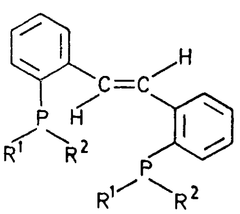
A Tridentate Unsaturated Tertiary Phosphine obtained by Dehydrogenation of 2,2′-Bis(diphenylphosphino)bibenzyl in the Presence of Rhodium Complexes; *X*-Ray Crystal Structure of the Chelate Olefin Complex $RhCl(o\text{-}Ph_2P{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}PPh_2\text{-}o),CH_2Cl_2$

By M. A. BENNETT,* P. W. CLARK, G. B. ROBERTSON, and P. O. WHIMP
(*Research School of Chemistry, The Australian National University, P.O. Box* 4, *Canberra, A.C.T.* 2600, *Australia*)

Summary The chelate olefin complex $RhCl(o\text{-}Ph_2P{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}PPh_2\text{-}o)$ is formed by dehydrogenation of 2,2′-bis(diphenylphosphino)bibenzyl, $o\text{-}Ph_2P{\cdot}C_6H_4.CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}PPh_2\text{-}o$, in the presence of Rh^{I} or Rh^{III} compounds, and is shown to be essentially square planar by *X*-ray structural analysis; four- and five-co-ordinate iridium(I) complexes are also formed by the tridentate olefinic ligand.

IT has been shown[1] that the *o*-tolylphosphines $(o\text{-}MeC_6H_4)_3P$, $Ph(o\text{-}MeC_6H_4)_2P$, and $Ph_2(o\text{-}MeC_6H_4)P$ undergo coupling and dehydrogenation on heating with $RhCl_3,3H_2O$ in high-boiling alcohols to give rhodium(I) complexes, RhCl(ligand), derived from the tridentate olefinic tertiary phosphines (**1a**—**1c**) in yields of 35, 16, and 1%, respectively. We now find that $RhCl(o\text{-}Ph_2P{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}PPh_2\text{-}o)$ (**2**) is conveniently obtained by reaction of 2,2′-bis(diphenylphosphino)bibenzyl, $[o\text{-}Ph_2P{\cdot}C_6H_4{\cdot}CH_2]_2$ (**3**) with $RhCl_3,3H_2O$, $RhCl(PPh_3)_3$, or $[RhCl(1,5\text{-}cod)]_2$ (1,5-cod = cyclo-octa-1,5-diene). For example, (**3**) reacts with $[RhCl(1,5\text{-}cod)]_2$ in refluxing toluene to give (**2**) in 78% yield, and the ligand (**1c**), 2,2′-bis(diphenylphosphino)stilbene (bdps), can be isolated in 80% yield by treatment of (**2**) with NaCN in refluxing aqueous 2-methoxyethanol. The ^1H n.m.r. and i.r. spectral data for (**1c**) and (**2**), RhBr(bdps), IrCl(bdps),-CH_2Cl_2 (**4**), $Ir(CO)(bdps),CH_2Cl_2,IrCl(bdps)(PPh_3)$ are very similar to those reported from the analogous *o*-tolyl compounds,[1] and they strongly suggest a *trans*-configuration for the olefin. The structural assignment for the series of complexes is confirmed by a single crystal *X*-ray structural analysis of (**2**).



(1)
a; $R^1 = R^2 = o\text{-}MeC_6H_4$
b; $R^1 = Ph, R^2 = o\text{-}MeC_6H_4$
c; $R^1 = R^2 = Ph$

Crystals of $[RhCl(Ph_2P{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}PPh_2)],CH_2Cl_2$ are triclinic, space group $P\bar{1}$, $a = 9{\cdot}38$, $b = 20{\cdot}75$, $c = 9{\cdot}38$ Å, $\alpha = 93{\cdot}14°$, $\beta = 76{\cdot}80°$, $\gamma = 101{\cdot}26°$, $Z = 2$. Refinement, using 4463 independent reflections with $I/\sigma(I) \geqslant 3{\cdot}0$ collected on a Picker FACS-I automatic diffractometer, has converged with $R = 0{\cdot}062$. E.s.d.s are: Rh–Cl, TABLE[a]

I.r. and n.m.r. spectral data for Rh *and* Ir *complexes of bdps*[b]

Compound	Olefinic C–H deformation (cm^{-1})	δ(Olefinic H)[c]
bdps (**1c**)	955	7·62 (m, $J_{PH} < 1{\cdot}0$ Hz)
RhCl(bdps),CH_2Cl_2 (**2**)	917	3·68 (sextet,[d] J_{PH} 1·8; J_{RhH} 1·0 Hz)
RhBr(bdps)	915	3·76 (sextet,[d] J_{PH} 2·5; J_{RhH} 2·0 Hz)
IrCl(bdps),CH_2Cl_2 (**4**)	943	2·78 (t J_{PH} 3·0 Hz)
IrCl(CO)(bdps),CH_2Cl_2	958	3·66, 3·34 (m, J_{PH} 5·0; J_{AB} 5·5 Hz)
IrCl(bdps)(PPh_3)	971	3·08 (t, J_{PH} 4·0 Hz)

[a] All compounds gave satisfactory analyses. [b] bdps = 2,2′-bis(diphenylphosphino)stilbene. [c] p.p.m. downfield of internal Me_4Si. [d] 1 : 1 : 2 : 2 : 1 : 1.

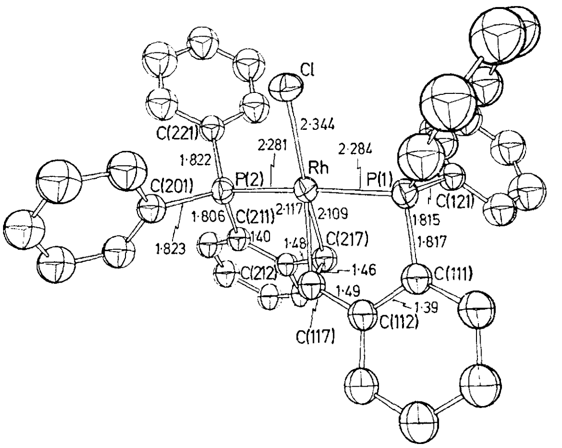


FIGURE. *Structure of* RhCl(*o*-$Ph_2P{\cdot}C_6H_4{\cdot}CH:CH{\cdot}C_6H_4{\cdot}PPh_2$-*o*)

0·002; Rh–P, 0·002; Rh–C, 0·008; C–C, 0·012 Å. Refinement will be continued using data corrected for absorption effects.

The stereochemistry about the metal atom is essentially square planar (Figure), the dihedral angle between the plane of the co-ordinated olefin [Rh, C(117), C(217)] and the metal co-ordination plane [Rh, Cl, P(1), P(2)] being 79·8°. The deviation from the expected value of 90° probably reflects the strain involved in tridentate chelation. Such strain is also shown by the angles Rh–P(1)–C(111) and Rh–P(2)–C(211) (102·8° and 103·9° respectively), which are significantly less than those generally observed for transition metal complexes of tertiary phosphines (*ca.* 115°). The olefinic bond [C(117)–C(217), 1·45(1) Å] shows the expected lengthening on co-ordination. The Rh–Cl distance [2·334(2) Å] is significantly shorter than those found in RhCl(CS)$(PPh_3)_2$[2·386 Å, *trans* to CS],[2] RhCl(PPh_3)-$(PF_2NEt_2)_2$[2·375 Å, *trans* to PF_2NEt_2],[3] and RhCl$(PPh_3)_3$ [2·373 Å, *trans* to PPh_3],[4] which suggests that the olefin exerts little or no *trans*-bond weakening effect. The Rh–C distances [Rh–C(117), 2·117 Å; Rh–C(217), 2·110 Å] are equal within experimental error, and agree well with the average value of 2·135(20) Å found for Rh(acac)-$(C_2H_4)_2$.[5]

Attempts to dehydrogenate (**3**) with iridium complexes have failed, but IrCl(bdps) (**4**) is obtained by reaction of (**1c**) with [IrCl(1,5-cod)]$_2$. Its ^{1}H n.m.r. spectrum (Table) shows the expected 1 : 2 : 1 triplet for the olefinic protons. (**4**) also forms 1 : 1 adducts with CO and PPh_3. The olefinic protons in the five-co-ordinate complex IrCl(CO)(bdps) are inequivalent and appear as an AB pattern (further complicated by ^{31}P coupling), whereas in IrCl(PPh_3)(bdps), the olefinic proton resonances appear as a 1 : 2 : 1 triplet, presumably owing to rapid exchange of co-ordinated triphenylphosphine.

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