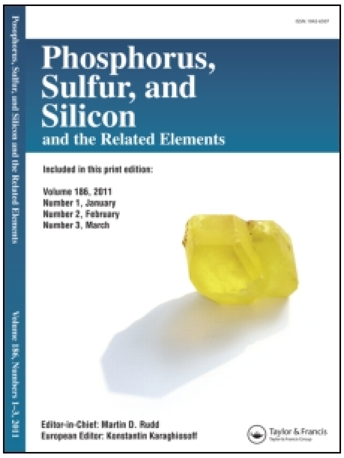

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PHOSPHORUS AND ARSENIC CHALCOGENIDES AS REAGENTS TOWARD TRANSITION METAL-LIGAND SYSTEMS

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Abstract The compounds obtained by reacting the P_4S_3, P_4Se_3 and As_4S_3 cage molecules with various transition metal-ligand moieties are reported. The transition metal-ligand systems are bound either to the intact molecules or to fragments (hexa- or tri-atomic) originating from the cage molecules. Such compounds provide examples of selective activation of cage molecules by metal moieties.

INTRODUCTION

It has been reported in recent years that white phosphorus reacts with hydrated salts of 3d transition metals or with platinum group complexes in the presence of polyphosphane ligands yielding either compounds in which the intact P_4 molecule is bound to the metal, or complexes containing the cyclic triphosphorus, P_3, unit.[1]

We now report on the reactivity of the pnicogen chalcogenides P_4S_3, P_4Se_3 and As_4S_3, toward various metal-ligand systems. These cage like molecules have similar structures based on a distorted tetrahedral array of phosphorus or arsenic atoms with bridging sulfur or selenium atoms.

RESULTS AND DISCUSSION

The reaction of the trigonal pyramidal nickel(0) and palladium(0) complexes $(np_3)M$ (M = Ni, Pd; np_3 = tris(2-diphenylphosphinoethyl)amine) with P_4X_3 (X = S, Se) yields the compounds $|(np_3)M(P_4X_3)|\cdot nC_6H_6$ (M = Ni, Pd; X = S, Se).

The two isomorphous nickel compounds $|(np_3)Ni(P_4S_3)|\cdot 2C_6H_6$ (Figure 1) and $|(np_3)Ni(P_4Se_3)|\cdot 2C_6H_6$ have been shown by X-ray diffraction studies to contain the P_4S_3 (or P_4Se_3) molecule coordinated to the metal through its apical P atom.

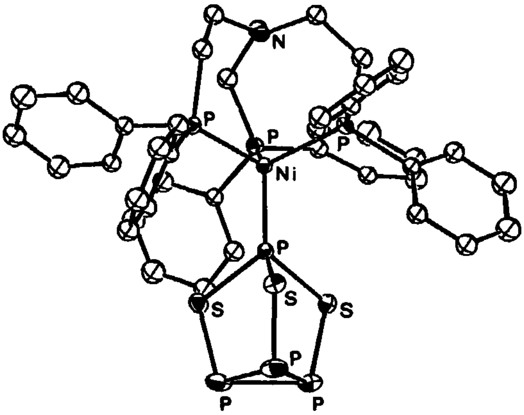

FIGURE 1 A view of the $|(np_3)Ni(P_4S_3)|$ molecule.

The metal atom is in a distorted tetrahedral environment formed by the three phosphorus atoms of the np_3 ligand (the nitrogen atom being uncoordinated) and by the P_4S_3 (or P_4Se_3) apical P atom. The easy detachment of the np_3 nitrogen from the metal atom is of crucial importance to the formation of the present P_4S_3 and P_4Se_3 adducts in mild conditions. A similar structure to that of the nickel derivatives is assigned to the palladium complexes mainly on the basis of the analytical and mass spectrometric data.

The P_4S_3 and P_4Se_3 molecules react with $|RhCl(cod)|_2$, cod = = cyclo-octa-1,5-diene, in presence of the tripod ligand triphos (triphos = 1,1,1-tris(diphenylphosphinomethylethane) yielding the compounds $|(triphos)Rh(P_3X_3)|\cdot C_6H_6$ (X = S, Se). The (triphos)Rh moiety in the |(triphos)Rh(P_3S_3)| molecule replaces one basal P atom of the P_4S_3 cage, Figure 2.

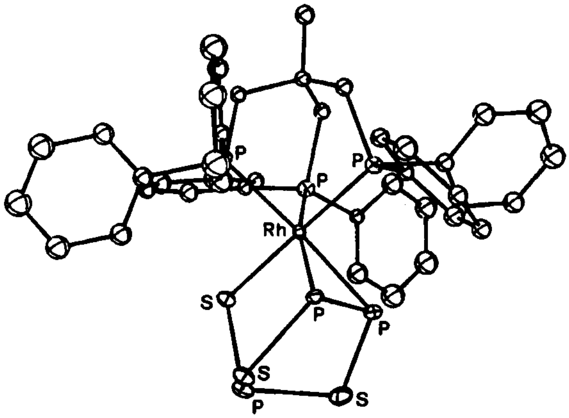

FIGURE 2 A view of the |(triphos)Rh(P_3S_3)| molecule.

The metal atom is coordinated by the three phosphorus atoms of the triphos ligand and by one S and two P atoms of the P_3S_3 fragment in a six-coordinate environment. The same structure is assigned to the isomorphous selenium derivative.

The P_4S_3, P_4Se_3 and As_4S_3 cage molecules react with cobalt(II) tetrafluoroborate in presence of the ligand triphos to give complexes of formula |(triphos)Co(D_2X)|$BF_4 \cdot C_6H_6$ (D = P, X = S, Se; D = As, X = S). The crystal structures of the isomorphous compounds |(triphos)Co(P_2S)|$BF_4 \cdot C_6H_6$ (Figure 3), |(triphos)Co(P_2Se)|$BF_4 \cdot C_6H_6$ and |(triphos)Co(As_2S)|$BF_4 \cdot C_6H_6$ consist of |(triphos)Co(D_2X)|$^+$cations, BF_4^- anions and interposed benzene molecules from the solvent.

The metal atom in the cation in each of the above compounds is in a six-coordinate environment formed by the three phosphorus atoms of the ligand and by the atoms of the heterocyclic D_2X unit in a staggered arrangement.

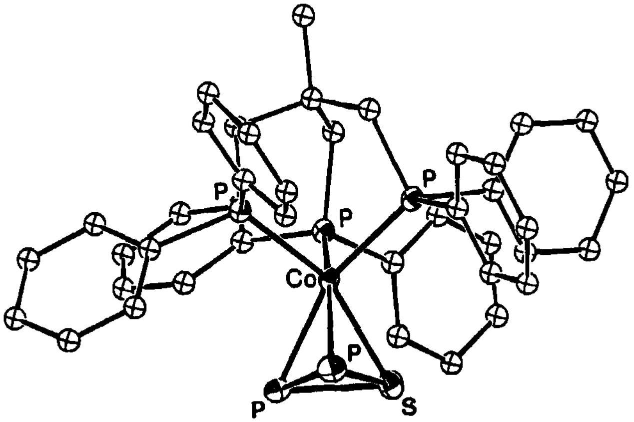

FIGURE 3 A view of the $|(\text{triphos})\text{Co}(P_2S)|^+$ cation.

The compounds described above evidentiate the different behaviour of different metal-ligand systems toward the cage molecules: (a) the d^{10} $(np_3)M$ complexes are coordinated by the intact molecules, (b) the d^8 (triphos)Rh moiety replaces one P atom in the P_4X_3 phosphorus chalcogenides, (c) the d^7 (triphos)Co unit reacts with the cage molecules leading to triatomic fragments. Such reactions provide examples of selective activation of cage molecules controlled by transition metal-ligand moieties.

REFERENCES

1. M. Di Vaira and L. Sacconi, Angew. Chem. Int. Ed. Engl., 21, 330 (1982).