Cleavage of P_4S_3 and P_4Se_3 Cage Molecules Controlled by Transition Metal–Ligand Systems. *X*-Ray Crystal Structure of $[\{MeC(CH_2PPh_2)_3\}Rh(P_3S_3)]\cdot C_6H_6$

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The reaction of tetraphosphorus trisulphide and tetraphosphorus triselenide with $[RhCl(cod)]_2$ (cod = cyclo-octa-1,5-diene) in the presence of triphos [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] yields the compounds $[(triphos)Rh(P_3X_3)]\cdot C_6H_6$, X = S or Se, which have been shown by *X*-ray analysis to contain the (triphos)Rh moiety replacing a basal P atom in the cage molecule.

We have recently found that the P_4X_3 (X = S, Se) cage molecules react with transition metal–ligand moieties, where the ligand is a tripod-like polytertiary phosphine, yielding different products, depending on the nature of the metal atom and its oxidation number. The intact P_4X_3 molecules are co-ordinated through their apical P atom to d^{10} transition metal atoms when tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$, is used as co-ligand.[1] On the other hand, the cage molecules undergo fragmentation by reaction with $M(BF_4)_2\cdot 6H_2O$ (M = Co, Ni) in presence of the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$ (triphos), yielding compounds in which either the homocyclic P_3 unit (M = Ni)[2] or the heterocyclic P_2X (X = S, Se) units (M = Co)[3] are formed. Such triatomic units are co-ordinated to the metal atom acting as *trihapto* (η^3)-ligands.

We now report that the P_4S_3 or P_4Se_3 molecules react with $[RhCl(cod)]_2$ (cod = cyclo-octa-1,5-diene) in the presence of triphos yielding the compounds $[(triphos)Rh(P_3X_3)]\cdot C_6H_6$ (X = S, Se) in which the P_3X_3 moiety may be considered to originate from the corresponding P_4X_3 molecule by loss of a basal P atom. Tetraphosphorus trichalcogenide (P_4S_3 or P_4Se_3) (1 mmol) dissolved in benzene (15 cm^3) was added to a hot solution obtained by mixing $[RhCl(cod)]_2$ (0.5 mmol) in tetrahydrofuran (50 cm^3) with solid triphos (1 mmol). n-Butanol (20 cm^3) was added and the resulting solution was refluxed under nitrogen for 5 h. Yellow (X = S) or orange (X = Se) crystals of the compounds were obtained by concentrating under nitrogen the hot solution (yield 35%); C, H, P, and S elemental analyses agreed with the formulae $[MeC(CH_2PPh_2)_3Rh(P_3S_3)]\cdot C_6H_6$ and $[MeC(CH_2PPh_2)_3Rh(P_3Se_3)]\cdot C_6H_6$. The compounds are air stable in the solid state but slowly decompose in solution. The structure of the sulphur derivative has been established by a single-crystal *X*-ray diffraction study.

Crystal data: $C_{47}H_{45}P_6Rh_1S_3$, $M = 994.82$, orthorhombic, space group $P2_1nb$, $Z = 4$, $a = 19.109(5)$, $b = 19.445(5)$, $c = 12.319(4)$ Å. 2230 Structure factors with $I > 3\sigma(I)$ were derived from 4506 intensities collected using a four-circle diffractometer and Mo-K_α radiation. The structure was solved by heavy atom procedures and refined by full matrix least squares to the present R value of 0.054 ($R_w = 0.051$), with Rh, P, and S anisotropic and hydrogen atoms in calculated positions.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

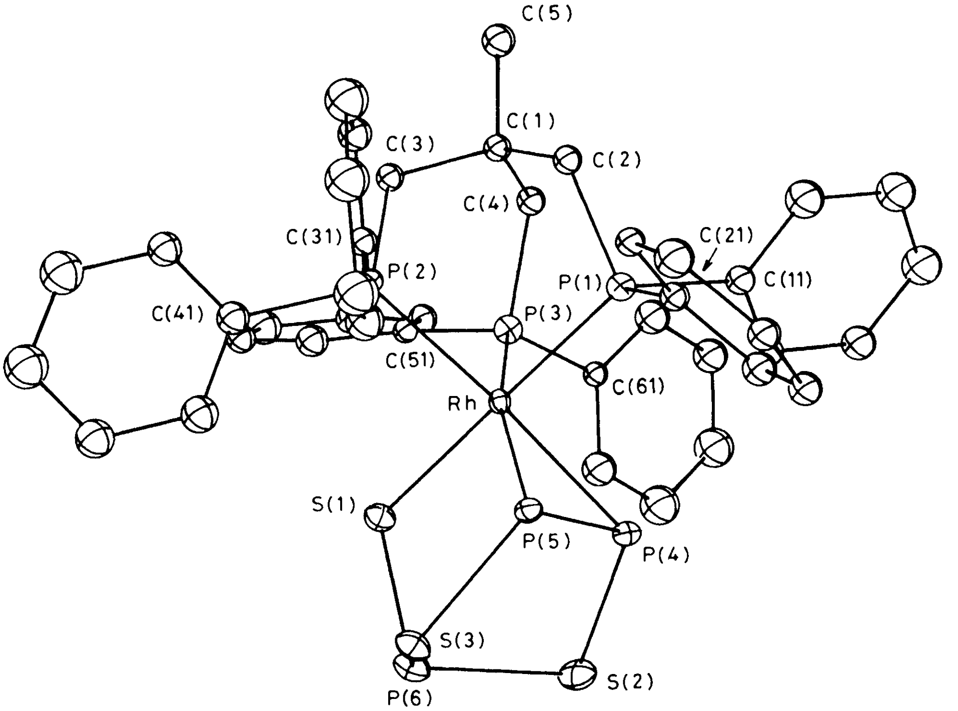

Figure 1. A view of the [(triphos)Rh(P_3S_3)] molecule. Bond distances: Rh–P(1), 2.31(1); Rh–P(2), 2.38(1); Rh–P(3), 2.34(1); Rh–P(4), 2.42(1); Rh–P(5), 2.41(1); Rh–S(1), 2.40(1) Å. Bond angles: P(1)–Rh–P(2), 88.3(2); P(1)–Rh–P(3), 88.1(1); P(2)–Rh–P(3), 92.1(2); P(4)–Rh–P(5), 53.3(2); S(1)–Rh–P(4), 90.9(2); S(1)–Rh–P(5), 93.1(2)°.

The structure consists of isolated [(triphos)Rh(P_3S_3)] and benzene molecules. The (triphos)Rh moiety in the [(triphos)-Rh(P_3S_3)] molecule replaces one basal P atom in the P_4S_3 cage (Figure 1). The metal atom is co-ordinated by the three phosphorus atoms of the triphos ligand and by one sulphur and two phosphorus atoms of the P_3S_3 fragment in a distorted six-co-ordinate environment. Values of bond distances and selected bond angles about the metal atom are given in the caption. The P(4)–P(5) distance, of 2.17(1) Å, in the P_3S_3 fragment is shorter than the basal P–P distance, of 2.235(11) Å, in the isolated P_4S_3 molecule.[4] The P(6)–S(1) bond length [2.03(1) Å] is shorter than the P(6)–S(2) and P(6)–S(3) lengths, both of 2.11(1) Å, and is also shorter than the apical P–S distance in the free cage molecule [2.088(9) Å].[4] The [(triphos)Rh(P_3Se_3)]·C_6H_6 compound may be safely assigned the same structure as that of the sulphur derivative based on their isomorphism and on the similarity in diffracted intensities. The present compounds provide examples of intermediate cleavage of the P_4X_3 molecules controlled by transition metal–ligand moieties, compared to that occurring in the processes which lead to the triatomic P_3 or P_2X fragments.[2,3]

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References

1 M. Di Vaira, M. Peruzzini, and P. Stoppioni, *Inorg. Chem.*, in the press.
2 M. Di Vaira, L. Sacconi, and P. Stoppioni, *J. Organomet. Chem.*, 1983, **250**, in the press.
3 M. Di Vaira, M. Peruzzini, and P. Stoppioni, *J. Chem. Soc., Chem. Commun.*, 1982, 894.
4 Y. C. Leung, J. Waser, S. van Houten, A. Vos, G. A. Wiegers, and E. H. Wiebenga, *Acta Crystallogr.*, 1957, **10**, 574.