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Selective Monodecarbonylation of $Ru(CO)_2X_2L_2$ Complexes

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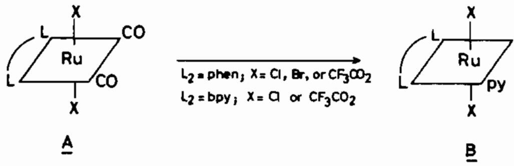
Complexes of the type $Ru(CO)_2X_2L_2$ (*e.g.* L_2 = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bpy), X = Cl [1]) are a potential starting point for synthesis of a wide variety of ruthenium complexes. However, their substitution reactions have not been extensively studied, and there is evidence [1] that they have low lability. Recent studies have shown [2] that $Ru(CO)_2X_2L_2$ (L_2 = phen or bpy; X = Cl) complexes can be labilised by conversion into trifluoromethanesulphonate derivatives, providing a convenient route to $[Ru(CO)_2(\text{bidentate})_2]^{2+}$ complexes. We now report that selective replacement of one carbon monoxide ligand of $Ru(CO)_2X_2L_2$ complexes can be readily achieved by reaction with trimethylamine oxide in pyridine. Monocarbonylruthenium(II) compounds are of particular current interest because of the ability of $[Ru(bpy)_2(CO)Cl]Cl$ to catalyse a photochemical water-gas shift reaction [3].

The complexes $Ru(CO)pyX_2L_2$ (L_2 = phen, X = Cl, Br, or CF_3CO_2; L_2 = bpy, X = Cl or CF_3CO_2; L_2 = $(Ph_3P)_2$, X = Cl or Br) were isolated after treatment of the corresponding $Ru(CO)_2X_2L_2$ derivatives (preparations [1, 2, 4]) with trimethylamine oxide (mole ratio 1:5) in pyridine for 2 h at room temperature (Eqn. (1)].

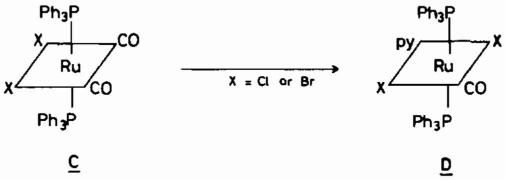
$$Ru(CO)_2X_2L_2 + py + Me_3NO \rightarrow [Ru(CO)pyX_2L_2 + CO_2 + Me_3N \qquad (1)$$

After crystallisation from ethanol, the compounds were obtained analytically pure (C, H, N, Halogen) in 45–70% yield, and the trifluoroacetato complexes and $Ru(CO)pyCl_2(bpy)$ were sufficiently volatile to give the parent ions in their mass spectra.

The stereochemistry of the products, established from spectroscopic data (below), and the reactants [1, 2, 5, 6] is given in reactions (2) and (3).



(2)



(3)

All $Ru(CO)pyX_2L_2$ complexes show a single ν(CO) absorption at 1942–1938 cm^{-1} (X = Cl or Br) or 1958–1955 cm^{-1} (X = CF_3CO_2). Each chloro derivative has a single ν(Ru–Cl) infrared absorption at *ca.* 320 cm^{-1}, indicative of *trans* chlorines (*cf.* two bands at 300 and 275 cm^{-1} for *bc*-dicarbonyl-*de*-dichloro-*af*-bis(triphenylphosphine)ruthenium(II) [5]).

It was not possible to locate ν(Ru–Br) of the $Ru(CO)pyBr_2L_2$ complexes, but the similarity of their ν(CO) frequencies to those of the corresponding chloro derivatives points to a similar stereochemistry. Structure *B* is also potentially distinguishable from the alternative with *cis* halogens and pyridine *trans* to the carbonyl by ^1H NMR spectroscopy, since the two pyridine rings of 1,10-phenanthroline and 2,2′-bipyridyl are inequivalent in *B* but not in the alternative. Where features due to the bidentate ligands can be distinguished from those of pyridine, they appear more complex than expected for symmetrical coordination, and in most cases there is not a single resonance for H2,9 (L_2 = phen) or H6, 6′ (L_2 = bpy), thereby indicating structure *B.* With *trans* halogens for $Ru(CO)pyX_2(PPh_3)_2$ complexes (above), there remain two isomeric possibilities, with *cis* or *trans* phosphines. Observation of a single ^{31}P NMR resonance establishes the latter (structure *D*).

The formation (2) of the complexes $Ru(CO)pyX_2L_2$ (L_2 = phen or bpy) proceeds with retention of stereochemistry. This is consistent with loss of a carbonyl group to give a square pyramidal intermediate, followed by addition of pyridine to the vacant site. By contrast, formation of $Ru(CO)pyX_2(PPh_3)_2$ complexes (*D*) involves isomerization [reaction (3)]. Probably, carbon monoxide elimination again proceeds with retention of stereochemistry to give *b*-carbonyl-*de*-dihalogeno-*c*-pyridine-*af*-bis(triphenylphosphine)ruthenium(II) derivatives, which then isomerize into *D*. It is known that an excess of trimethylamine oxide, used in the present reactions, and the reaction product trimethylamine [see reaction (1)] can cause isomerization [7].

In the present case, coordination of either compound to the remaining carbonyl group could labilise a cis chlorine and lead to rearrangement.

Attempts to remove both carbonyls of $Ru(CO)_2Cl_2L_2$ (L_2 = phen or bpy) derivatives by reaction with trimethylamine oxide in boiling pyridine failed and $Ru(CO)pyCl_2L_2$ complexes were again obtained [reaction (1), X = Cl]. The selective monodecarbonylation can probably be related to stronger ruthenium–carbon bonding in the monocarbonyls (ν(CO), 1958–1938 cm^{-1} (above)) than in the reactant dicarbonyls (ν(CO), 2100–2000 cm^{-1} [1, 2, 8]). It is known that trimethylamine oxide induced decarbonylations are generally restricted to complexes with $\nu(CO) > 2000$ cm^{-1} [7].

References

1 J. V. Kingston, J. W. S. Jamieson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *29*, 133 (1967).

2 D. St. C. Black, G. B. Deacon and N. C. Thomas, *Transition Metal Chem.*, *5*, 317 (1980).

3 D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.*, 1213 (1980).

4 J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, *87*, 4008 (1965).

5 S. Cenini, A. Fusi and G. Capparella, *Inorg. Nucl. Chem. Lett.*, *8*, 127 (1972).

6 D. R. Fahey, *J. Org. Chem.*, *38*, 80 (1973).

7 D. J. Blumer, K. W. Barnett and T. L. Brown, *J. Organometal. Chem.*, *173*, 71 (1979).

8 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *28*, 945 (1966).