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Preliminary communication

SYNTHESES OF DI- AND TRI-μ-HALIDE COMPLEXES OF RUTHENIUM(II)-CONTAINING CARBONYL AND TERTIARY PHOSPHINE LIGANDS

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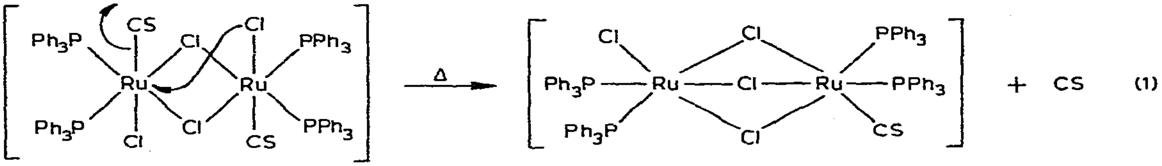
We have recently shown that the reaction of $[RuCl_2(PPh_3)_3]$ and carbon disulphide gives, in addition to the previously reported [1] di-μ-chloro complex $[RuCl_2(CS)(PPh_3)_2]_2$ (I) and the η-CS_2 cation $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$ (II), the tri-μ-chloro complex $[(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2]$ (III) which has been characterised by X-ray analysis [2] and ^{31}P NMR studies. Initially, it was thought that (III) was probably formed from (I) by an intramolecular transfer of chloride ion accompanied by displacement of a thiocarbonyl group (eqn. 1), but attempts to carry out this conversion under the conditions of the original reaction were unsuccessful.



Therefore, a speculative mechanism was suggested which involved formation of $[RuCl_2(CS)(PPh_3)_2]$ (probably via abstraction of Ph_3PS from (II)) and then, either dimerisation of this five coordinate intermediate to give (I) or combination with some unreacted $[RuCl_2(PPh_3)_3]$* to give (III) (eqn. 2).

Although this latter mechanism is difficult to verify for the thiocarbonyl compounds, we have now obtained good evidence for the feasibility of such a mechanism by synthesis of the corresponding carbonyl complexes by this method.

Thus, if the recently reported $[RuCl_2CO(PPh_3)_2dmf]$ (ν(CO) 1911 cm^{-1}; dmf = *N,N'*-dimethylformamide) [4] is gently refluxed in dichloromethane,

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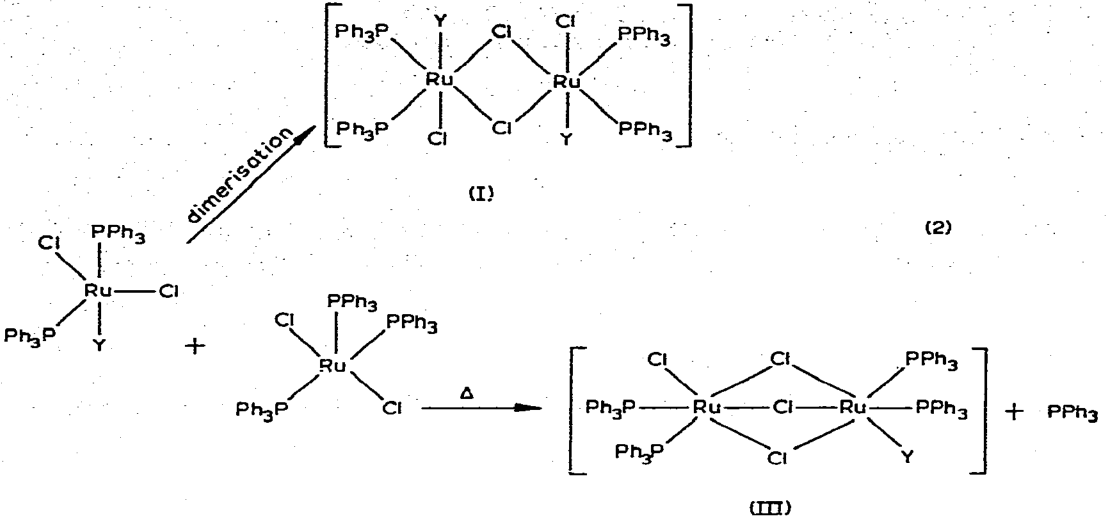
*Recent ^{31}P NMR studies of this compound in this and other laboratories (S. Cenini, private communication) show that in the complete absence of oxygen, this compound is not dissociated in solution but when traces of oxygen are present, free triphenylphosphine oxide is rapidly produced.



(2)

dimerisation occurs to give the pale orange $[RuCl_2(CO)(PPh_3)_2]_2$ (I, Y = CO) (ν(CO) 1960 (br) cm^{-1}) whereas if the dmf complex is refluxed with $[RuCl_2(PPh_3)_3]$ in acetone (1/1 molar ratio), red crystals of the tri-μ-chloro complex $[(PPh_3)_2ClRuCl_3Ru(CO)(PPh_3)_2]$ (III, Y = CO) (ν(CO) 1951 cm^{-1}) are formed. This latter compound is isomorphous with the corresponding thiocarbonyl complex and the ^{31}P proton decoupled NMR spectra in $CDCl_3$ which consists of two AB quartets centred at 48.0* and 40.3 ppm. (Y = CO) and 48.3 and 36.1 ppm (Y = CS) respectively confirm that the same structure is retained in solution.

The tri-μ-bromo complex can be similarly prepared from $[RuBr_2(PPh_3)_3]$ and $[RuBr_2CO(PPh_3)_2dmf]$ and by reaction of 1/1 molar mixtures of $[RuCl_2CO(PPh_3)_2dmf]/[RuBr_2(PPh_3)_3]$ and $[RuBr_2CO(PPh_3)_2dmf]/[RuCl_2(PPh_3)_3]$ respectively, the mixed tri-μ-halide complexes $[(PPh_3)_2BrRuBrCl_2Ru(CO)(PPh_3)_2]$ and $[(PPh_3)_2ClRuClBr_2Ru(CO)(PPh_3)_2]$ are readily isolated. Preliminary work indicates that such coupling reactions can also be used to synthesise mixed tertiary phosphine complexes e.g. $[(PPh_3)_2ClRuCl_3Ru(CO)(PEt_2Ph)_2]$ from $[RuCl_2(PPh_3)_3]$ and $[RuCl_2CO(PEt_2Ph)_2dmf]$.

Therefore, this work provides both an independent verification of the proposed mechanism of formation of the thiocarbonyl compounds described in ref. 3 and also a general route to the preparation of a wide range of binuclear metal compounds with different bridging and terminal ligands and probably even different metal ions.

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*Chemical shifts are reported in ppm to high frequency of 85% H_3PO_4.

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