

Preliminary communication

Metal–metal bond formation promoted by steric effects: the structural chemistry of μ -dichlorobis(di-*t*-butyl-*p*-tolylphosphine) tetracarbonyl-diruthenium(I)

R. MASON and K.M. THOMAS

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

D.F. GILL and B.L. SHAW

School of Chemistry, The University, Leeds LS2 9JT (Great Britain)

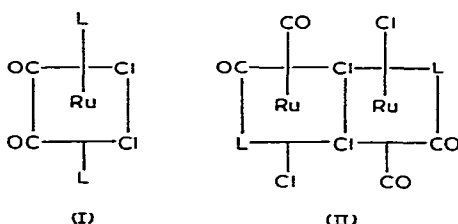
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SUMMARY

The bulky tertiary phosphines P-*t*-Bu₂Ph and P-*t*-Bu₂-*p*-tol, provide binuclear ruthenium(I) complexes. An X-ray analysis of [Ru₂Cl₂(CO)₄(P-*t*-Bu₂-*p*-tol)₂] shows the RuCl₂Ru bridge to be non-planar and to have an Ru–Ru distance of 2.632Å.

Sterically overcrowded tertiary phosphines provide complexes of metals in unusual valency states and coordination numbers and promote internal metallation reactions^{1, 2, 3}. They are now shown to promote metal–metal bond formation.

The treatment of ruthenium trichloride in boiling 2-methoxyethanol with carbon monoxide for 16 h provides a yellow solution; addition of sterically non-bulky phosphines (PEt₃, PPr₂Ph, PPh₃ etc.) gives, in high yield, the colourless complexes [RuCl₂(CO)₂L₂], having the configuration(I)⁴, whereas reaction with the bulky phosphines, P-*t*-Bu₂Ph or



P-*t*-Bu₂-*p*-tol, provides orange binuclear, diamagnetic complexes [Ru₂Cl₂(CO)₄L₂]. Crystals (methanol) of [Ru₂Cl₂(CO)₄(P-*t*-Bu₂-*p*-tol)₂] are orthorhombic with $a = 9.507(4)$, $b = 15.531(6)$, $c = 25.922(12)$ Å; $Z = 4$, space group $P2_12_12_1$. 2436 independent

reflexions ($\text{Mo-K}\alpha$; four circle diffractometry; $F_O^2 \geq 2.8\sigma F_O^2$) formed the basis of the X-ray analysis and least squares refinement has converged to $R = 0.047$. The stereochemistry is shown in Fig. 1; e.s.d.'s in the bond lengths are 0.002\AA (Ru-Ru) 0.004\AA (Ru-P and Ru-Cl) and 0.02\AA (C-C and C-O).

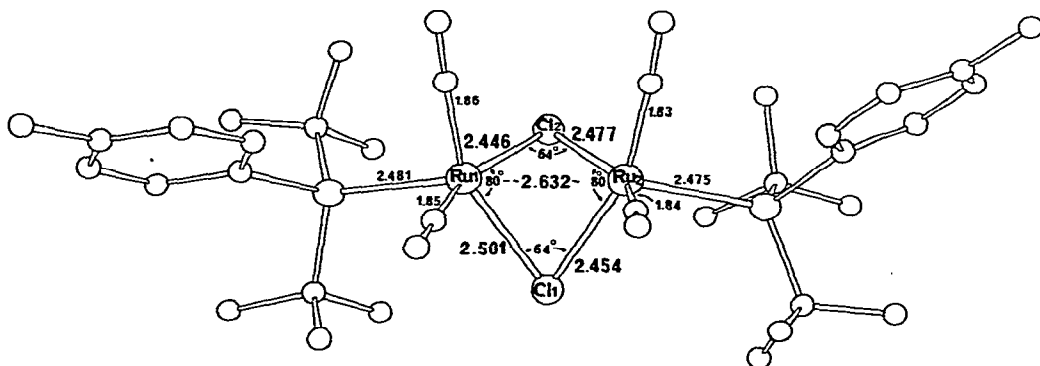
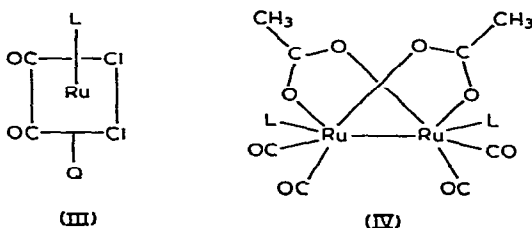


Fig. 1. Stereochemistry of $[\text{Ru}_2\text{Cl}_2(\text{CO})_4(\text{P-t-Bu}_2\text{-p-tol})_2]$.

The metal-metal distance is much shorter than those found in other bi- and polynuclear complexes of Ru^0 and Ru^{I} . This result, the non-planarity of the bridge system (the dihedral angle between the two planes, $\text{Cl}_2\text{-Ru}_2\text{-Cl}_1$ and $\text{Cl}_2\text{-Ru}_1\text{-Cl}_1$, is 92°) and the rare gas rule can be rationalised by postulating a bent metal-metal bond formed from the overlap of essentially octahedral hybrid orbitals. There is no reason to believe that the bridge conformation reflects any steric effects, the complex has approximate C_2 symmetry and the two independent $\text{RuCl}_2(\text{CO})_2$ groups are planar.

On treatment of a chloroform solution of $[\text{Ru}_2\text{Cl}_2(\text{CO})_4\text{L}_2]$ ($\text{L} = \text{P-t-Bu}_2\text{Ph}$, $\text{P-t-Bu}_2\text{-p-tol}$) with chlorine in carbon tetrachloride, the white complexes $[\text{RuCl}_2(\text{CO})_2\text{L}_2]_n$ are formed. These chlorobridged (IR) complexes probably have the stereochemistry (II), since they react with pyridine or dimethylphenylphosphine (Q) to give the complexes $[\text{RuCl}_2(\text{CO})_2\text{LQ}]$ of configuration (III) (IR and NMR).



$[\text{Ru}_2\text{Cl}_2(\text{CO})_4(\text{P-t-Bu}_2\text{Ph})_2]$ is reformed on heating $[\text{Ru}_2\text{Cl}_4(\text{CO})_4(\text{P-t-Bu}_2\text{Ph})_2]$ in 2-methoxyethanol alone (30 min) or with $\text{P-t-Bu}_2\text{Ph}$ (1 min). Reaction of the dichloride with silver acetate in acetone gives the diacetate complex, whose probable structure is (IV); the infrared data ($\nu(\text{C}\equiv\text{O})$ and $\nu(\text{C}=\text{O})$) are very similar to those reported for $[\text{Ru}_2(\text{OAc})_2(\text{CO})_4(\text{PPh}_3)_2]$ and for which a similar structure has been proposed⁵.

We suggest that the phosphines, P-t-Bu₂Ph and P-t-Bu₂-p-tol, are too sterically overcrowded to allow the formation of six coordinate complexes such as [RuCl₂(CO)₂L₂]. It is possible that complexes with only one coordinated phosphine ligand can be formed which then undergo reduction to the six coordinate, binuclear species.

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