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Preliminary communication

The reaction of a ruthenium(0) complex with methyl iodide, and opposing photochemical and thermal isomerizations of ruthenium(II) complexes

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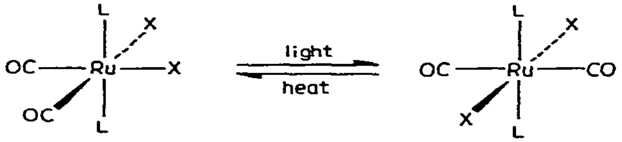
It has been reported[1,2] that the ruthenium(0) complex $Ru(CO)_3(PPh_3)_2$ undergoes an oxidative addition reaction with iodomethane to give $Ru(CO)_2(PPh_3)_2IMe$, although no details of the reaction conditions, no analytical data and no properties of the product were given. Since such a compound is of obvious interest as a model for the species believed to be involved in catalytic olefin hydrogenation[3] and aldehyde decarboxylation[4], we attempted to repeat the preparation. This communication describes the results of our attempts and some related experiments.

We were unable to observe any reaction between $Ru(CO)_3(PPh_3)_2$[5] and MeI in benzene either at room temperature or under reflux. In tetrahydrofuran, there was no reaction at room temperature, but prolonged heating under reflux using excess MeI led to the formation of yellow crystals of the ionic species $[PPh_3Me][Ru(CO)_2PPh_3I_3]$. (Found: C, 43.69; H, 3.14; $C_{39}H_{33}O_2I_3P_2Ru$ calcd.: C, 43.49; H, 3.06%.) The IR spectrum of the complex in acetone exhibited strong bands due to C–O stretching modes at 2036 and 1976 cm^{-1}, and the proton NMR spectrum in dimethylsulphoxide-d_6 contained bands in the region δ 7.84–7.40 due to aromatic protons, and a doublet (δ 3.13, $^2J(P-H) = 14$ Hz) due to the methyl protons in the cation (*cf.* $[PPh_3Me]I$ in the same solvent: δ 3.24, $^2J(P-H) = 14$ Hz).

Although it is possible that such a compound might result from the reaction of initially formed $Ru(CO)_2(PPh_3)_2IMe$ with the excess of MeI (there is a precedent for this type of reaction[6]), we were not able to isolate $Ru(CO)_2(PPh_3)_2IMe$ from the reaction of $Ru(CO)_3(PPh_3)_2$ with the stoichiometric amount of MeI, and it is equally possible that the ionic compound is formed via $Ru(CO)_2(PPh_3)_2I_2$. We have found that this compound, obtained as yellow crystals from $Ru(CO)_2(PPh_3)_2Cl_2$[7] by metathesis[8] (Found: C, 48.91; H, 3.30; $C_{38}H_{30}O_2I_2P_2Ru$ calcd.: C, 48.79; H, 3.20%), also reacts with MeI in tetrahydrofuran to give $[PPh_3Me][Ru(CO)_2PPh_3I_3]$. Reaction of the ionic complex with PPh_3 regenerated $Ru(CO)_2(PPh_3)_2I_2$.

During this work, we discovered an intriguing reversible isomerization of $Ru(CO)_2(PPh_3)_2I_2$. Exposure to daylight of a benzene solution of the yellow isomer mentioned above (whose IR spectrum contains two strong bands in the C–O stretching region, at 2055 and 1990 cm^{-1}, showing that the two carbonyl groups are mutually *cis*) caused these bands to weaken, and a new band to appear at 2001 cm^{-1}. The mixture reached equilibrium over a period of two days, but could be driven back entirely to the yellow species by heating the solution under reflux for 30 min. The species responsible for the new IR band was isolated as red crystals of a tetrahydrofuran solvate, $Ru(CO)_2(PPh_3)_2I_2 \cdot C_4H_8O$, by irradiating a solution of the yellow isomer in tetrahydrofuran. (Found: C, 50.24; H, 3.72; $C_{42}H_{38}O_3I_2P_2Ru$ calcd.: C, 50.07; H, 3.77%.) As expected, the IR spectrum of a nujol mull of the red crystals exhibited a single band in the C–O stretching region (at 1998 cm^{-1}), showing that the two carbonyl groups are mutually *trans* in the red isomer. The presence of the solvent of crystallization was confirmed by the NMR spectrum of the complex in benzene solution. Complete reconversion to the yellow isomer was achieved by dissolving the red isomer in benzene and heating the solution under reflux, whereas on allowing a solution of the red isomer to stand in daylight, an equilibrium mixture similar to that obtained from the yellow isomer under the same conditions resulted.

Both yellow and red isomers of $Ru(CO)_2(PPh_3)_2I_2$ have been previously described[9] (whereas the reversible interconversion has not) and assigned structures (I) and (II) respectively. We believe these structures to be correct, since the corresponding isomers of $Ru(CO)_2(PPh_2Me)_2I_2$ possess related IR spectra and both have NMR spectra (recorded in benzene solution) containing 1/2/1 triplets for the methyl protons (*cis*-carbonyls isomer, δ 2.90, $|^2J(P\text{–}H) + {}^4J(P\text{–}H)| = 8.0$ Hz; *trans*-carbonyls isomer, δ 2.56, $|^2J(P\text{–}H) + {}^4J(P\text{–}H)| = 7.2$ Hz), confirming that the phosphorus ligands are mutually *trans*. (Whereas daylight was sufficient for the photochemical isomerization of $Ru(CO)_2(PPh_3)_2I_2$, the rearrangement of $Ru(CO)_2(PPh_2Me)_2I_2$ required UV irradiation).



(I)
(for L=PPh_3, X=I, yellow)

(II)
(for L=PPh_3, X=I, red)

Preliminary results indicate that this reversible interconversion is possible for many complexes $Ru(CO)_2L_2X_2$ (L = phosphorus(III) or arsenic(III) ligand; X = Cl, Br or I), although the wavelength of the light required for the photochemical step and the rate of the thermal step at a given temperature both vary from complex to complex. Although there has been a brief mention[10], in a communication on iridium(III) complexes, of photochemically induced isomerizations of two ruthenium(II) complexes, we believe that this paper represents the first report of opposing photochemical and thermal isomerizations in such complexes. Further studies to establish the scope and details of the mechanisms of these reactions are in progress.

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