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Polyphosphine Complexes of Ruthenium(II)

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Introduction

Three tertiary phosphine complexes of ruthenium (II), *viz.* $Ru(PPh_3)_3Cl_2$,[1,2] $Ru(PPh_3)HCl$[1] and $Ru(PPh_3)_3H(O_2CCH_3)$,[3,4] have been studied extensively in connection with their homogeneous catalytic activity. While it is well established that in the solid state these complexes have very similar square pyramidal coordination polyhedra,[5] there are more uncertainties concerning their structures in solution: as with some complexes of Rh(I) and Pt(0), there appeared to be considerable dissociation of one or more of the triphenylphosphine ligands from the coordination sphere; the most recent ^{31}P n.m.r. study suggests, however, that it is only $Ru(PPh_3)_3Cl_2$ which undergoes solution dissociation in 'spectroscopically detectable' amounts.[6]

We have shown that complexes of platinum(0)[7] and cobalt(I)[8] based on chelating polyphosphine ligands are much more stable with respect to dissociation in solution, a feature which allows an unambiguous structure analysis and the determination of metal–phosphorus and phosphorus–phosphorus coupling constants which cannot be obtained systematically from monodendate phosphine species, given ligand dissociation and rapid exchange processes. Our object then was to extend our studies of the polyphosphine complexes of d^{10} and d^8 metal ions to ones involving ruthenium(II) and to investigate the effects of ligand substitution on catalytic behaviour.

Experimental and Discussion

Addition of the diphosphine ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 1,2,3) to an acetone suspension of $Ru(PPh_3)_3Cl_2$, under nitrogen, gave yellow compounds of composition, $Ru(diphos)_2Cl_2$. The ^{31}P n.m.r. spectra of these complexes (in dichloromethane) show but one resonance (Table), invariant within the temperature range –80 °C to 30 °C; the obvious implication is that the complexes are octahedral with *trans*-chloro ligands and non-exchanging phosphorus nuclei. There are significant differences in the phosphorus chemical shifts between the complexes $Ru(dppe)_2Cl_2$, which contains a five-membered chelate ring, and those based on four and six-membered chelate rings, $Ru(dppm)_2Cl_2$ and $Ru(dppp)_2Cl_2$ (dppe = $Ph_2P(CH_2)_2PPh_2$; dppm = $Ph_2PCH_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$). Similar data are to hand for complexes of chromium, molybdenum and tungsten[9] but the possible 'ring contribution' [10] to the deshielding effect in five-membered chelate ring complexes has yet to be placed on a firm theoretical basis.

The Table lists the ^1H magnetic resonance data and shows that coupling between the phosphorus and methylene protons is resolved only for $Ru(dppm)_2Cl_2$ where J_{PH} = 4.3 Hz; an unresolved multiplet at τ 7.3 is observed for $Ru(dppe)_2Cl_2$ while in $Ru(dppp)_2Cl_2$ there are two unresolved multiplets with relative intensities of 2:1 which can reasonably be attributed to the central methylene protons (τ 8.05) and the two sets of terminal methylene protons at τ = 7.39.

TABLE. NMR Data for the Ruthenium Complexes.

Complex	^{31}P [a]			^1H [b]		
	δ, ppm[c]	Δ, ppm	T(K)	$\tau(C_6H_5)$	$\tau(-CH_2-)$	$\tau(CH_3)$
$Ru(dppm)_2Cl_2$	147.9	–16.7	303, 213	2.86	4.97[d]	
$Ru(dppe)_2Cl_2$	96.0	–55.2	303, 213	2.90	7.26	
$Ru(dppp)_2Cl_2$ [e]	145.2	–13.1	303, 213, 193	2.85	7.39(2) 8.05(1)	
$Ru(triphos)_2Cl_2$ [e]	140.6(2) 166.7(1)	–25.5 0	303	2.96	7.41(2)	8.33(1)

[a] In CH_2Cl_2 solution. [b] In $CDCl_3$ solution at 303 K. [c] Relative to trimethylphosphite. [d] J_{P-H} = 4.3 Hz. [e] Relative intensities in parentheses.

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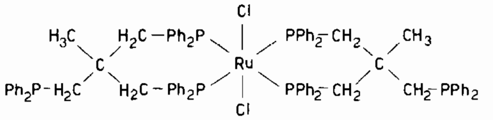
The reaction, under nitrogen, of the triphosphine ligand, $CH_3C(CH_2PPh_2)_3$, with $Ru(PPh_3)_3Cl_2$ provided a white compound which, analytically, is characterised as $Ru(triphos)_2Cl_2$. The ^{31}P n.m.r. of this complex (in dichloromethane) has resonances at 166.7 ppm and 140.6 ppm (relative to trimethylphosphite), the relative intensities being 1:2. The uncoordinated triphosphine has a single phosphorus resonance at 166.1 ppm and the magnetic resonance spectrum of bis(triphos)Pt(0) is very similar to the ruthenium(II) species; the d^{10} complex has been characterised by X-ray crystallography as a tetrahedral species with two non-coordinated phosphorus atoms.[11] There seems, therefore, little doubt that the structure of $Ru(triphos)_2Cl_2$ is,



The reaction of $Ru(PPh_3)_3H(O_2CCH_3)$ with the diphosphine ligands, dppe and dppp, was attempted but the low solubility of the resulting yellow complexes of stoichiometry $Ru(dppe)_2H(O_2CCH_3)$ and $Ru(dppp)_2H(O_2CCH_3)$ precluded any n.m.r. studies of their solution structures. A monomeric formulation and the analogy with the ruthenium complex would suggest that the acetate ligands are monodendate; the asymmetric carbon–oxygen stretching frequencies (1601 cm^{-1} and 1598 cm^{-1} for the dppe and dppp complexes respectively) are similar to those in *trans*-$Ru(dppe)_2(O_2CCH_3)_2$ where they are 1603 cm^{-1} and 1570 cm^{-1} and where the monodendate character of the acetate group is established.[12] The Ru–H stretching frequencies in our complexes are 2017 cm^{-1} (dppe) and 2004 cm^{-1} (dppp complex).

All the polydendate phosphine complexes which we have synthesised and tested for catalytic hydrogenation of alkenes are less active than the corresponding monodendate phosphine complexes. The satisfactory analytical data obtained for all complexes were obtained by the Analytical Laboratory, University of Sussex. Fourier transform ^{31}P n.m.r. spectra were recorded on a Jeol PFT-100 spectrometer.

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Note added in press (November 14, 1975)

A similar study of polyphosphine complexes of ruthenium (II) has just been reported by M. Bressan and P. Rigo (*Inorg. Chem., 14, 2286 (1975)*).