

Preliminary communication

REACTION OF COBALT AND NICKEL MOIETIES WITH THE SILYLPHOSPHANE $P_7(\text{SiMe}_3)_3$

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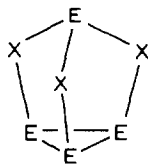
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Summary

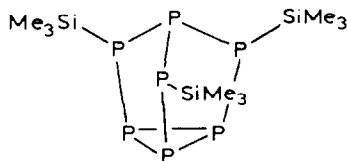
Tris(trimethylsilyl)heptaphosphanortricyclene, $P_7(\text{SiMe}_3)_3$, undergoes cleavage in the presence of triphos-nickel and -cobalt species (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) to give compounds containing the cyclic triphosphirene unit. From the chemical properties of the cage molecule it seems that the presence of a triphos-metal entity is important for the formation of the three-membered cyclic units.

The cage molecules of tetrapnicogen trichalcogenides E_4X_3 ($E = \text{As}, \text{P}; X = \text{S}, \text{Se}$), Ia, contain several lone pairs on both the chalcogen and pnictogen atoms, and could be expected to exhibit a wide range of coordination modes toward transition metal—ligand systems. This potentiality has not so far been realised. Only a few transition metal adducts of P_4S_3 [1] and P_4Se_3 [2] have been described and all such compounds have the cage molecules bonded to the metal atom through the apical phosphorus atom.



$E = \text{As}, \text{P}$
 $X = \text{S}, \text{Se}$

(Ia)



(Ib)

While the coordinating abilities of the cage species seem to be poor, we have found that in the presence of transition metal–ligand moieties such species either undergo unusual reactions [3] or act as precursors for unprecedented inorganic units [4, 5]. In particular E_4X_3 ($E = \text{As, P}$; $X = \text{S, Se}$) species react with cobalt(II) and nickel(II) in the presence of triphos (triphos = 1,1,1-tris-(diphenylphosphinomethyl)ethane) to give the complexes $[\text{Co}(E_2X)(\text{triphos})]\text{-BF}_4$ ($E = \text{As, P}$; $X = \text{S, Se}$) [4], $[\text{Ni}(\text{P}_3)(\text{triphos})]\text{BF}_4$ [6] and $[(\text{triphos})\text{Ni}(\text{As}_3)\text{-Ni}(\text{triphos})](\text{BF}_4)_2$ [7]. Both the cobalt and nickel derivatives contain a three-membered cyclic unit trihapto bonded to the metal. The formation of the homoatomic triphosphirene and triarsirene in the nickel derivatives and of the heteroatomic thiadiphosphirene, thiadiarsirene, selenadiphosphirene and selenadiarsirene units in the cobalt complexes is evidence for a change in the mode of the cleavage of the cage molecules with change in the metal atom.

With the aim of investigating whether tendencies of the cage to undergo cleavage or the properties of the $\text{M}(\text{triphos})$ moieties are more important for the formation of the three membered inorganic rings at the metal atom, we have begun a study on the reactions of various cage molecules with $\text{M}(\text{triphos})$ ($\text{M} = \text{Co, Ni}$) species.

Treatment under nitrogen of a mixture of $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Co, Ni}$) (0.5 mmol) in ethanol (5 ml) and triphos (0.5 mmol) in tetrahydrofuran (25 ml) with tris(trimethylsilyl)heptaphosphanortricyclene, $\text{P}_7(\text{SiMe}_3)_3$ [8] in toluene (10 ml) gave the yellow-orange $[\text{Co}(\text{P}_3)(\text{triphos})]$ and the dark-green $[(\text{triphos})\text{Ni}(\text{P}_3)\text{Ni}(\text{triphos})](\text{BF}_4)_2$ in yields of ca. 30%. The identities of the products were determined by elemental analyses (C, H, P and Co or Ni) and by comparing their ^{31}P NMR spectra and conductivities with those of the authentic samples [9].

The recently described *closo*-silylphosphane (Ib) [8] has the same cage structure as E_4X_3 molecules but with only phosphorus atoms in the cage skeleton; each of the bridging phosphorus atoms bears a bulky trimethylsilyl substituent [10]. Such a molecule, in contrast with tetrapnicogen trichalcogenides and other silylpoliphosphanes [11] having a cage structure, does not form adducts with metal carbonyls [12]. The mass spectrum of the compound shows the molecular ion as the base peak and several fragments which may be ascribed to two distinct decomposition pathways of the molecule: (a) loss of fragments from the substituted phosphorus atoms while the skeleton of the molecule remains intact; (b) cleavage of the cage skeleton to afford ions containing three and five phosphorus atoms which bear two or three SiMe_3 groups [8].

$\text{P}_7(\text{SiMe}_3)_3$ shows chemical behaviour and modes of mass-spectral fragmentation which differ significantly from those of the tetrapnicogen trichalcogenides; the latter, which have E_3X^+ as base peak, appear to undergo easier cleavage [13]. Such differences have been rationalized in terms of a greater electron delocalization of the electrons of the cage skeleton by the SiMe_3 groups [12]. The above features of $\text{P}_7(\text{SiMe}_3)_3$, and the extrusion from the molecule of the P_3 unit which does not bear substituent, show that this reagent behaves differently from tetrapnicogen trichalcogenides in presence of the $\text{Co}(\text{triphos})$ and $\text{Ni}(\text{triphos})$ moieties. It is noteworthy that cobalt(II) and nickel(II) in presence of triphos always cause extrusion of a three-membered cyclic unit even from species which differ in their overall properties [14]. The $\text{M}(\text{triphos})$ units

evidently have orbitals of such symmetry that they are especially able to stabilize such inorganic three-membered rings and this feature of the M(triphos) species is more important than the ease of cleavage of the cyclic substrates.

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- 14 The dominant effect of the M(triphos) moiety is confirmed by the synthesis of [(triphos)M(As₃)M-(triphos)](BF₄)₂ (M = Co, Ni) (which contain the triarsirene as bridging unit between two M(triphos)) by reaction of cyclo-(AsPh)₆ with nickel(II) or cobalt(II) salts in the presence of triphos. Further studies on such reactions and related species are in progress.