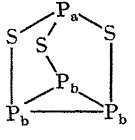
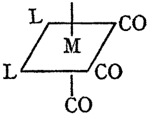
# Transition Metal Complexes of Tetraphosphorus Trisulphide, $P_4S_3$

By R. JEFFERSON, H. F. KLEIN, and J. F. NIXON*
(*Chemical Laboratory, University of Sussex, Brighton,* BNI 9QJ)

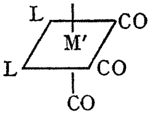
WE report syntheses of the first co-ordination complexes of the 'cage' phosphine, tetraphosphorus trisulphide, $P_4S_3$ (I). Treatment of $C_7H_8M(CO)_4$ [M = Cr,Mo,W] and $C_7H_8M'(CO)_3$ [M' = Cr,Mo] with $P_4S_3$ in refluxing carbon disulphide solution afforded the orange-yellow complexes *cis*-$(P_4S_3)_2M(CO)_4$(II) [M = Cr,Mo,W] and *cis*-$(P_4S_3)_3M'(CO)_3$ (III) [M' = Cr,Mo] respectively.



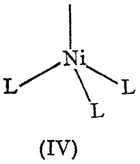
(I)=L



(II)



(III)



(IV)

The i.r. spectra of these complexes in the C–O stretching region are consistent with the proposed *cis*- stereochemistry, the stretching frequencies lying between those quoted for the related $P(OMe)_3$ and $PCl_3$ compounds.[1]

Compound (II; M = Mo) reacted slightly with phosphorus trifluoride (60°, 16 hr.) to give small amounts of the volatile *cis*- $(PF_3)_2Mo(CO)_4$[2] complex, but was recovered unchanged on heating with a 2 : 1 molar ratio of sulphur($S_8$). Heating with a large excess of sulphur led to some breakdown of (II) and formation of $P_4S_7$.

The co-ordination site within the 'cage' phosphine was established by $^{31}P$ n.m.r. spectroscopy. The $^{31}P$ n.m.r. spectrum of (I) is known to consist of a high-field doublet for the three equivalent $P_b$ nuclei and a low field quartet for the $P_a$ atom.[3] We have pointed out[4] that a downfield phosphorus chemical shift is invariably observed when phosphines become co-ordinated to zerovalent transition metals, the effect being most pronounced for the first member of a particular Group (*e.g.* Cr > Mo > W;[5,6] Fe > Ru,[7] Co > Rh > Ir [8]). In the $P_4S_3$ complexes (II) reported here the low-field phosphorus resonance of the unique phosphorus atom $P_a$ moves significantly further downfield from the free ligand value suggesting it is the atom which has become bonded to the transition metal. As expected the co-ordination shift [$\delta_P$(complex)–$\delta_P$ (ligand)] is greatest for the chromium complex. The unco-ordinated phosphorus atoms $P_b$ show a very much smaller low-field shift and the spacing of the double pattern [roughly a measure of $J(P_aP_b)$] is substantially smaller than the free ligand value. These complexes represent $[X_3A]_2$ nuclear spin systems [$X = P_b$; $A = P_a$] but broadness of the bands precluded evaluation of $^2J(P_aMP_a)$ (*i.e.* the coupling constant through the metal atom).

The zerovalent nickel complex, tetrakis(tetraphosphorus trisulphide)nickel(0), $Ni(P_4S_3)_4$, (IV), can be obtained by displacement of both cyclopentadienyl rings from nickelocene, but the very insoluble product is difficult to separate from polymeric material, and was more conveniently synthesised from bis-$\pi$-allylnickel[9] at −30° in ether solution.

$$\pi\text{-}(C_3H_5)_2Ni + 4P_4S_3 \longrightarrow Ni(P_4S_3)_4 + C_6H_{10}$$

Compound (IV) reacted with iodine in carbon disulphide solution to produce nickel iodide, $P_4S_3I_2$ and other phosphorus thioiodides,[10] but no displacement of $P_4S_3$ was observed when (IV) was heated with trifluorophosphine at 60°.

We thank Messrs. Albright and Wilson Ltd. for a Research Grant to support this work.

(*Received, March* 17*th*, 1969; *Com.* 382.)

---

[1] G. R. Dobson, I. W. Stolz, and R. K. Sheling, *Adv. Inorg. Chem. Radiochem.*, 1968, **8**, 1.

[2] C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc.* (*A*), 1968, 2216; R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, 1965, **4**, 1771.

[3] C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Amer. Chem. Soc.*, 1957, **79**, 2719.

[4] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[5] S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Amer. Chem Soc.*, 1967, **89**, 5573.

[6] T. R. Johnson and J. F. Nixon, unpublished results.

[7] Th. Kruck and A. Prasch, *Z. anorg. Chem.*, 1968, **356**, 118.

[8] W. Lang, Ph.D. thesis, Technische Hochschule, Munich, 1966.

[9] G. Wilke and B. Bogdanovic, *Angew. Chem.*, 1961, **73**, 756; G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 111; J. K. Beaconsal, B. F. Job and S. O'Brien, *J. Chem. Soc.* (*A*), 1967, 423.

[10] W. D. Treadwell and C. Beeli, *Helv. Chim. Acta*, 1935, **18**, 1161.