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Decarboxylation of 2,2′-Bipyridinyl-4,4′-dicarboxylic Acid Diethyl Ester during Microwave Synthesis of the Corresponding Trichelated Ruthenium Complex

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Microwave reaction of $RuCl_3$ with 2,2′-bipyridinyl-4,4′-dicarboxylic acid diethyl ester (debpy) in ethylene glycol generated $Ru(bpy)_3^{2+}$ instead of the expected $Ru(debpy)_3^{2+}$. Gas chromatography–mass spectrometry analysis of the headspace revealed CO_2, and $Ru(bpy)_3^{2+}$ was recovered from the filtrate. Further experiments suggest that $RuCl_3$ decarboxylates debpy during microwave synthesis.

The use of microwave reactors is a rapidly expanding area of synthetic chemistry in both organic and inorganic syntheses. The technique offers several advantages over traditional synthesis especially in the synthesis of ruthenium and osmium complexes, which typically require many hours of refluxing in high-boiling solvents to affect a reaction. Similar reactions, when performed in a microwave reactor, can occur in a matter of minutes. Matsumura-Inoue and Tanabe reported efficient and rapid synthesis of ruthenium polypyridine complexes using microwave irradiation.[1] This method was used to synthesize a variety of tris-bidentate complexes as well as bis-tridentate complexes. For example, $Ru(bpy)_3^{2+}$ was prepared by microwave heating of a ruthenium chloride solution with 3 equiv of 2,2′-bipyridine in ethylene glycol for 15 min in 95% yield, which is slightly higher than the literature value of 86%.[1] A number of related examples have recently appeared in the literature.[1−6]

Over the past decade, numerous ruthenium bipyridine and phenanthroline complexes have been created for sensing applications or for applications where enhanced photophysical properties or electrochemical properties are required. Many of the complexes rely on the creation of an ester or amide linkage to the carboxylic acid derivative of 2,2′-bipyridine or 1,10-phenanthroline.[7−18] The ruthenium complex prepared from 2,2′-bipyridinyl-4,4′-dicarboxylic acid diethyl ester (debpy), for example, has a significantly enhanced excited-state lifetime of 2000 ns measured in dichloromethane when compared to the lifetime of the parent complex, $Ru(bpy)_3^{2+}$, of 600 ns.[7]

The commonly reported synthesis for $Ru(debpy)_3^{2+}$ is rather arduous and produces low yields. Specifically, $[Ru(DMSO)_4Cl_2]$ is refluxed with ~4 equiv of debpy in ethanol for 1 week with a reported 15% yield.[19] We have tried other synthetic schemes to prepare this complex, but these also suffered from poor yields and complex mixtures of ruthenium compounds. Specifically, reaction of debpy with $Ru(COD)Cl_2$[20] or $[Ru(CO)_2Cl_2]_n$[21,22] in 2-methoxyethanol produced mixtures and only small amounts of the desired product.

Attempted microwave synthesis of $Ru(debpy)_3^{2+}$ in a CEM Explorer (Matthews, NC) reactor produced an unexpected

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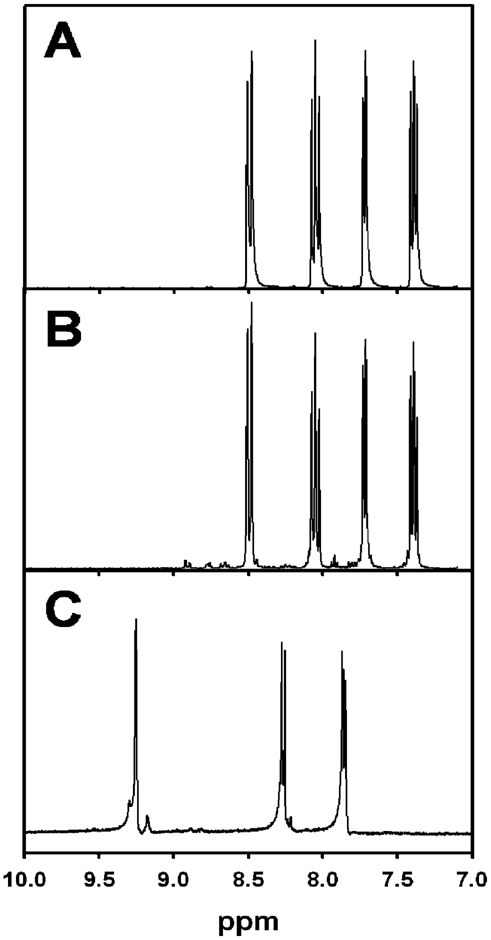

Figure 1. ^{1}H NMR spectra of (A) $[Ru(bpy)_3][PF_6]_2$, (B) reaction product, and (C) $[Ru(debpy)_3][PF_6]_2$ all in CD_3CN.

product. A mixture of ruthenium trichloride trihydrate (13.1 mg, 0.0632 mmol) and ethyl ester (57.0 mg, 0.190 mmol) in ∼5 mL of ethylene glycol was reacted for 5 min. During the reaction, the pressure in the sealed vessel rose to >300 psi as the temperature was increased to 225 °C, at which point the instrument shut down because the pressure limit had been exceeded. The solution was filtered to remove a small amount of black solid, and then 2 mL of saturated aqueous ammonium hexafluorophosphate was added to the filtrate to recover an orange solid (60.5% yield). ^{1}H NMR spectra of pure $[Ru(bpy)_3][PF_6]_2$, as prepared by Nocera's method,[20] product from the microwave synthesis, and $[Ru(debpy)_3][PF_6]_2$, prepared as described by Murray et al.,[19] are shown in Figure 1A−C, respectively. A comparison of the spectra in Figure 1 clearly indicates that the product obtained from the microwave reaction was $Ru(bpy)_3^{2+}$. UV−vis spectroscopy and electrospray mass spectrometry (MS), when compared to high-quality samples of $Ru(bpy)_3^{2+}$ and the corresponding ethyl ester, also confirmed the product to be $Ru(bpy)_3^{2+}$. The evidence clearly indicates that during the synthesis the ethyl ester undergoes a decarboxylation, resulting in the loss of the entire ester side chain. The increase in pressure, which is not typically observed, is also consistent with the formation of volatile products. Analysis of the headspace gases by gas chromatography (GC) and GC−MS revealed the presence of CO_2 and ethanol.

The control reaction of debpy in ethylene glycol in the absence of ruthenium trichloride was also performed. Under these conditions, GC−MS analysis of the solution indicated that neither debpy nor ethylene glycol undergoes reaction. Furthermore, there is no increase in the pressure in the reactor during the reaction beyond what is typically observed from heating of the solvent. In another control experiment, $Ru(debpy)_3(PF_6)_2$, synthesized by another method,[19] was exposed to microwaves under the same reaction conditions and found to be unreactive.

To verify that properties specific to ruthenium chloride were required for the reaction, a few other metal chlorides were examined. ^{1}H NMR of the product isolated from the reaction of iron(III) chloride, under identical conditions, indicated that the complexed debpy remained intact. The reaction was repeated using osmium(III) chloride trihydrate, and again there was no evidence of decarboxylation. Thus, the trivial mechanism whereby ruthenium trichloride behaves as a general Lewis acid can be eliminated.

To obtain further information on the role of ruthenium trichloride, reactions were performed for 30 min with $Ru(bpy)_2Cl_2$. In this case, a series of trischelated complexes was obtained, as indicated by ^{1}H NMR and electrospray MS. Specifically, no significant amounts of ethyl ester products were obtained. Instead, the corresponding ethylene glycol esters were present along with nearly equal amounts of $Ru(bpy)_3^{2+}$. In addition, complexes containing carboxylic acids were also present in similar amounts, as were the various permutations of acids and esters.[23] These results, and the detection of CO_2 and ethanol, strongly suggest that the reaction involves successive loss of alcohol, with intermediate transesterification with ethylene glycol, and finally decarboxylation of the acid form. The reaction was also performed in ethylene glycol-*d*$_2$. ^{1}H and ^{13}C NMR revealed that the product, $Ru(bpy)_3^{2+}$, was selectively deuterated at the 4 and 4′ positions. These results are also consistent with the decarboxylation of a carboxylic acid form of the coordinated ligand.

The fact that $Ru(bpy)_3^{2+}$ is formed exclusively in the reaction with $RuCl_3$ and $Ru(debpy)_3^{2+}$ is inert under the same reaction conditions presented some mechanistic difficulties. However, the reaction of $Ru(bpy)Cl_4$[24] with excess dimethylbipyridine (dmbpy) under the same reaction conditions gave $Ru(dmbpy)_3^{2+}$ as well as $Ru(dmbpy)_2(bpy)^{2+}$. This observation indicates that there is exchange of the ligands particularly in the early stages of the reaction. Thus, there appears to be a stepwise reduction in the reactivity induced by ruthenium as bipyridine ligands are added.

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(23) Electrospray MS of the products gave the following mass peaks and relative intensities: 24% and 285, $Ru(bpy)_3^{2+}$; 2% and 307 $Ru(bpy)_2(bpyCOOH)^{2+}$; 6% and 329, $(Ru(bpy)_2(bpy(COOH)_2)^{2+}$; 16% and 351, $Ru(bpy)_2(bpyCOOHCOOCH_2CH_2OH)^{2+}$; 40% and 373, $Ru(bpy)_2(bpy(COOCH_2CH_2OH)_2)^{2+}$.

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In summary, the debpy ligand undergoes a quantitative decarboxylation reaction under reaction conditions that are typically used in the microwave preparation of ruthenium complexes. The reaction involves the metal and results in the formation of unsubstituted bipyridyl complexes. Thus, microwave synthesis of ruthenium complexes using derivatives of 4,4′-dicarboxybipyridine should be approached with caution. Although the reaction is not productive in this specific example, the ability to decarboxylate esters may have applications in organic synthesis where such reactions are difficult to perform. Further experiments with other esters and amides are planned.

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