Binuclear Halide-bridged Ruthenium(II) Complexes containing Terminal Alkene, Alkyne, and Dinitrogen Ligands

Tom Easton,[a] Graham A. Heath,[a] T. Anthony Stephenson,[a] and Manfred Bochmann[b]†

[a] *Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, U.K.*
[b] *New Science Group, ICI plc, Runcorn, Cheshire WA7 4QE, U.K.*

Convenient, high-yield routes to the new redox-active complexes $[(PEt_2Ph)_3Ru(\mu\text{-}Cl)_3RuL(PEt_2Ph)_2]BF_4$ ($L = C_2H_4$, $PhC{\equiv}CH$, N_2 *etc.*) and $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$ ($L' = C_2H_4$ or $PhC{\equiv}CH$) are described.

A wide range of triple chloride bridged compounds of stoicheiometry $L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}$, ($L$ = soft Lewis base such as PR_3, AsR_3, PF_3, CO, or CS), in oxidation states varying from $Ru_2^{II,II}$ to $Ru_2^{III,III}$ have been synthesised in recent years.[1] Although several monomeric dinitrogen ruthenium complexes are known, the only examples of well defined binuclear species containing terminally bound N_2 appear to be $[Ru_2X_4N_2(PPh_3)_4]$ ($X = Cl$[2] or H[3]) and $[Ru_2H_6N_2(PPh_3)_4]$.[4]

We now describe a simple, high-yield method of incorporating ligands such as N_2, alkenes, alkynes, *etc.* into the terminal positions of $L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}$ by displacement of terminal chloride using $M[BF_4]$ (M = Ag, Na, or Tl). For example, reaction of $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ in CH_2Cl_2 with equimolar amounts of $Tl[BF_4]$ in the presence of an excess of L at ambient temperature and pressure, ($L = N_2$, C_2H_4, $PhC{\equiv}CH$, $MeO_2CC{\equiv}CCO_2Me$, MeCN, $MeNO_2$, or PEt_2Ph), produces the cationic complexes $[(PEt_2Ph)_3RuCl_3RuL(PEt_2Ph)_2]BF_4$ in almost quantitative yield.‡

The cyclic voltammogram§ of $[Ru_2Cl_3(C_2H_4)(PEt_2Ph)_5]BF_4$ (**1**) in CH_2Cl_2 (Scheme 1) shows a reversible one-electron oxidation and a second irreversible oxidation, much like the overall pattern for the analogous ionic dimer $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ (Scheme 2).[1] The abundant evidence for isolated valencies[1,5] in these binuclear species and the reversible nature of the first wave suggest that the initial oxidation in (**1**) takes place at the $-Ru(PEt_2Ph)_3$ centre.

The N_2 and C_2H_4 compounds are stable in both solid and solution phase at ambient temperature under N_2 and C_2H_4 (1 atm) respectively and can be reversibly interconverted. The N_2 and C_2H_4 ligands are readily replaced by chloride ion to regenerate $[Ru_2Cl_4(PEt_2Ph)_5]$, and by the other ligands L mentioned above to generate $[Ru_2Cl_3L(PEt_2Ph)_5]BF_4$ complexes which are stable under argon.

Under argon, in the absence of other potential ligands, treatment of $[Ru_2Cl_4(PEt_2Ph)_5]$ with $M[BF_4]$ in CH_2Cl_2 leads to formation of $[Ru_2Cl_3(PEt_2Ph)_6]BF_4$ and $[RuCl_2(PEt_2Ph)_2]_n$, presumably *via* attack of a co-ordinatively unsaturated intermediate on unchanged $[Ru_2Cl_4(PEt_2Ph)_5]$.

Finally, reduction of the mixed valence complex $[Ru_2^{II,III}Cl_5(PEt_2Ph)_4]$ with $Na[BH_4]$ in the presence of C_2H_4 or $PhC{\equiv}CH$ (L′) leads to the unusual bis(alkene) and bis(alkyne) complexes $[(PEt_2Ph)_3ClRu(\mu\text{-}Cl)_2RuL'_2Cl(PEt_2Ph)]$. The asymmetric ligation of these complexes is demonstrated by their ^1H and ^{31}P n.m.r. spectra.

$$
\begin{array}{cr}
[(PEt_2Ph)_3Ru^{II}Cl_3Ru^{II}(C_2H_4)(PEt_2Ph)_2]^{+} & (36e) \\
(\mathbf{1}) & \\
+1.48\ \text{V} \updownarrow & \\
[(PEt_2Ph)_3Ru^{III}Cl_3Ru^{II}(C_2H_4)(PEt_2Ph)_2]^{2+} & (35e) \\
+2.00\ \text{V}\P \downarrow & \\
[(PEt_2Ph)_3Ru^{III}Cl_3Ru^{III}(C_2H_4)(PEt_2Ph)_2]^{3+} & (34e)
\end{array}
$$

Scheme 1

$$
\begin{array}{cr}
[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{+} & (36e) \\
+1.20\ \text{V} \updownarrow & \\
[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+} & (35e) \\
+1.75\ \text{V} \updownarrow & \\
[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{3+} & (34e)
\end{array}
$$

Scheme 2

We thank Johnson Matthey plc for loans of '$RuCl_3 \cdot xH_2O$', the S.E.R.C. and I.C.I. plc for financial support (to T. E.), and Drs. W. N. Brooks and C. S. Cundy of I.C.I. New Science Group for useful discussions.

Received, 5th November 1984; Com. 1571

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† Present address, Department of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

‡ The complexes have been fully characterised by elemental analyses, and i.r. and n.m.r. (^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$) spectroscopy.

§ $E_{\frac{1}{2}}$ V measured by cyclic voltammetry (scan rate, 0.1 V/s) at 293 K in $Bu_4NBF_4\text{–}CH_2Cl_2$ (0.5 M) *vs.* a $Ag/AgI/CH_2Cl_2$ reference electrode. $E_{\frac{1}{2}}$ for ferrocene–ferrocinium is 0.60 V in this cell.

¶ Rapid rearrangement observed (no cyclic voltammetric return wave) in the scan rate range 0.05 to 50 V/s, even at 235 K.