Interconversion of Methyl and Acetyl Complexes of Ruthenium(II)

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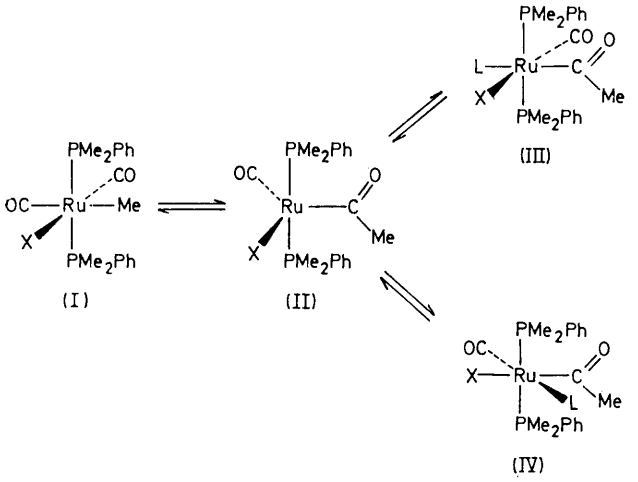
Summary Complexes $[Ru(CO)_2XMe(PMe_2Ph)_2]$ (X = Cl, Br, or I) react rapidly and reversibly with CO to form acetyl complexes $[Ru(CO)_2X(COMe)(PMe_2Ph)_2]$; the rate and stereochemistry of the interconversion are strongly dependent on the nature of the ligand X.

RECENTLY we reported[1] the preparation of new alkyl complexes of ruthenium(II), intended to serve as models for similar species which seem to be likely intermediates in several reactions involving ruthenium compounds as catalysts or reactants. Here we describe the rapid and reversible conversion of methyl complexes $[Ru(CO)_2XMe(PMe_2Ph)_2]$ (X = halogen) into acetyl complexes, reactions which may well be relevant to the mechanism of ruthenium-catalysed hydroformylation of alkenes[2] and decarbonylation of aldehydes by $[Ru_2Cl_3(PEt_2Ph)_6]Cl$.[3]

In $CHCl_3$ at 293 K there is an immediate reaction between $[Ru(CO)_2ClMe(PMe_2Ph)_2]$ [(I; X = Cl): Scheme] and CO. The i.r. spectrum of the solution (two bands in the terminal and one in the acyl C–O stretching region) is compatible with the formation of the acetyl complex $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$. The reaction can be reversed by passing nitrogen through the solution, and attempts to isolate the product yielded only the methyl complex.

Saturation with CO of a $CDCl_3$ solution of $[Ru(CO)_2ClMe(PMe_2Ph)_2]$ at 313 K causes the disappearance of the ^1H n.m.r. signal due to the methyl ligand, but no acetyl resonance appears in its place. At 253 K, however, the



SCHEME

latter is observed as a sharp singlet, and the PMe_2Ph methyl protons give rise to two 1:2:1 triplets of equal area [the use of the ligand PMe_2Ph in determining the stereochemistry of ruthenium(II) complexes has been described by Shaw and his co-workers[4]]. Thus the structure of the product $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$ must be (III) (see Scheme: X = Cl, L = CO). If insufficient CO is added to cause complete conversion, separate signals are observed for the methyl and acetyl ligands at 253 K: these broaden and collapse simultaneously on warming. Evidently the equilibrium between (I) and (III) is very rapid at 313 K and heavily in favour of (III) in CO-saturated solution.

The reaction of $[Ru(CO)_2IMe(PMe_2Ph)_2]$ with CO, also reversible, yields an isolable product $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$. Its i.r. spectrum, however, contains only a single terminal C–O stretching band (plus the expected band in the acyl C–O stretching region) and its n.m.r. spectrum differs from that of $[Ru(CO)_2Cl(COMe)(PMe_2Ph)_2]$ in two ways: the resonance due to the acetyl protons is still a sharp singlet at 313 K {even in the presence of $[Ru(CO)_2IMe(PMe_2Ph)_2]$} and the PMe_2Ph methyl protons give rise to a single 1:2:1 triplet resonance. Thus interconversion between methyl and acetyl complexes is slow on the n.m.r. time scale at 313 K, and the structure of $[Ru(CO)_2I(COMe)(PMe_2Ph)_2]$ must be (IV) (see Scheme: X = I, L = CO) rather than (III). Reaction of $[Ru(CO)_2BrMe(PMe_2Ph)_2]$ with CO yields an equilibrium mixture of isomers (III) and (IV) of $[Ru(CO)_2Br(COMe)(PMe_2Ph)_2]$; n.m.r. studies show that $[Ru(CO)_2BrMe(PMe_2Ph)_2]$ interconverts with isomer (III) much faster than with (IV).

The complex $[Ru(CO)_2ClMe(PMe_2Ph)_2]$ also reacts reversibly with PMe_2Ph to yield $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$, showing that the acetyl ligand is formed by combination of co-ordinated methyl and carbonyl ligands {separate experiments ruled out initial carbonyl substitution by PMe_2Ph followed by CO attack on $[Ru(CO)ClMe(PMe_2Ph)_3]$}. The product was assigned structure (III) (X = Cl, L = PMe_2Ph) on the basis of its i.r. and n.m.r. spectra. Collapse of the acetyl proton resonance for $[Ru(CO)Cl(COMe)(PMe_2Ph)_3]$ on warming above 283 K can be inhibited by addition of free PMe_2Ph: this undergoes rapid exchange with the unique PMe_2Ph ligand (L) at a rate which is independent of the concentration of free PMe_2Ph.

A mechanism compatible with all these results is shown in the Scheme. Combination of methyl and carbonyl ligands yields (II) (see earlier discussions[5] of the stereochemistry of such five-co-ordinate species). In a separate step, (II) is attacked by L, the normal direction of attack being *trans* to the strongly *trans*-directing acetyl ligand,† yielding (III). The *trans*-effect of the acetyl ligand[6]† also facilitates the loss of L from (III), thus allowing the very rapid interconversion of (I) and (III) observed at 313 K. In the reaction between $[Ru(CO)_2IMe(PMe_2Ph)_2]$ and CO, it is probably steric repulsion between iodide and acetyl ligands which disfavours formation of (III). Isomer (IV), once formed, reverts less rapidly to (I) because the ligand L which must be lost is *not trans* to the acetyl ligand.

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† The relationship between *trans*-directing and *trans*-labilizing effects of a ligand is discussed in ref. 5.

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