

## Structural and Chemical Aspects of Phosphino-ethers as Chelating Ligands in Rhodium(I) Cationic Complexes. X-Ray Crystal Structures of Two Phosphino-ether Rhodium Carbonyl Complexes

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**Summary** Crystal structures of phosphino-ether rhodium carbonyl complexes provide examples of a tridentate chelate, and of a macrocyclic aquo-complex.

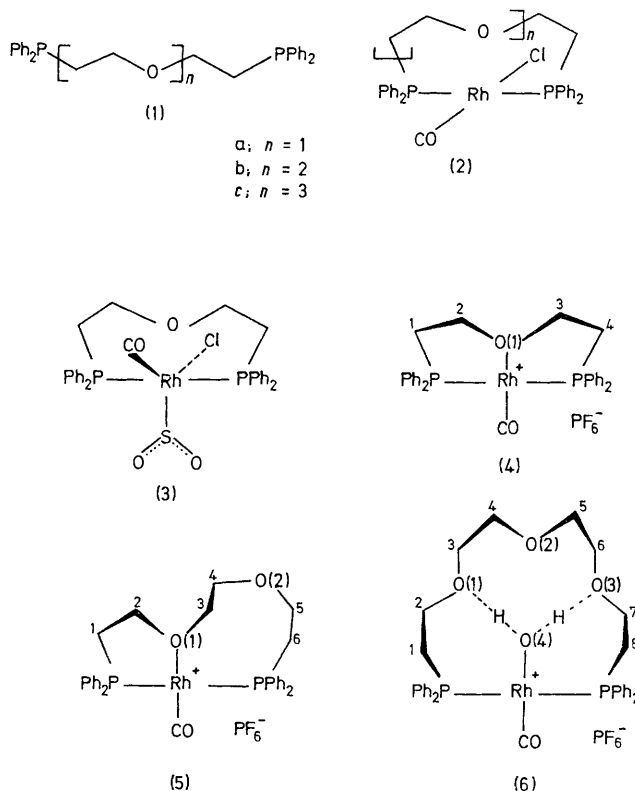
MULTIDENTATE ligands possessing both hard and soft donor centres have potential application to homogeneous catalysis. The  $\beta$ -phosphino-ethers (**1a—c**)† represent simple examples and we have begun a study of the structure and reactivity of their complexes. They displace CO from tetracarbonyldirhodium dichloride in methanol giving yellow microcrystalline neutral complexes (**2a—c**) resembling the known<sup>1</sup> *trans*-chlorocarbonyl(bis-triphenylphosphine)rhodium in chemical properties. These show no marked tendency to oxidative addition; for example, (**2a**) does not react in solution with O<sub>2</sub>, H<sub>2</sub>, or CO, although reversible reaction occurs with SO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, giving (**3**) ( $\nu_{C-O}$  2030 cm<sup>-1</sup>,  $\nu_{O-S-O}$  1220, 1190, and 1060 cm<sup>-1</sup>),<sup>2</sup> and with HCl in CH<sub>2</sub>Cl<sub>2</sub> to give a six-co-ordinate adduct ( $K$  14.5 ± 1,  $\nu_{C-O}$  2080 cm<sup>-1</sup>,  $\nu_{Rh-H}$  2200 cm<sup>-1</sup>).

Complexes (**2a—c**) each react with AgPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> followed by crystallisation from methanol to give the salts (**4**), (**5**), and (**6**). The structures of (**4**) and (**6**) (Figures) have been solved by single crystal X-ray methods.

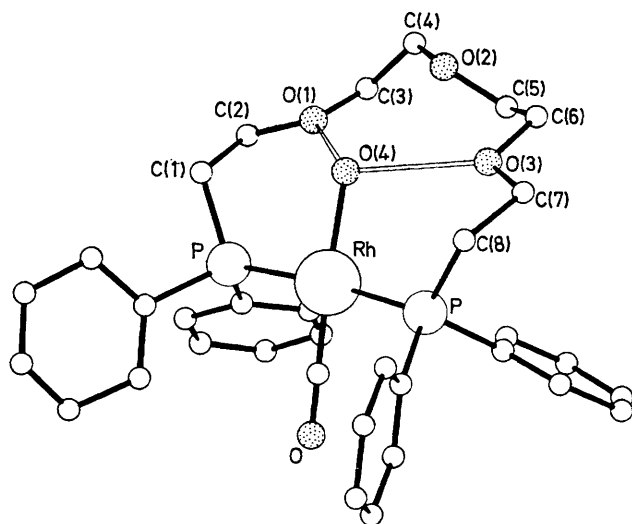
**Crystal data:** (**4**), C<sub>28</sub>H<sub>28</sub>F<sub>6</sub>O<sub>2</sub>P<sub>3</sub>Rh, triclinic,  $a = 10.907$  (3),  $b = 11.048$  (2),  $c = 13.405$  (3) Å,  $\alpha = 94.19$  (2),  $\beta = 82.30$  (2),  $\gamma = 107.98$  (2)°,  $Z = 2$ , space group  $P\bar{1}$ , 2384 observed reflections. (**6**), C<sub>33</sub>H<sub>38</sub>F<sub>6</sub>O<sub>5</sub>P<sub>3</sub>Rh; triclinic,  $a = 9.837$  (2),  $b = 11.416$  (2),  $c = 17.554$  (3) Å,  $\alpha = 94.08$  (1),  $\beta = 79.64$  (1),  $\gamma = 111.98$  (1)°,  $Z = 2$ , space group  $P\bar{1}$ , 3106 observed reflections. Data were collected on a Syntex P2<sub>1</sub> four-circle diffractometer; the structures were solved by direct methods and refined to current  $R$ -factors of 0.069 and 0.089 (anisotropic temperature factors for Rh and P only).

† Prepared by successive reaction of PPh<sub>2</sub> with Bu<sup>n</sup>Li and the appropriate chloro-ether in benzene-hexane.

In (**4**) the phosphine functions as a terdentate ligand, unlike the situation in nickel complexes of (**1**) and (**2**).<sup>3</sup> There are slight, but significant deviations from square



planarity, notably the PRhP angle of  $165.80$  ( $0.15^\circ$ ), brought about by the constraints of binding a 7-atom chain at three coplanar sites. Hybridisation at oxygen is close to  $sp^3$ , with O(1)-C(2) and O(1)-C(3) *syn* to the metal-ligand plane. Rapid inversion at oxygen occurs in solution, since axial and equatorial protons at C(2) are equivalent in the n.m.r. spectrum down to  $-80^\circ\text{C}$ . In (6), by contrast, a



Structure of cation (6)

water molecule has been incorporated and this despite synthesis under ostensibly dry conditions. Apart from the stabilisation provided by H-bonding of this water to O(1) and O(3) in the chain, part of the driving force for formation may derive from non-bonded H-H interactions which must arise in any terdentate analogue of (4) where O(1) or O(2) is bonded to the metal. O(4) is pyramidal whereas O(1) and O(3) appear to be essentially trigonal,  $sp^2$  hybridised [ $\angle C(2)O(1)C(3)$   $119(1)^\circ$ ,  $\angle C(6)O(3)C(7)$   $113(1)^\circ$ ] with the hydrogen-bonded protons almost coplanar with the respective C-O-C groups (assuming linear H-bonds) (Table). Binding is strong, for several cycles of dissolution in chloroform and evacuation at  $10^{-3}$  mmHg produced no change in the  $^1\text{H}$  n.m.r. spectrum [ $\delta(\text{H}_2\text{O})$   $6.04$  p.p.m.].

<sup>1</sup> L. Vallarino, *J. Chem. Soc.*, 1957, 2287.

<sup>2</sup> Cf. J. Valentine, D. Valentine, Jr., and J. P. Collman, *Inorg. Chem.*, 1971, 10, 219.

<sup>3</sup> P. T. Greene and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 866; P. Dapporto and L. Sacconi, *ibid.*, 1971, 1914.

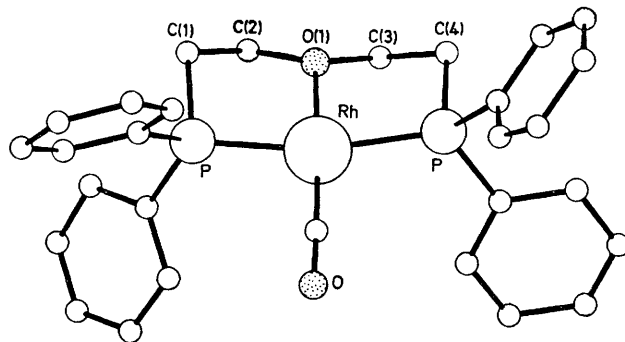
<sup>4</sup> M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, 40, 393; R. J. Haines, R. Mason, J. A. Zubieta, and C. R. Nolte, *J.C.S. Chem. Comm.*, 1972, 990.

<sup>5</sup> A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, 1973, 947.

TABLE. Geometry at oxygen in (4) and (6), measured by the angle of inclination  $\alpha$  of  $\text{O}\cdots\cdots\text{X}$  to the Y-O-Z plane [tetrahedral  $\equiv 54.7^\circ$ ].

O(1) (4)	$39^\circ$	Rh	C(2)	C(3)
O(2) (6)	$6^\circ$	O(4)	C(2)	C(3)
O(3) (6)	$9^\circ$	O(4)	C(6)	C(7)
O(4) (6)	$64^\circ$	Rh	O(1)	O(3)

No direct structural evidence is yet available on (5). On the basis of chemical shift equivalence of protons at C(2) and C(2)' down to  $-80^\circ\text{C}$ , and their progression, namely (4), 4.42, (5) 4.04, and (6) 3.73 p.p.m., the proposed formula with rapid interconversion of tautomers is indicated.



Structure of cation (4)

Ether complexes of group VIIIb metals are relatively rare and our examples illustrate the importance of chelation in stabilising otherwise weak metal-ligand bonds.<sup>4</sup> In addition, we note the differences in co-ordination chemistry between polymethylene- $\alpha\omega$ -diphosphines and  $\beta$ -phosphino-esters.<sup>5</sup>

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