Crystal Structure of Trichlorobis(tri-n-butylphosphine)trimethylphosphiterhodium(III)

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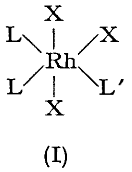
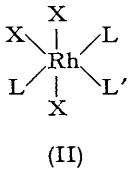
Summary The X-ray crystal structure of $[RhCl_3(Bu^n{}_3P)_2(\{MeO\}_3P)]$ confirms the structure deduced from ^{31}P n.m.r.

WE believe that it is possible from ^{31}P n.m.r. data alone to assign the correct structure to any isomeric form of a compound of the type $[RhX_3L_2L']$, where L is a tertiary phosphine, L′ a tertiary phosphite and X an anion. This prediction is verified by X-ray analysis of one compound

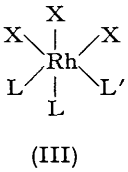
The first-order ^{31}P n.m.r. spectra of these compounds, neglecting P–H coupling, is: (I), 24 lines; (II), 10 lines; (III), 10 lines. Both $[RhCl_3(Bu^n{}_3P)_2(\{MeO\}_3P)]$ (A) and $[RhCl_3(Bu^n{}_3P)_2(\{PhO\}_3P)]$[1,2] (B) give 10 line spectra.‡



(I)



(II)



(III)

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The ${}^{31}P$ spectrum of A consists of two low-field triplets (a)[‡] and two-high field doublets (b).

	(a)	(b)
δ (from P_4O_6) p.p.m. ..	19·6	106·0
J_{Rh-P} Hz	185	80·2
J_{P-P} Hz	unresolved	29·1

The ratio of the areas (a) : (b) is 1 : 2.

It is known that for the complexes of the type $[PtX_2(Bu^n{}_3P)_2]$ and $[PtX_4(Bu^n{}_3P)_2]$, the coupling constant J_{Pt-P} in the *cis*-isomer is about 1·5 times larger than in the corresponding *trans*-isomer.[3] We find that for a series of compounds *mer*-$[RhX_3(R_3P)_3]$[1,4] the ratio between J_{Rh-P} for phosphorus *trans* to X compared with phosphorus *trans* to phosphorus is about 1·34. It has also been noted[3,5] that *J*(phosphite)/*J*(phosphine) is nearly independent of the acceptor, being 1·62 for *cis*-$[PtCl_2(\text{phosphite})_2]$/*cis*-$[PtCl_2(\text{phosphine})_2]$ and 1·53 for $[\text{phosphite}–BH_3]/[\text{phosphine}–BH_3]$.

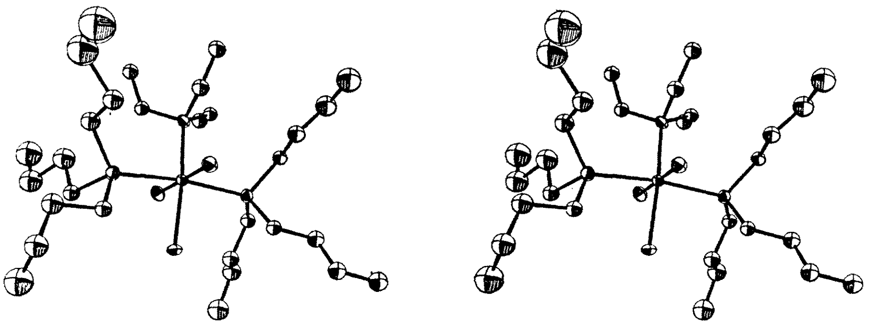

FIGURE 1. *Stereoscopic view of the molecule*

The coupling constants in *mer*-$[RhCl_3(Bu^n{}_3P)_3]$ are: J_{Rh-P} (P *trans* to P) 82·6 Hz and J_{Rh-P} (P *trans* to Cl) 113·2 Hz.[§]

If the relationship between *J*(phosphite)/*J*(phosphine) holds for rhodium complexes then for phosphite *trans* to chlorine J_{Rh-P} will be, *ca.* 1·6 × 113 = 181 Hz and for phosphite *trans* to phosphine, *ca.* 1·6 × 83 = 133 Hz. The low-field lines in the spectrum of A arise from the trimethyl phosphite phosphorus since not only do phosphite resonances generally appear to the low field of phosphine but the ratio of the areas (a) : (b) is 1 : 2. The measured value of J_{Rh-P} = 185 Hz indicates that trimethyl phosphite is *trans* to chlorine.

The high-field lines (b) give a value of $J_{Rh-P} = 80$ Hz and this is approximately the same as the value found for J_{Rh-P} (phosphorus *trans* to phosphorus) in the series of compounds *mer*-$[RhX_3(R_3P)_3]$.[1,4]

Hence the n.m.r. evidence alone strongly indicates structure (II) and this assignment is confirmed by the *X*-ray data below. Using similar arguments the structure of B would also be (II). [*J*(Rh–phosphite) = 202·8 Hz, *J*(Rh–phosphine) = 79·3 Hz].

Crystals of A are monoclinic, space-group $P2_1/n$; $a = 18{\cdot}45$, $b = 18{\cdot}73$, $c = 11{\cdot}18$ Å, $\beta = 100{\cdot}70°$, $D_m = 1{\cdot}29$ g cm^{-3}, $Z = 4$ (flotation), $D_c = 1{\cdot}287$ g cm^{-3}.

Intensity data were estimated visually from equi-inclination Weissenberg photographs (Cu-K_α) of layers *h*0—13 *l* and *hk*0—5. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares, including anisotropic temperature factors for the rhodium, phosphorus, and chlorine atoms. The final *R* index for 3775 observed reflections is 0·124. A stereoscopic view of the molecule is shown in Figure 1. Rh–Cl and Rh–P distances are shown in Figure 2. All calculations were carried out at the California Institute of Technology on an IBM 7094 computer under the CRYRM system.[6]

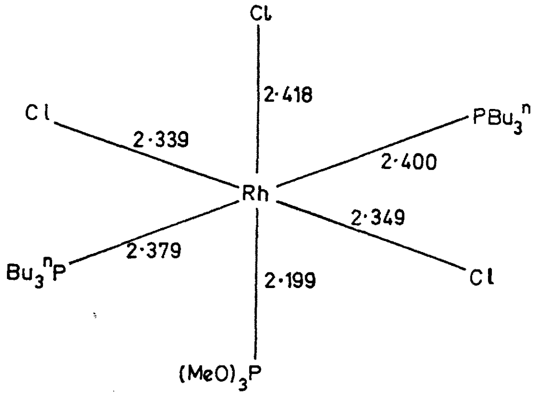

FIGURE 2. *Bond lengths in* Å (*e.s.d.* 0·005 Å)

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[‡] The low-field triplets are unresolved in compound A.

[§] Remeasured.

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