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The Preparation of [$Ru_2Cl_5(PEtPh_2)_4$·Ag($PEtPh_2$)] by Direct Interaction of Silver(I) Chloride with Triply Chloride Bridged Diruthenium Complexes

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The reaction of [$Ru_2Cl_4(PEtPh_2)_5$], [$Ru_2Cl_3(PEtPh_2)_6$]Cl, or [$RuCl_2(PEtPh_2)_3$] with equimolar amounts of AgCl at ambient temperature in methanol gives the novel, fluxional, heterotrimetallic complex [$Ru_2Cl_5(PEtPh_2)_4$·Ag($PEtPh_2$)] whose structure has been determined by *X*-ray crystallography and $^{31}P\{^1H\}$ n.m.r. spectroscopy.

The heterotrimetallic complex [$Ru_2Cl_5(PEtPh_2)_4$·Ag($PEtPh_2$)] (**1**) is readily prepared in high yield by direct reaction of equimolar amounts of [$Ru_2Cl_4(PEtPh_2)_5$] and AgCl in methanol at room temperature. Recrystallisation from CH_2Cl_2–MeOH yields red crystals of the dichloromethane solvate, shown by *X*-ray analysis to have the novel structure depicted in Figure 1.† This reveals a formal insertion of AgCl into a Ru–$PEtPh_2$ linkage to produce a four-co-ordinate Ag^I ion linked to one terminal- and two bridging-chloride ligands of the newly formed [$(PEtPh_2)_2ClRu^{II}(\mu\text{-}Cl)_3Ru^{II}Cl(PEtPh_2)_2$]$^-$ unit. As shown in Figure 1, the co-ordination of the silver atom produces no significant changes in the co-ordination of the two ruthenium atoms.

Interestingly, compound (**1**) can also be synthesised in high yield by reaction of either [$Ru_2Cl_3(PEtPh_2)_6$]Cl or [$RuCl_2(PEtPh_2)_3$] at ambient temperature with equimolar amounts of AgCl. Both these reactions clearly involve cleavage of

[$Ru_2Cl_5(PEtPh_2)_4$·Ag($PEtPh_2$)]
(**1**)

ruthenium–phosphorus bonds, probably with the pre-formation of [$Ru_2Cl_4(PEtPh_2)_5$], whereas, in the absence of AgCl, conversion of [$Ru_2Cl_3(PEtPh_2)_6$]Cl into [$Ru_2Cl_4(PEtPh_2)_5$] requires pyrolysis at elevated temperatures.[1]

Variable temperature $^{31}P\{^1H\}$ n.m.r. studies on (**1**) in CD_2Cl_2 are fully consistent with retention of the solid state structure in solution. Thus at 183 K (Figure 2), two AB patterns from the $PEtPh_2$ ligands attached to ruthenium and two characteristic doublets from the $PEtPh_2$ group attached to silver are observed. These spectroscopic data indicate that, as

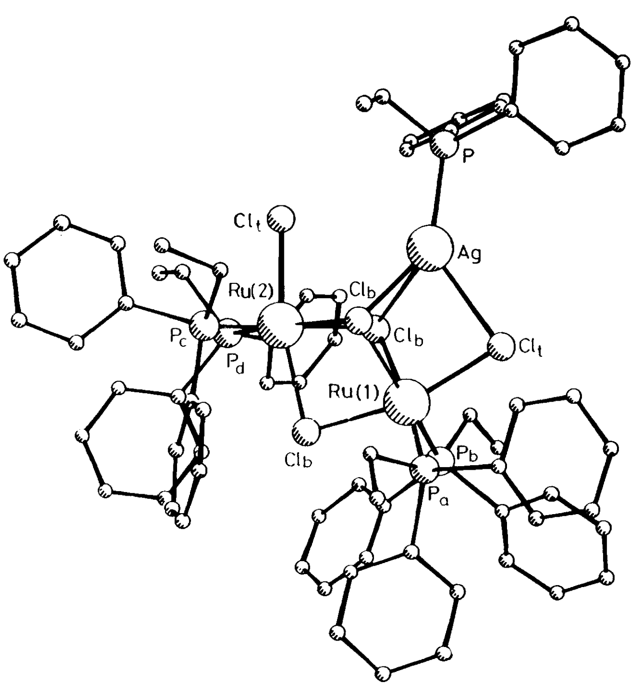


Figure 1. The structure of [$Ru_2Cl_5(PEtPh_2)_4$·Ag($PEtPh_2$)] (**1**). Selected bond lengths (Å) (e.s.d.s all 0.006 Å): Ru(1)–P$_a$ 2.280, Ru(1)–P$_b$ 2.282, Ru(1)–Cl$_t$ 2.433, Ru(1)–Cl$_b$ (*trans* to P, attached to Ag) 2.493, 2.578, Ru(1)–Cl$_b$ (*trans* to Cl$_t$) 2.378, Ru(2)–P$_c$ 2.274, Ru(2)–P$_d$ 2.280, Ru(2)–Cl$_t$ 2.441, Ru(2)–Cl$_b$ (*trans* to P, attached to Ag) 2.499, 2.570, Ru(2)–Cl$_b$ (*trans* to Cl$_t$) 2.449, Ag–Cl$_b$ 2.657, 2.788, Ag–Cl$_t$ 2.675, Ag · · · Cl$_t$ 3.457, Ag–P 2.376.

† *Crystal data* for (**1**) $C_{70}H_{75}AgCl_5P_5Ru_2 \cdot CH_2Cl_2$, M = 1643.5, monoclinic, space group $P2_1/a$, a = 26.005(5), b = 19.315(6), c = 15.515(3) Å, β = 106.98(1)°, U = 7453(3) Å^3, Z = 4, D_c = 1.40 g cm^{-3}. The structure was based on 3475 data out of 6766 measured to sin θ/λ = 0.48 Å^{-1}; R = 0.060, R_w = 0.070. The structure was solved by Patterson methods. In the refinement, all phenyl rings were constrained to be ideal hexagons, and all hydrogen atoms were held in calculated positions. In the final cycles, 318 parameters were refined, including two positions for a disordered molecule of CH_2Cl_2 solvent of crystallisation. The final electron density map showed no peaks above 0.6 e Å^{-3}. 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.

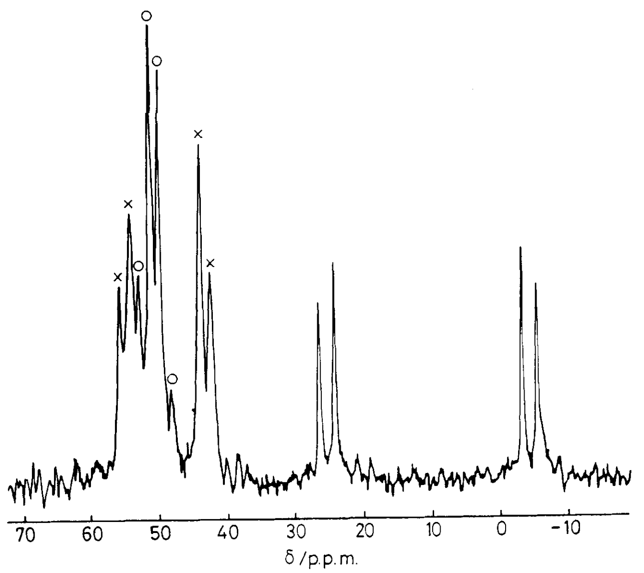
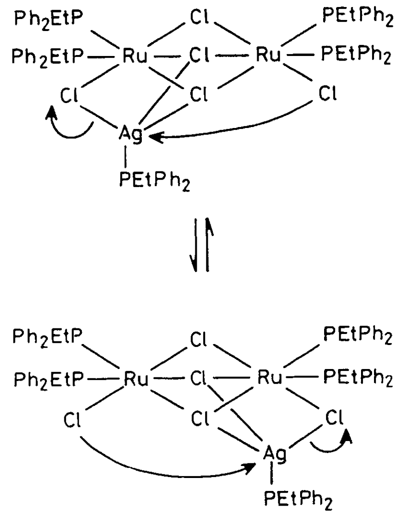


Figure 2. $^{31}P\{^1H\}$ n.m.r. spectrum of $[Ru_2Cl_5(PEtPh_2)_4 \cdot Ag(PEtPh_2)]$ in CD_2Cl_2 at 183 K. Two AB patterns centred at δ 50.0 (○) [$\Delta\nu(P_cP_d)$ 57.9 Hz, $J(P_cP_d)$ 41.9 Hz] and 48.4 (×) [$\Delta\nu(P_aP_b)$ 284.1 Hz, $J(P_aP_b)$ 36.4 Hz] and two doublets centred at 10.0 p.p.m. [$J(^{109}Ag^{31}P)$ 771.5 Hz, $J(^{107}Ag^{31}P)$ 668.9 Hz].

in the solid phase, there is no plane of symmetry relating the two ruthenium atoms, nor through the three metal atoms because of the preferred orientation of the substituents on the $Ag(PEtPh_2)$ moiety. At 223 K, a temperature-reversible coalescence of the AB signals, to give a singlet at δ 48.9 p.p.m., indicates magnetic equivalence of all four $PEtPh_2$ groups bound to ruthenium, and this is attributed to ready switching of the $Ag(PEtPh_2)$ moiety between the two equivalent sites offered by the $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^-$ unit [see equation (1)]. The *X*-ray structure reveals the proximity of the alternative chloride ligand [Ag ··· Cl_t, 3.457(6) Å]. At ambient temperature, collapse of the $Ag(PEtPh_2)$ resonance but retention of the $Ru(PEtPh_2)$ singlet, indicates the onset of specific intermolecular tertiary phosphine exchange at the silver site [*cf.* the kinetic lability of simple silver(I) tertiary phosphine compounds].[2]

Whereas the asymmetrically ligated $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuCl_2(PEt_2Ph)]^-$ anion is readily prepared by electroreduction of $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuCl_2(PEt_2Ph)]$,[3,4] the



(1)

symmetric $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^-$ anion represents a new structural category among triply chloride bridged diruthenium compounds. Such distinctions substantially determine mixed valency behaviour.[4]

Cyclic voltammetric studies establish that upon reduction of (**1**), silver metal is released and experiments are now in progress to generate $[(PEtPh_2)_2ClRu(\mu\text{-}Cl)_3RuCl(PEtPh_2)_2]^{-/0}$ species on a preparative scale.

Finally, preliminary studies indicate that $[Ru_2Cl_4(PEtPh_2)_5]$ and $[Ru_2Cl_3(PEtPh_2)_6]Cl$ will react with other metal compounds such as AuCl, CuCl, $PtCl_2$, and $PdCl_2$.

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