Syntheses of Some Triple Chloro-bridged Complexes of Ruthenium(II) Including a Novel Phosphine Ligand Transfer Reaction

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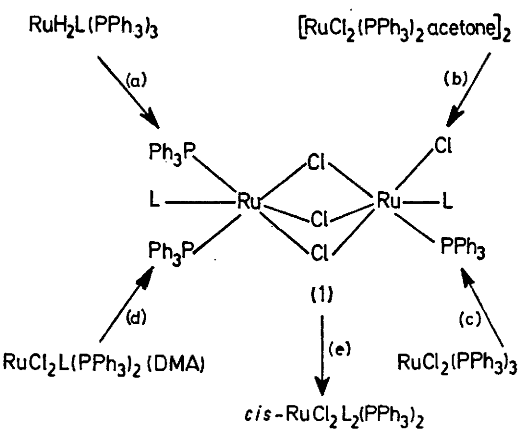
Summary Several different synthetic routes to triple chloro-bridged complexes of ruthenium(II) are described, including an unusual phosphine ligand exchange reaction.

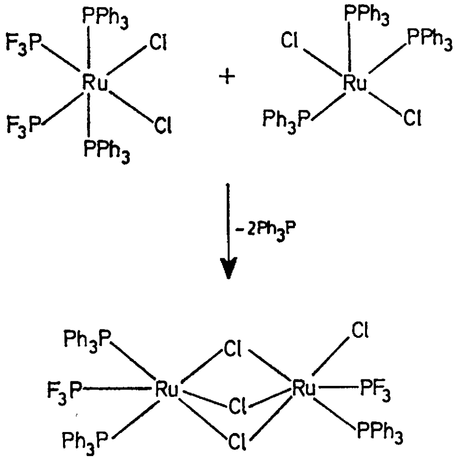
Recent reports of the synthesis of some tri-μ-halide complexes of ruthenium(II)[1] prompts us to describe several alternative preparative routes to this type of complex and we also report an interesting phosphine ligand transfer reaction during the formation of one of these triple bridged structures.



(a) 2HCl(gas), L = CO, PF_3 (b) L = $2PF_3$ (c) 1:1 molar ratio; L = PF_3, Me_2NPF_2 in benzene (d) Heat; L = PF_3, Me_2NPF_2 (e) Excess PF_3

Scheme 1

The different synthetic approaches are summarised in Scheme 1 and involve (a) treatment of the dihydridoruthenium complexes $RuH_2L(PPh_3)_3$ (L = CO, PF_3)[2,3] with gaseous hydrogen chloride; (b) displacement of acetone and triphenylphosphine from the di-μ-chloro-complex $[RuCl_2(PPh_3)_2acetone]_2$; (c) treatment of $RuCl_2(PPh_3)_3$ with an equimolar amount of L (L = PF_3, Me_2NPF_2); and (d) *via* the thermal decomposition of complexes of the type $RuCl_2(L)(PPh_3)_2(DMA)$, (L = PF_3, Me_2NPF_2). In (d) the behaviour contrasts with that previously reported[1] for the analogous carbonyl complex which gives a di-μ-chloro-bridged complex. Complex (**1**, L = PF_3) reacts with an



Scheme 2

excess of PF_3 to yield the monomeric complex *cis*-$RuCl_2(PF_3)_2(PPh_3)_2$ which we have prepared by other routes.[3]

The triple chloro-bridged complex, $(PPh_3)_2(PF_3)RuCl_3RuCl(PPh_3)_2$, (**2**) is readily obtained from the reaction of a 2:1 mixture of $RuCl_2(PPh_3)_3$ and trifluorophosphine while the mixed carbonyl-trifluorophosphine-triphenylphosphine ruthenium complex $(PPh_3)_2)(CO)RuCl_3RuCl(PPh_3)(PF_3)$, (**3**), is the major product (> 90%) from the reaction between a 1:1 mixture of $(PPh_3)_2(CO)RuCl_3RuCl(PPh_3)_2$[1] and PF_3.

An interesting and unexpected phosphine ligand transfer reaction is observed when a 1:1 mixture of $RuCl_2(PPh_3)_3$ and *cis*-$RuCl_2(PF_3)_2(PPh_3)_2$ is refluxed in acetone, the product being (**1**, L = PF_3) (Scheme 2).

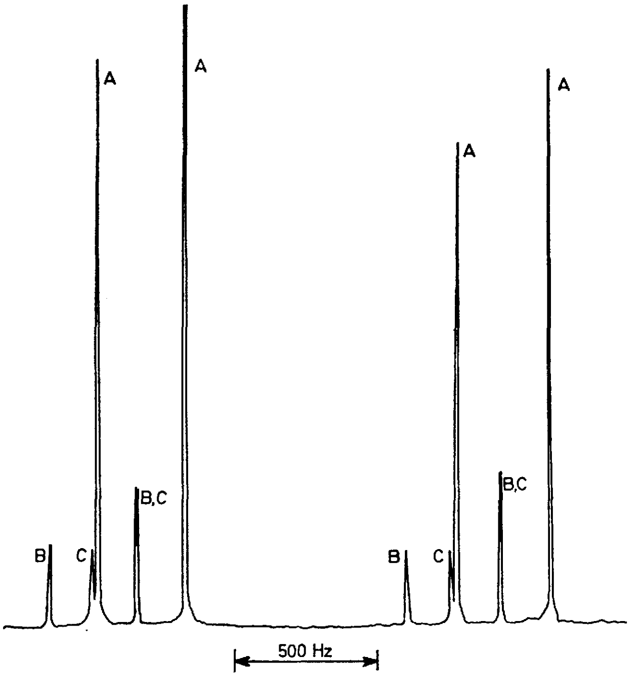
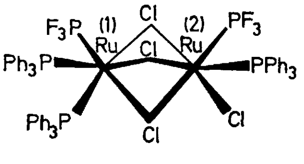


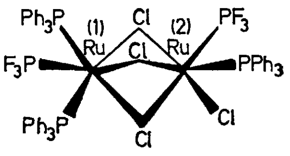
Figure ^{19}F n.m.r. spectrum of (**1**, L = PF_3) showing the relative abundance of geometric isomers [A], [B] and [C].

In the absence of $RuCl_2(PPh_3)_3$ the *cis*-$RuCl_2(PF_3)_2(PPh_3)_2$ complex can be recovered unchanged from refluxing acetone.

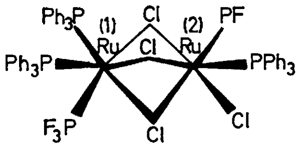
All new complexes were fully characterised by elemental analysis, and their i.r. and n.m.r. spectra. In particular the ^{31}P and ^{19}F n.m.r. spectra of complexes (**1**—**3**) reveal the presence of different geometric isomers, thus (**1**, L = PF_3) exists as the three geometric isomers [A], [B], and [C] and these can be assigned from the ^{19}F n.m.r. spectrum shown in the Figure.



[A]



[B]



[C]

The strongest lines in the ^{19}F n.m.r. spectrum are assigned to isomer [A] in which the two PF_3 groups are eclipsed, each line appearing as a widely spaced doublet due to coupling with phosphorus [^1J(PF) 1290 Hz]. The resonance of the PF_3 attached to Ru(2) appears at highest field and is further doubleted by the single PPh_3 ligand also attached to Ru(2) [^2J(PF) 4 Hz]. In both the isomers [B] and [C] the PF_3 attached to Ru(2) is eclipsed by a Ph_3P ligand on Ru(1) and this causes the PF_3 resonances on Ru(2) in both isomers to have the same chemical shift. (The signal is further split into a doublet through coupling to the PPh_3 attached to Ru(2), [^3J(PF) 4 Hz].) Two distinct resonances are observed, however, for the PF_3 bonded to Ru(1) since in isomer [B] it eclipses a PPh_3 ligand while in isomer [C] it eclipses a chlorine atom. The relative abundancies of the three isomers are 74%, 16%, and 10%.

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[3] R. A. Head and J. F. Nixon, unpublished results.

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