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New Dimeric Ruthenium(II) Carbonyl Complexes containing a Bridging 2,2′-Bipyrimidine Ligand

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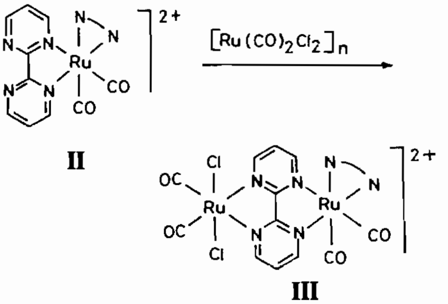
Previously [1] we have described the synthetic utility of $Ru(CO)_2(O_3SCF_3)_2L$ (**I**) complexes (L = 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy)) containing labile trifluoromethanesulfonate ligands. These complexes readily form $[Ru(CO)_2L_2]^{2+}$ complexes which in turn decarbonylate to yield $[RuL_3]^{2+}$ compounds [2]. In this communcation the reaction of **I** with the bridging bidentate ligand 2,2′-bipyrimidine (bpyrm) is shown to yield $[Ru(CO)_2(bpyrm)L]^{2+}$ complexes, which on reaction with $[Ru(CO)_2Cl_2]_n$ form the novel dimeric species $[Ru(CO)_2Cl_2(bpyrm)Ru(CO)_2L](PF_6)_2$. Ruthenium complexes containing bpyrm and related ligands are potential electron transfer agents and consequently have a variety of possible applications including solar energy conversion [3–5].

A mixture of **I** (L = phen or bpy) (0.60 mmol) and bpyrm (0.65 mmol) in absolute ethanol (30 ml) was boiled in air for *ca.* 15 min during which time a pale yellow precipitate formed. Recrystallization of the solid from acetone/ethanol and subsequently acetone/ether gave $[Ru(CO)_2(bpyrm)L](O_3SCF_3)_2$ (**II**) as white powders in 70% yield (reaction (1)).

$$Ru(CO)_2(O_3SCF_3)_2L + bpyrm \longrightarrow [Ru(CO)_2(bpyrm)L](O_3SCF_3)_2 \qquad (1)$$

The presence of two strong bands in the ν(CO) stretching region, 2200–2000 cm^{-1}, indicates *cis*-CO groups and consequently structure **II** for these complexes. The ^1H NMR spectra and elemental analyses (C, H, N) support the above formulation for **II**. The low solubility of **II** in the reaction solvent presumably precluded the formation of the dimeric species $\{[Ru(CO)_2L]_2bpyrm\}^{4+}$ during reaction (1).

A solution of **II** (0.25 mmol) and $[Ru(CO)_2Cl_2]_n$ (0.28 mmol) in methanol (25 ml) was heated under reflux in an atmosphere of nitrogen for 30 min. After removal of solvent, the residue was dissolved in water (10 ml), filtered and added to excess aqueous KPF_6. The resultant precipitate was recrystallized twice from methanol/ether yielding $[Ru(CO)_2Cl_2(bpyrm)Ru(CO)_2L](PF_6)_2$ (**III**) as yellow powders in 60% yield (reaction (2)).



II

III

(2)

The infrared spectra of these diruthenium complexes show four strong bands in the 2200–2000 cm^{-1} region indicating two sets of *cis*-CO groups, and a single band at *ca.* 320 cm^{-1} implying *trans*-chlorine ligands. Based on this data structure **III** can be assigned for the complexes. In addition, both the elemental analyses (C, H, N) and ^1H NMR spectra, which indicate 14 distinguishable proton resonances for each complex, are consistent with this formulation.

The bipyridyl complex $[Ru(CO)_2Cl_2(bpyrm)Ru(CO)_2(bpy)](PF)_2$ was sufficiently volatile to enable measurement of the Fast Atom Bombardment mass spectrum. Ions with *m/e* values at 844, 816, 699 and 617 corresponding to $[M-PF_6]^+$, $[M-PF_6-CO]^+$, $[M-2PF_6]^+$ and $[M-2PF_6-3CO]^+$ fragments respectively, were observed in the mass spectrum.

The reaction of $[Ru(CO)_2(bpyrm)L]^{2+}$ complexes with other transition metals compounds is presently under investigation.

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