

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

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Convenient, high-yield routes to the new redox-active complexes [(PEt<sub>2</sub>Ph)<sub>3</sub>Ru(μ-Cl)<sub>3</sub>RuL(PEt<sub>2</sub>Ph)<sub>2</sub>]BF<sub>4</sub> (L = C<sub>2</sub>H<sub>4</sub>, PhC≡CH, N<sub>2</sub> etc.) and [(PEt<sub>2</sub>Ph)<sub>3</sub>ClRu(μ-Cl)<sub>2</sub>RuL'Cl(PEt<sub>2</sub>Ph)] (L' = C<sub>2</sub>H<sub>4</sub> or PhC≡CH) are described.

A wide range of triple chloride bridged compounds of stoichiometry L<sub>3-x</sub>Cl<sub>x</sub>RuCl<sub>3</sub>RuCl<sub>y</sub>L<sub>3-y</sub>, (L = soft Lewis base such as PR<sub>3</sub>, AsR<sub>3</sub>, PF<sub>3</sub>, CO, or CS), in oxidation states varying from Ru<sup>II,II</sup> to Ru<sup>III,III</sup> have been synthesised in recent years.<sup>1</sup> Although several monomeric dinitrogen ruthenium complexes are known, the only examples of well defined binuclear species containing terminally bound N<sub>2</sub> appear to be [Ru<sub>2</sub>X<sub>4</sub>N<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (X = Cl<sup>2</sup> or H<sup>3</sup>) and [Ru<sub>2</sub>H<sub>6</sub>N<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>].<sup>4</sup>

We now describe a simple, high-yield method of incorporating ligands such as N<sub>2</sub>, alkenes, alkynes, etc. into the terminal positions of L<sub>3-x</sub>Cl<sub>x</sub>RuCl<sub>3</sub>RuCl<sub>y</sub>L<sub>3-y</sub> by displacement of terminal chloride using M[BF<sub>4</sub>] (M = Ag, Na, or Tl). For example, reaction of [(PEt<sub>2</sub>Ph)<sub>3</sub>RuCl<sub>3</sub>RuCl(PEt<sub>2</sub>Ph)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> with equimolar amounts of Tl[BF<sub>4</sub>] in the presence of an excess of L at ambient temperature and pressure, (L = N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, PhC≡CH, MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me, MeCN, MeNO<sub>2</sub>, or PEt<sub>2</sub>Ph), produces the cationic complexes [(PEt<sub>2</sub>Ph)<sub>3</sub>RuCl<sub>3</sub>RuL(PEt<sub>2</sub>Ph)<sub>2</sub>]BF<sub>4</sub> in almost quantitative yield.<sup>‡</sup>

The cyclic voltammogram§ of [Ru<sub>2</sub>Cl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)(PEt<sub>2</sub>Ph)<sub>5</sub>]BF<sub>4</sub> (**1**) in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 1) shows a reversible one-electron oxidation and a second irreversible oxidation, much like the overall pattern for the analogous ionic dimer [Ru<sub>2</sub>Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>6</sub>]BF<sub>4</sub> (Scheme 2).<sup>1</sup> The abundant evidence for isolated valencies<sup>1,5</sup> 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<sub>2</sub>Ph)<sub>3</sub> centre.

The N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> compounds are stable in both solid and solution phase at ambient temperature under N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> (1 atm) respectively and can be reversibly interconverted. The N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> ligands are readily replaced by chloride ion to regenerate [Ru<sub>2</sub>Cl<sub>4</sub>(PEt<sub>2</sub>Ph)<sub>5</sub>], and by the other ligands L mentioned above to generate [Ru<sub>2</sub>Cl<sub>3</sub>L(PEt<sub>2</sub>Ph)<sub>5</sub>]BF<sub>4</sub> complexes which are stable under argon.

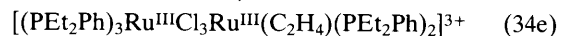
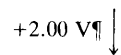
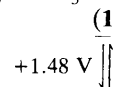
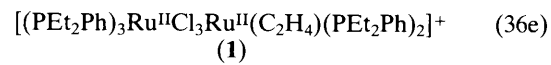
Under argon, in the absence of other potential ligands, treatment of [Ru<sub>2</sub>Cl<sub>4</sub>(PEt<sub>2</sub>Ph)<sub>5</sub>] with M[BF<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> leads to formation of [Ru<sub>2</sub>Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>6</sub>]BF<sub>4</sub> and [RuCl<sub>2</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>]<sub>n</sub>, presumably *via* attack of a co-ordinatively unsaturated intermediate on unchanged [Ru<sub>2</sub>Cl<sub>4</sub>(PEt<sub>2</sub>Ph)<sub>5</sub>].

Finally, reduction of the mixed valence complex [Ru<sup>II,III</sup>Cl<sub>5</sub>(PEt<sub>2</sub>Ph)<sub>4</sub>] with Na[BH<sub>4</sub>] in the presence of C<sub>2</sub>H<sub>4</sub> or PhC≡CH (L') leads to the unusual bis(alkene) and bis(alkyne) complexes [(PEt<sub>2</sub>Ph)<sub>3</sub>ClRu(μ-Cl)<sub>2</sub>RuL'Cl(PEt<sub>2</sub>Ph)]. The asymmetric ligation of these complexes is demonstrated by their <sup>1</sup>H and <sup>31</sup>P n.m.r. spectra.

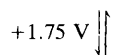
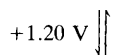
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‡ The complexes have been fully characterised by elemental analyses, and i.r. and n.m.r. (<sup>1</sup>H, <sup>31</sup>P-<sup>1</sup>H), and <sup>13</sup>C-<sup>1</sup>H} spectroscopy.

§ E<sub>1</sub> V measured by cyclic voltammetry (scan rate, 0.1 V/s) at 293 K in Bu<sub>4</sub>NBF<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub> (0.5 M) vs. a Ag/AgI/CH<sub>2</sub>Cl<sub>2</sub> reference electrode. E<sub>1</sub> for ferrocene-ferrocinium is 0.60 V in this cell.



### Scheme 1



### Scheme 2

We thank Johnson Matthey plc for loans of 'RuCl<sub>3</sub> · xH<sub>2</sub>O', 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.

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