Trimethylphosphine Complexes of Rhodium(I) and Ruthenium(II); *X*-Ray Crystal Structures of Chlorotristrimethylphosphinerhodium and Tetrakistrimethylphosphinerhodium Chloride†

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Summary The syntheses are reported of the rhodium(I) and ruthenium(II) trimethylphosphine complexes $RhCl(PMe_3)_3$, $[Rh(PMe_3)_4]Cl$, η^5-$C_5H_5Rh(PMe_3)_2$, $CHg_6Rh_4(PMe_3)_{12}$, *trans*-$RuCl_2(PMe_3)_4$, $[Ru_2Cl_2(PMe_3)_8]Cl_2$, and $[RuCl(PMe_3)_4]BF_4$ and of ruthenium(I), $Ru_2Cl_2(PMe_3)_4$; the structures of $RhCl(PMe_3)_3$ and $[Rh(PMe_3)_4]Cl$ have been determined by single crystal *X*-ray analysis.

Although numerous trisalkyl-phosphine complexes of stoicheiometry $RhCl(PR_3)_3$ have been reported,[1] our attempts to synthesize the trimethylphosphine complex by the complicated procedure given did not give a pure product. Much rhodium metal was produced and carbonyl species were formed. It is likely that the other complexes quoted are also mixtures. We have now made authentic $RhCl(PMe_3)_3$, (**A**), from $[Rh(PMe_3)_4]Cl$, (**B**), which in turn is quantitatively obtained from $RhCl(PPh_3)_3$[2] by phosphine exchange in petroleum. The cobalt analogue of (**A**) is known[3] and $[Ir(PMe_3)_4]Cl$,[4] and $[Ni(PMe_3)_4]BPh_4$[5] have also been reported briefly.

The structures of the two complexes (**A**) and (**B**) have been determined by single crystal *X*-ray analysis. *Crystal data:* (**A**) $C_9H_{27}ClP_3Rh$, $M = 366{\cdot}59$, triclinic, $a = 8{\cdot}842(1)$, $b = 8{\cdot}982(1)$, $c = 11{\cdot}825(1)$ Å, $\alpha = 98{\cdot}74(1)$, $\beta = 92{\cdot}38(1)$, $\gamma = 116{\cdot}09(1)°$, $U = 827{\cdot}4$ Å^3, space group $P\bar{1}$, $Z = 2$,

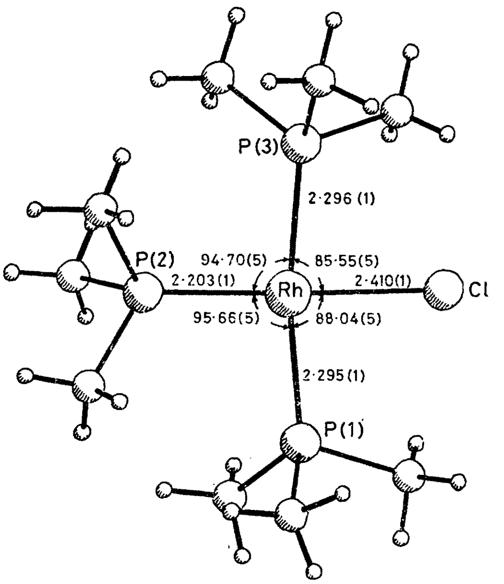

Figure 1. The structure of $RhCl(PMe_3)_3$ (**A**) showing bond lengths (Å) and angles (°) in the co-ordination sphere. ∠Cl–Rh–P(2), 163·15(5) and P(1)–Rh–P(3), 163·99(5)°.

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† No reprints available.

D_c = 1·47 g cm^{-3}, $F(000)$ = 376, μ(Mo-K_α) = 13·3 cm^{-1}. (**B**) $C_{12}H_{36}ClP_4Rh$, M = 442·67, orthorhombic, a = 12·366(2), b = 13·584(2), c = 12·554(2) Å, U = 2108·8 Å^3, space group *Ccmm*, Z = 4, D_c = 1·39 g cm^{-3}, $F(000)$ = 920, μ(Mo-K_α) = 11·2 cm^{-1}.

Intensity data were recorded on a Nonius CAD4 diffractometer as described previously[6] and the structures solved and refined by standard methods. Current R values are 0·0235 for (**A**) [2695 reflections with $F_0 > 3\sigma(F_0)$] and 0·0304 for (**B**) [1476 reflections with $F_0 > 3\sigma(F_0)$].‡

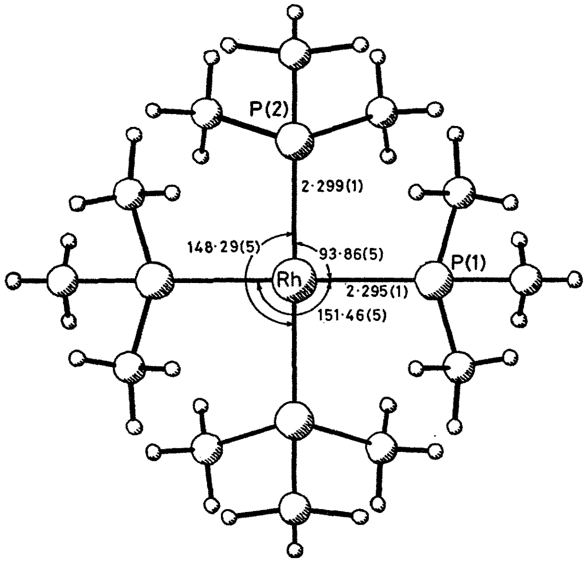

FIGURE 2. The structure of the cation $[Rh(PMe_3)_4]^+$ (**B**) showing bond lengths (Å) and angles (°) in the co-ordination sphere.

The structures found are shown in Figures 1 and 2. Both the molecule (**A**) and the cation (**B**) can be considered to have the square-planar geometries expected for rhodium(I) with distortion towards tetrahedral, as a result of the steric crowding between the phosphine ligands. In the case of the cation this is quite severe (see Figure 2).

Although $[Rh(PMe_3)_4]Cl$ is a 1:1 electrolyte in polar solvents, the precipitation of the cation from aqueous solutions by BPh_4^- or PF_6^- gives salts of the *tris*-ion $[Rh(PMe_3)_3]^+$. The analogous tris-triphenylphosphine ion has recently[7] been characterised in $[Rh(PPh_3)_3]ClO_4$. Spectroscopic studies show that the ion $[Rh(PMe_3)_3]^+$ is non-rigid and also that in $[Rh(PMe_3)_3]BPh_4$, there is no π-bonded phenyl ring as found in other rhodium(I) tetraphenylborates.[8]

Interaction of $RhCl(PMe_3)_3$ or $[Rh(PMe_3)_4]Cl$ with hydrogen (1 atm, 25 °C) gives, as the chloride, the cation $[RhH_2(PMe_3)_4]^+$, obtained previously as PF_6^- and ClO_4^- salts from cationic diene complexes.[9] Interaction of $[Rh(PMe_3)_4]Cl$ with (a) CO gives *trans*-$RhCl(CO)(PMe_3)_2$, and (b) NaC_5H_5 in tetrahydrofuran (thf) gives η^5-$C_5H_5Rh(PMe_3)_2$, the latter as red-brown, petroleum soluble crystals (the cobalt analogue of the latter is known[10]). With sodium amalgam, a dark-red, very air sensitive, but petroleum soluble crystalline cluster of formula $CHg_6Rh_4(PMe_3)_{12}$, is obtained; its structure has been determined and will be described separately.

Although *trans*-$RuCl_2(PMe_3)_4$ has been obtained from $RuCl_2(PPh_3)_3$ by phosphine exchange in petroleum[11] it can also be obtained by interaction of $Ru_2(CO_2Me)_4Cl$ with Na–Hg in thf containing PMe_3 and LiCl. At refluxing temperature, however, the ion $[(Me_3P)_4Ru(\mu\text{-}Cl)_2Ru(PMe_3)_4]^{2+}$ is obtained as the chloride; spectroscopic data suggest a structure similar to that[12] for $\{Ru_2Cl_2[P(OEt)Ph_2]_8\}^{2+}$.

The pentaco-ordinate ion $[RuCl(PMe_3)_4]^+$ as its BF_4^- salt can be obtained by the interaction of trityltetrafluoroborate with the products of the reaction of $Ru_2(O_2CMe)_4Cl$, PMe_3, and $(2\text{-}MeOC_6H_4)_2Mg$. Spectroscopic studies indicate that it is fluxional in solution as found for $[NiX(PMe_3)_4]BF_4$.[13]

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Added in proof: An alternative synthesis of (**B**) from $[RhCl(C_8H_{12})]_2$ has been recently reported by H. Werner, R. Feser, and W. Buchner, *Chem. Ber.*, 1979, **112**, 834.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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