969).
17. W. Ibàñez, M. González and C. E. Clavijo, Z. Anorg. Allg. Chem. **432**, 253 (1977).
18. A. W. Cordes, R. D. Joyner, R. D. Shores and E. D. Dill, Inorg. Chem. **13**, 132 (1974).
19. P. Bourgund, C. Brevard, L. G. Hubert-Pfalzgraf and J. G. Riess, see note 94 in Ref. 13.
20. M. Di Vaira, M. Peruzzini and P. Stoppioni, Inorg. Chem. **22**, 2196 (1983).
21. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Organomet. Chem. **258**, 373 (1983).
22. Y. C. Leung, J. Waser, S. van Houten, A. Vos, G. A. Wiegers and E. H. Wiebenga, Acta Crystallogr. **10**, 574 (1957). E. Keulen and A. Vos, Acta Crystallogr. **12**, 323 (1959).
23. S. Kang, T. A. Albright and J. Silvestre, Croat. Chem. Acta **57**, 1355 (1984).
24. G. Fritz and R. Uhlmann, Z. Anorg. Allg. Chem. **440**, 168 (1978). W. Hönle and H. G. von Schnering, Z. Anorg. Allg. Chem. **440**, 171 (1978).
25. G. Fritz, Comments Inorg. Chem. **1**, 329 (1982).
26. G. Fritz and R. Uhlmann, Z. Anorg. Allg. Chem. **465**, 59 (1980).
27. G. Fritz, S. Lang, E. Layher, M. Jarmer, J. Reuter and T. Vaahs, XI International Conference on Phosphorus Chemistry, Tallinn, USSR, 1989, Abstracts of Lectures, pp. 3–10.
28. W. Hönle and H. G. von Schnering, Z. Anorg. Allg. Chem. **465**, 72 (1980).
29. G. Fritz, R. Uhlmann, K. D. Hoppe, W. Hönle and H. G. von Schnering, Z. Anorg. Allg. Chem. **491**, 83 (1982).
30. A. P. Ginsberg, W. E. Lindsell, K. J. McCullough, C. R. Sprinkle and A. J. Welch, J. Am. Chem. Soc. **108**, 403 (1986).
31. O. J. Scherer, M. Swarowsky and G. Wolmershäuser, Organometallics **8**, 841 (1989).
32. O. J. Scherer, M. Swarowsky and G. Wolmershäuser, Angew. Chem. Int. Ed. Engl. **27**, 405 (1988). O. J. Scherer, J. Vondung and G. Wolmershäuser, Angew. Chem., Int. Ed. Engl. **28**, 1355 (1989) and references therein.
33. M. Baudler, Angew. Chem., Int. Ed. Engl. **26**, 419 (1987).
34. C. A. Ghilardi, S. Midollini and A. Orlandini, Angew, Chem., Int. Ed. Engl. **22**, 790 (1983); Angew. Chem. Suppl. 1066 (1983).
35. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Dalton Trans. 291 (1985).
36. E. D. Jemmis and R. Hoffmann, J. Am. Chem. Soc. **102**, 2570 (1980).
37. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Chem. Commun. 903 (1983).
38. M. Di Vaira, P. Stoppioni and M. Peruzzini, Inorg. Chim. Acta **132**, 37 (1987).
39. M. Di Vaira, B. E. Mann, M. Peruzzini and P. Stoppioni, Inorg. Chem. **27**, 3725 (1988).
40. M. Elian and R. Hoffmann, Inorg. Chem. 14, 1058 (1975).

41. C. A. Ghilardi, S. Midollini and L. Sacconi, Inorg. Chem. **19**, 301 (1978). M. Di Vaira, M. Peruzzini and P. Stoppioni, Polyhedron **6**, 351 (1987).
42. A. S. Faust, M. S. Foster and L. F. Dahl, J. Am. Chem. Soc. **91**, 5631 (1969).
43. A. Gleiter, H. Koppel, P. Hoffmann, H. R. Schmidt and J. Ellermann, Inorg. Chem. **24**, 4020 (1985).
44. M. Di Vaira, P. Innocenti, S. Moneti, M. Peruzzini and P. Stoppioni, Inorg. Chim. Acta **83**, 161 (1984).
45. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Chem. Commun. 894 (1982).
46. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Dalton Trans. 359 (1984).
47. M. Di Vaira, P. Stoppioni and M. Peruzzini, J. Organomet. Chem. **364**, 399 (1989).
48. M. Di Vaira and L. Sacconi, Angew. Chem., Int. Ed. Engl. **21**, 330 (1982).
49. M. Di Vaira, L. Sacconi and P. Stoppioni, J. Organomet. Chem. **250**, 183 (1983). M. Di Vaira, M. Peruzzini and P. Stoppioni, Acta Crystallogr. **C39**, 1210 (1983).
50. P. Stoppioni, and M. Peruzzini, J. Organomet. Chem. **262**, C5 (1984).
51. M. Di Vaira, M. Peruzzini and P. Stoppioni, Polyhedron **5**, 945 (1986).
52. I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter and M. L. Ziegler, Angew. Chem., Int. Ed. Engl. **23**, 438 (1984). H. Brunner, K. Ulrich, W. Meier, J. Wachter, O. Serhadle and M. L. Ziegler, J. Organomet. Chem. **335**, 339 (1987).
53. H. Brunner, H. Kauermann, B. Nüber, J. Wachter and M. L. Ziegler, Angew. Chem., Int. Ed. Engl. **25**, 557 (1986).