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New Decarbonylation Reactions of Carbonylruthenium(II) Complexes

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We have recently shown that the complexes $Ru(CO)_2X_2L_2$ (X = Cl, Br, or CF_3CO_2; L_2 = 1,10-phenanthroline (phen), 2,2′-bipyridyl(bpy), or *trans*-$(Ph_3P)_2$) undergo selective monodecarbonylation reactions with trimethylamine oxide in pyridine at room temperature to give $Ru(CO)pyX_2L_2$ complexes [1]. The remaining carbonyl group could not be removed even in boiling pyridine and this was related [1] to stronger ruthenium–carbon bonding in the monocarbonyls (ν(CO), *ca.* 1940 cm^{-1}) than in the reactant dicarbonyls (ν(CO), 2100–2000 cm^{-1} [2–4]) and to the observation that trimethylamine oxide induced decarbonylations are generally restricted to carbonyls with $\nu(CO) > 2000$ cm^{-1} [5]. We now report that both carbonyl groups of $Ru(CO)_2Cl_2L_2$ complexes can be removed on reaction with bidentate ligands and trimethylamine oxide in boiling 2-methoxyethanol even though the reaction proceeds through an intermediate monocarbonyl with $\nu(CO) < 2000$ cm^{-1}. This method was also used for decarbonylation of $Ru(CO)pyCl_2L_2$, $Ru(CO)_2Cl_2(py)_2$, and $Ru(CO)_2L_2L_2'^{2+}$ (L_2, L_2' = phen or bpy) complexes.

In typical reactions, suspensions of $Ru(CO)_2Cl_2L_2$ (L_2 = phen or bpy) complexes in 2-methoxyethanol were heated under reflux with two mol equivalents of a bidentate ligand (phen, bpy or 3,4,7,8-tetramethyl-1,10-phenanthroline (phen′)) and three mol equivalents of trimethylamine oxide for 2 h in a nitrogen atmosphere. On cooling, aqueous ammonium or potassium hexafluorophosphate was added. Evaporation to dryness and addition of ethanol gave suspensions of $[Ru(L_2)_3](PF_6)_2$ or $[RuL_2(L_2')_2](PF_6)_2$ ($L_2' \neq L_2$ = phen, bpy, or phen′) complexes which were obtained in yields of 50–80% after recrystallization from ethanol or methanol, *e.g.*

$$Ru(CO)_2Cl_2L_2 + 2L_2' + 2Me_3NO \rightarrow$$
$$[RuL_2(L_2')_2]^{2+} + 2Cl^- + 2Me_3N + 2CO_2$$

No decarbonylation was achieved in the absence of trimethylamine oxide. A similar reaction using one mol equivalent of 2,2′-6′,2″-terpyridyl(tpy) gave the complex $[RuCl(bpy)(tpy)]PF_6$. The complexes $[Ru(L_2)_3](PF_6)_2$ were identified by U.V./visible [6] and ^1H n.m.r. [7, 8] spectroscopy, whilst $[RuL_2(L_2')_2](PF_6)_2$ complexes and $[RuCl(bpy)(tpy)]PF_6$ were identified by microanalysis, ^1H n.m.r. spectra, and, in the last case, by ν(Ru–Cl) absorption at 367 cm^{-1}. In addition, the spectra of $[Ruphen(bpy)_2](PF_6)_2$ and $[Rubpy(phen)_2(PF_6)_2$ were identical with those of samples obtained by the reported preparation [6], and the U.V./visible spectrum of the terpyridyl complex was in agreement with that of the corresponding perchlorate [9].

To provide insight into the decarbonylation path, the reaction of $Ru(CO)_2Cl_2bpy$ with one mol equivalent of 2,2′-bipyridyl and 2.5 mol equivalents of trimethylamine oxide in 2-methoxyethanol under nitrogen at room temperature was followed by infrared spectroscopy, which indicated slow formation of a monocarbonyl species with ν(CO) = 1945 cm^{-1}. This complex could not be isolated in a pure state, but presumably was $[Ru(CO)(bpy)_2(MeOCH_2CH_2OH)]Cl_2$ or $[Ru(CO)Cl(bpy)_2]Cl$; (ν(CO) of $[Ru(CO)Cl(bpy)_2]ClO_4$ = 1963 cm^{-1} (Nujol) [10]).

The successful complete decarbonylation of $Ru(CO)_2Cl_2L_2$ complexes despite involvement of an intermediate with $\nu(CO) < 2000$ cm^{-1} led to examination of analogous reactions of $Ru(CO)pyCl_2L_2$ (L_2 = phen or bpy) complexes, which have ν(CO) = 1942–1938 cm^{-1} [1]. Treatment with bidentate ligands (phen, bpy) and trimethylamine oxide in boiling 2-methoxyethanol gave $Ru(L_2)_3^{2+}$, $Ruphen(bpy)_2^{2+}$, and $Rubpy(phen)_2^{2+}$, which were isolated as hexafluorophosphates in 50–70% yield, *e.g.*

$$Ru(CO)pyCl_2phen + 2bpy + Me_3NO \rightarrow$$
$$Ruphen(bpy)_2^{2+} + 2\,Cl^- + py + CO_2 + MeN_3$$

Similarly, decarbonylation of $Ru(CO)_2Cl_2(py)_2$ and $Ru(CO)_2(L_2)_2^{2+}$ (L_2 = phen or bpy) has been achieved giving $Ru(L_2)_3^{2+}$, $Ruphen(bpy)_2^{2+}$, or $Rubpy(phen)_2^{2+}$, *e.g.*

$$Ru(CO)_2(phen)_2^{2+} + bpy + 2Me_3NO \xrightarrow{MeOCH_2CH_2OH}$$
$$Rubpy(phen)_2^{2+} + 2CO_2 + 2Me_3N$$

Other workers have recently reported photochemical decarbonylation of $Ru(CO)_2(bpy)_2^{2+}$ giving $Ru(bpy)_2L_2^{2+}$ (L = MeOH, H_2O, or MeCN) complexes [11]. Decarbonylation has also been used to give ruthenium(II) complexes with three different bidentate ligands. Thus treatment of $[Ru(CO)_2bpy(phen)](PF_6)_2$ with di(2-pyridylamine)(dpa) and trimethylamine oxide in boling 2-methoxyethanol yielded

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[Rubpy(phen)dpa]$(PF_6)_2$, which was obtained analytically pure in 70% yield on recrystallization from ethanol. Examination by h.p.l.c. indicated that only a single complex was present, and X-ray crystallography has confirmed the presence of the three bidentate ligands [12]. The complex [Rubpy(phen)bqy]$(PF_6)_2$ (bqy = 2,2′-biquinolyl) was also obtained by this method.

The present study has established that trimethylamine oxide induced decarbonylations can be achieved for metal carbonyls with $\nu(CO) < 2000$ cm^{-1}. Furthermore, decarbonylation reactions of $Ru(CO)_2Cl_2L_2$ and $Ru(CO)_2L_2(L'_2)^{2+}$ provide a viable alternative to reported syntheses [*e.g.* 6, 13, 14] of ruthenium(II) complexes with two or three different uncharged bidentate ligands.

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