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Reactions of Ruthenium(II) Carbonyl Complexes

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Although originally believed to have low lability [1], substitution reactions of $Ru(CO)_2X_2$(bidentate) complexes (e.g. X = Cl, Br; bidentate = 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy)) have been recently reported [2–4]. For instance, these complexes readily monodecarbonylate with trimethylamine-*N*-oxide (Me_3NO) in pyridine [2]. This reaction has now been studied with a variety of $[Ru(CO)_2X_2(bidentate)]^{n+}$ complexes (e.g. X = Cl, $MeCO_2$, $n = 0$; X = MeCN, $n = 2$] in pyridine (py) and acetonitrile (MeCN), and the reactivity of the products, $Ru(CO)X_2L$(bidentate) (X = Cl, $MeCO_2$; L = py, MeCN), is also reported.

In typical reactions the complexes $Ru(CO)_2X_2$(bidentate) (X = Cl, $MeCO_2$) were stirred with 3 mol equivalents of Me_3NO at room temperature for 2 h in MeCN or py. Evaporation to dryness and recrystallization of the residue obtained the pure $Ru(CO)X_2L$(bidentate) complexes (X = Cl, $MeCO_2$; L = MeCN, py), A single ν(Ru–Cl) infrared absorption for the dichloro complexes, or a single methyl ^1H NMR resonance for the bis(acetato) complexes indicates structure A for these compounds.

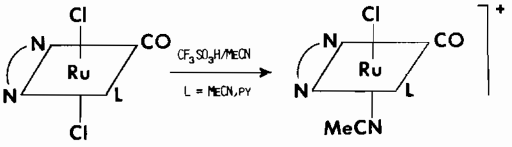
A similar reaction between $[Ru(CO)_2(MeCN)_2(bidentate)](PF_6)_2$ and Me_3NO in MeCN gave $[Ru(MeCN)_4(bidentate)](PF_6)_2$ (reaction (1)).

$$[Ru(CO)_2(MeCN)_2(bidentate)]^{2+} + 2Me_3NO + 2MeCN \longrightarrow [Ru(MeCN)_4(bidentate)]^{2+} + 2Me_3N + 2CO_2 \qquad (1)$$

Removal of both CO groups under these mild reaction conditions can be attributed to the weak Ru–CO bond as indicated by the high ν(CO) stretching frequencies at *ca.* 2100 and 2050 cm^{-1} for $[Ru(CO)_2(MeCN)_2(bidentate)]^{2+}$ complexes [5]. By contrast, $Ru(CO)_2Cl_2$(bidentate) complexes (with ν(CO) at *ca.* 2060 and 1990 cm^{-1} [5]) undergo complete decarbonylation with Me_3NO in 2-methoxyethanol at reflux temperature [3].

In pyridine, $[Ru(CO)_2(MeCN)_2(bidentate)]^{2+}$ complexes only monodecarbonylate with Me_3NO to give $[Ru(CO)py(MeCN)_2(bidentate)]^{2+}$. Failure to remove the second CO in pyridine can be related to the low ν(CO) value for $[Ru(CO)py(MeCN)_2(bidentate)]^{2+}$ (*ca.* 1990 cm^{-1}). By contrast, $[Ru(CO)(MeCN)_3(bidentate)]^{2+}$ (prepared below), which has a higher ν(CO) of *ca.* 2040 cm^{-1} and is presumably initially formed during reaction (1), readily decarbonylates with Me_3NO in py or MeCN to form $[Ru(L)(MeCN)_3(bidentate)]^{2+}$ (L = py, MeCN). Generally, Me_3NO induced decarbonylations are restricted to complexes with $\nu(CO) > 2000$ cm^{-1} [6].

The complexes $[Ru(CO)Cl(MeCN)L(bidentate)](PF_6)$ (L = py, MeCN) were prepared from the reaction of the corresponding $Ru(CO)Cl_2L$(bidentate) complex with trifluoromethanesulfonic acid (CF_3SO_3H) in boiling MeCN for 0.25 h. Evaporation to dryness, followed by addition of ethanol/ether gave the trifluoromethanesulfonate salts which, after treatment with aqueous KPF_6, were isolated as the hexafluorophosphates. The stereochemistry of the products (structure **B**, reaction (2)) was established from ^1H NMR data (below).

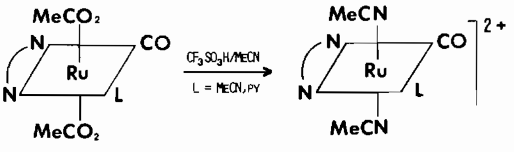


A **B**

(2)

A similar reaction between $Ru(CO)_2Cl_2$(bidentate) and CF_3SO_3H/MeCN resulted in no reaction. Presumably the additional CO ligand with its strong π-acceptor properties enhances the Ru–Cl bond strength, making the dicarbonyl complexes less labile.

Both anionic ligands of $Ru(CO)(MeCO_2)_2L$(bidentate) (L = py, MeCN) were displaced in CF_3SO_3H/MeCN forming the dicationic $[Ru(CO)(MeCN)_2L(bidentate)](PF_6)_2$ complexes (reaction (3))



A **C**

(3)

^1H NMR data indicates structure **C** for $[Ru(CO)(MeCN)_2L(bidentate)[(PF_6)_2$ complexes since the two pyridine rings of the bidentate ligands are inequivalent. Structure **B** is tentatively assigned for $[Ru(CO)Cl(MeCN)L(bidentate)](PF_6)$ complexes based on similar aromatic resonances, and the observation of two inequivalent MeCN groups (for L = MeCN).

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Some acetonitrile displacement reactions have also been investigated. For instance, in boiling 2-ethoxyethanol, $[Ru(MeCN)_4(bidentate)]^{2+}$ reacts with bpy or phen forming the corresponding $[Ru(bidentate)_3]^{2+}$ complexes. Under similar conditions $[Ru(CO)(MeCN)_3(bidentate)]^{2+}$ complexes react with 2,2'-6',2"-terpyridyl (tpy) yielding $[Ru(CO)(tpy)(bidentate)]^{2+}$ complexes.

All new complexes were characterized by elemental analysis (C, H, N or Cl), infrared and ^{1}H NMR spectroscopy. The previously reported complexes $[Ru(MeCN)_4(bidentate)]^{2+}$ [7], and $[Ru(bidentate)_3]^{2+}$ [8, 9] were identified by their reported spectroscopic properties.

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