Chloro-1,2-bis(diphenylphosphino)ethanecarbonylrhodium(I): an Exceptional Complex within a Series

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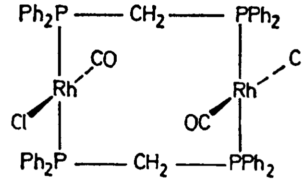
Summary The ^{31}P n.m.r. and i.r. spectra of the series of complexes $[\{RhCl(CO)(Ph_2P[CH_2]_nPPh_2)\}_m]$ ($n = 1$—4) have been studied; all the square-planar complexes are dimeric ($m = 2$) with a *trans* configuration about rhodium, except the complex ($n = 2$) which is monomeric and has a *cis* configuration.

The spectroscopic properties of complexes of the series $[\{RhCl(CO)(Ph_2P[CH_2]_nPPh_2)\}_m]$ (I–IV; $n = 1$–4) and the complexes *trans*-$[RhCl(CO)(PEtPh_2)_2]$ and $[\{Rh(cis\text{-}Ph_2PCH{:}CHPPh_2)_2\}\{RhCl_2(CO)_2\}]$ have been studied, and the unique structure of $[RhCl(CO)(Ph_2P[CH_2]_2PPh_2)]$ within the series has been demonstrated (see Table).†

The chlorine-bridged dirhodium complex $[Rh_2Cl_2(CO)_4]$ was cleaved by tertiary phosphines (or arsines) to give the complexes[1,2] *trans*-$[RhCl(CO)(PR_3)_2]$. In benzene solution equivalent amounts of $Ph_2P[CH_2]_nPPh_2$ and $[Rh_2Cl_2(CO)_4]$[3] or $[Rh_2Cl_2(1,5\text{-}C_8H_{12})_2]$[4] gave the complexes $[\{RhCl(CO)(Ph_2P[CH_2]_nPPh_2)\}_m]$. Complex (II) has been shown to be a monomer in solution.[3] Complex (I) was later shown to be a dimer in the solid state, with *trans* geometry.[5] The ligand $Bu^t{}_2P[CH_2]_{10}PBu^t{}_2$ forms a complex of similar structure.[6]

The monomeric character of (II) was clearly reflected in both the i.r. and ^{31}P n.m.r. spectra. The metal–carbonyl stretching band of (II) was 40—60 cm^{-1} higher than that shown by (I)—(IV) or *trans*-$[RhCl(CO)(PEtPh_2)_2]$ (V).[7] The ^{31}P n.m.r. spectrum consisted of two doublets of doublets separated by 20 p.p.m., reflecting the difference between phosphorus atoms *trans* to Cl and to CO ($J_{P-P'}$ 34 Hz). The ^{31}P n.m.r. spectra (^1H decoupled) of the dimeric complexes or of (V) showed in each case a unique environment for co-ordinated phosphorus (δ 85—96 p.p.m. to high field of P_4O_6). The signals were sharp doublets ($^1J_{Rh-P}$ 121—125 Hz) at −50 °C, but broader at room temperature. The similarity of both ^{31}P n.m.r. and i.r. spectra of the complexes (III) and (IV) with those of (I) or (V), and the unique environment of phosphorus atoms demonstrate that



(I)

Table. ^{31}P N.m.r. and i.r. spectroscopic data.

Complex	δ/p.p.m.[a]	$^1J_{Rh-P}$/Hz[a]	ν(CO)/cm^{-1} [b]	*M*[c]
$[\{RhCl(CO)(Ph_2PCH_2PPh_2)\}_2]$	96·8	[d]	1968	(refs. 3 and 5)
$[RhCl(CO)(Ph_2P[CH_2]_2PPh_2)]$[e]	42·2[f] 63·4[g]	158 124	2010	542[565] (ref. 3)
$[\{RhCl(CO)(Ph_2P[CH_2]_3PPh_2)\}_2]$	87·1	125	1954	949[1158]
$[\{RhCl(CO)(Ph_2P[CH_2]_4PPh_2)\}_2]$	89·1	121	1951	1090[1186]
trans-$[RhCl(CO)(PEtPh_2)_2]$[h]	85·9	122	1955	553[595]
$[\{Rh(cis\text{-}Ph_2PCH{:}CHPPh_2)_2\}\{RhCl_2(CO)_2\}]$	44·0	133	2054, 1970	1228[1126]

[a] All ^{31}P n.m.r. spectra (^1H decoupled) were run at −50 °C in $CDCl_3$ or CD_2Cl_2; signals were broader at room temperature. Chemical shifts are to high field of P_4O_6. [b] Pellets, 0·3% in KBr; all bands were very strong. [c] Osmometry; calculated values in brackets. [d] Second order: $|{}^1J_{Rh-P} + {}^3J_{Rh-P}| = 114$ Hz. [e] $J_{P-P'}$ 34 Hz. [f] P *trans* to CO. [g] P *trans* to Cl. [h] Results agree with reported values (see ref. 7).

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† **All complexes gave satisfactory elemental analyses, and their molecular weights were determined osmometrically.**

these are *trans* square-planar complexes of rhodium(I). It is unlikely that these ligands can bridge rhodium to co-ordinate in a *trans* manner. These data and molecular weight determinations therefore demonstrate that the structures of complexes (III) and (IV) are dimeric, analogous to (I).

None of the complexes resembled $[\{Rh(Ph_2PCH{:}CHPPh_2)_2\}\{RhCl_2(CO)_2\}]$[1] in either the ^{31}P n.m.r. or i.r. spectrum.

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[1] J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1969, **8**, 119.

[2] L. Vallarino, *J. Inorg. Nuclear Chem.*, 1958, **8**, 288.

[3] W. Hieber and R. Kummer, *Chem. Ber.*, 1967, **100**, 148.

[4] A. R. Sanger, unpublished results.

[5] J. T. Mague, *Inorg. Chem.*, 1969, **8**, 1975.

[6] F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 584.

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437; A. Sacco, R. Ugo, and A. Moles, *ibid.*, p. 1670; B. E. Mann, C. Masters, and B. L. Shaw, *ibid.*, 1971, 1104.