

New Decarbonylation Reactions of Carbonylruthenium(II) Complexes

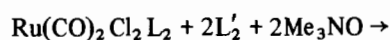
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We have recently shown that the complexes $\text{Ru}(\text{CO})_2\text{X}_2\text{L}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or } \text{CF}_3\text{CO}_2$; $\text{L}_2 = 1,10$ -phenanthroline (phen), 2,2'-bipyridyl(bpy), or *trans*-(Ph_3P)₂) undergo selective monodecarbonylation reactions with trimethylamine oxide in pyridine at room temperature to give $\text{Ru}(\text{CO})\text{pyX}_2\text{L}_2$ 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 ($\nu(\text{CO})$, ca. 1940 cm^{-1}) than in the reactant dicarbonyls ($\nu(\text{CO})$, 2100 – 2000 cm^{-1} [2–4]) and to the observation that trimethylamine oxide induced decarbonylations are generally restricted to carbonyls with $\nu(\text{CO}) > 2000\text{ cm}^{-1}$ [5]. We now report that both carbonyl groups of $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ 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 $\nu(\text{CO}) < 2000\text{ cm}^{-1}$. This method was also used for decarbonylation of $\text{Ru}(\text{CO})\text{pyCl}_2\text{L}_2$, $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{py})_2$, and $\text{Ru}(\text{CO})_2\text{L}_2\text{L}'_2$ ($\text{L}_2, \text{L}'_2 = \text{phen or bpy}$) complexes.

In typical reactions, suspensions of $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ ($\text{L}_2 = \text{phen or bpy}$) 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 $[\text{Ru}(\text{L}_2)_3](\text{PF}_6)_2$ or $[\text{RuL}_2(\text{L}'_2)_2](\text{PF}_6)_2$ ($\text{L}_2 \neq \text{L}'_2 = \text{phen, bpy, or phen}'$) complexes which were obtained in yields of 50–80% after recrystallization from ethanol or methanol, *e.g.*

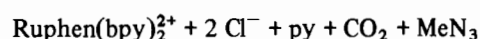
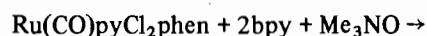


No decarbonylation was achieved in the absence of trimethylamine oxide. A similar reaction using one

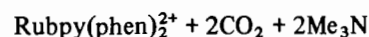
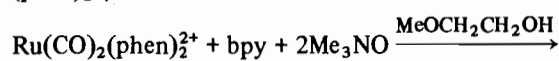
mol equivalent of 2,2'-6',2''-terpyridyl(tpy) gave the complex $[\text{RuCl}(\text{bpy})(\text{tpy})]\text{PF}_6$. The complexes $[\text{Ru}(\text{L}_2)_3](\text{PF}_6)_2$ were identified by U.V./visible [6] and ^1H n.m.r. [7, 8] spectroscopy, whilst $[\text{RuL}_2(\text{L}'_2)_2](\text{PF}_6)_2$ complexes and $[\text{RuCl}(\text{bpy})(\text{tpy})]\text{PF}_6$ were identified by microanalysis, ^1H n.m.r. spectra, and, in the last case, by $\nu(\text{Ru}-\text{Cl})$ absorption at 367 cm^{-1} . In addition, the spectra of $[\text{Ruphen}(\text{bpy})_2](\text{PF}_6)_2$ and $[\text{Rubpy}(\text{phen})_2](\text{PF}_6)_2$ 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 $\text{Ru}(\text{CO})_2\text{Cl}_2\text{bpy}$ 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 $\nu(\text{CO}) = 1945\text{ cm}^{-1}$. This complex could not be isolated in a pure state, but presumably was $[\text{Ru}(\text{CO})(\text{bpy})_2(\text{MeOCH}_2\text{CH}_2\text{OH})]\text{Cl}_2$ or $[\text{Ru}(\text{CO})\text{Cl}(\text{bpy})_2]\text{Cl}$; ($\nu(\text{CO})$ of $[\text{Ru}(\text{CO})\text{Cl}(\text{bpy})_2]\text{ClO}_4 = 1963\text{ cm}^{-1}$ (Nujol) [10]).

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



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



Other workers have recently reported photochemical decarbonylation of $\text{Ru}(\text{CO})_2(\text{bpy})_2^{2+}$ giving $\text{Ru}(\text{bpy})_2\text{L}_2^{2+}$ ($\text{L} = \text{MeOH}, \text{H}_2\text{O}, \text{or } \text{MeCN}$) complexes [11]. Decarbonylation has also been used to give ruthenium(II) complexes with three different bidentate ligands. Thus treatment of $[\text{Ru}(\text{CO})_2\text{bpy}(\text{phen})](\text{PF}_6)_2$ with di(2-pyridylamine)(dpa) and trimethylamine oxide in boiling 2-methoxyethanol yielded

[Rubpy(phen)dpa](PF₆)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](PF₆)₂ (bqy = 2,2'-biquinoly) was also obtained by this method.

The present study has established that trimethylamine oxide induced decarbonylations can be achieved for metal carbonyls with $\nu(\text{CO}) < 2000 \text{ cm}^{-1}$. Furthermore, decarbonylation reactions of Ru(CO)₂Cl₂L₂ and Ru(CO)₂L₂(L')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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