# Synthesis, Structure, and Physicochemical Characterizations of a New Cationic Ruthenium(I)−Ruthenium(I) Tetracarbonyl Bipyridine Dimer Precursor for the Electrochemical Synthesis of an Organometallic Ruthenium(0) Polymer

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The synthesis and structure of the Ru(I) dimer $[Ru(bpy)(CO)_2(CH_3CN)]_2(PF_6)_2$ (**1**; bpy = 2,2′-bipyridine) are described. The electrochemical properties of this complex have been examined. The irreversible two-electron reduction of **1** gives $[Ru(bpy)(CO)_2]_n$ polymer film on the electrode surface. The physicochemical properties of this metal−metal bond based polymer equal those of the polymers formed from the reduction of *trans*($CH_3CN$)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$ or *trans*(Cl)-$[Ru(bpy)(CO)_2Cl_2]$ monomer complexes previously described. The Ru(0) polymer can be oxidized in a stepwise manner, leading first to the Ru(I) dimer **1** and then to the Ru(II) monomer **2**: *cis*($CH_3CN$)-$[Ru(bpy)(CO)_2(CH_3CN)_2]^{2+}$. On the other hand, the dimer **1** exhibits an irreversible two-electron oxidation, leading to the same Ru(II) monomer (**2**). Carbon electrodes modified with the polymer resulting from **1** catalyze the electrochemical reduction of $CO_2$ into CO with a 98% electrical yield at a low potential in hydro-organic or pure aqueous electrolytes.

## Introduction

The modification of electrode surfaces by organic conducting polymer films functionalized by metal complexes has received much interest. These polymer-coated electrodes have potential applications, particularly in electrocatalysis.[1] A relatively unexplored approach to the chemical alteration of the electrode surface is the direct electrochemical deposition of a true metal−metal-bonded organometallic polymer onto it. This has been achieved in the electropolymerization of a series of Ru(II) monomer complexes, such as $[Ru^{II}(L)(CO)_2X_2]$ (L = bidentate ligand such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) derivatives; X = ionic labile ligand), to a polymer of the general formula $[Ru(L)(CO)_2]_n$.[2] Polymerization is achieved by the overall addition of two electrons per mole of complex and is associated with the loss of both coordinated X monodentate leaving ligands (reaction 1).

$$n[Ru^{II}(L)(CO)_2X_2] + 2ne^- \rightarrow [Ru^0(L)(CO)_2]_n + 2nX^- \quad (1)$$

The resulting polymeric $[Ru^0(L)(CO)_2]_n$ species consists of extended $Ru^0-Ru^0$ bond chains formed via transient dimeric and tetrameric species.[3] This polymer catalyzes the electrochemical reduction of $CO_2$ into CO or formate ions in pure aqueous electrolyte[4] and is an active catalyst in the water-gas shift reaction (WGSR).[5] Furthermore, initial studies show it to be potentially photochemically active.[6]

The air-sensitive and insoluble polymeric nature of $[Ru(bpy)(CO)_2]_n$ precludes its full structural characterization. In an effort to gain further insight into the structure and mechanism of the formation of the

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(1) See for example: (a) Kaneko, M.; Wörhle, D. In *Advances in Polymer Sciences*; Springer-Verlag: Berlin, 1998; Vol. 84, p 141. (b) Abruña, H. D. *Coord. Chem. Rev.* **1988**, 86, 135. (c) Mertz, A. In *Electrochemistry IV*; Topics in Current Chemistry 152; Steckhan, E., Ed.; Springer-Verlag: Berlin, 1990; p 51. (d) Deronzier, A.; Moutet, J.-C. *Coord. Clem. Rev.* **1996**, *147*, 339. (e) Curran, D.; Grimshaw, J.; Perera, S. D. *Chem. Soc. Rev.* **1991**, *20*, 391.

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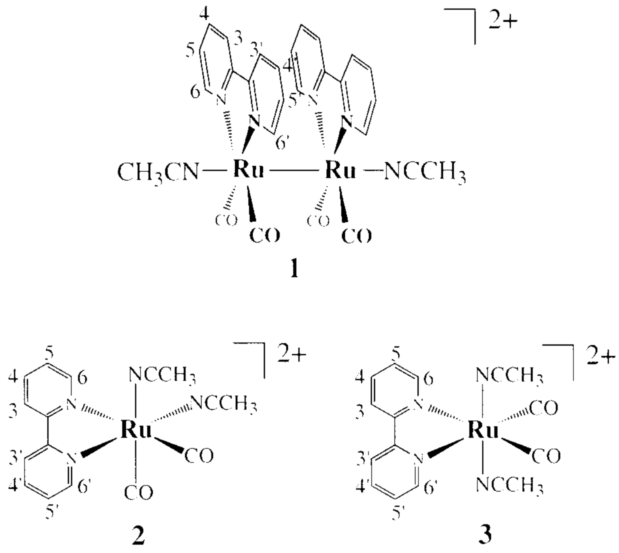

**Figure 1.** Structural formulas of Ru complexes **1**−**3**.

polymer, we undertook the study of related dimeric Ru(I) polypyridyl complexes. As the poor solubility of $[Ru(bpy)(CO)_2Cl]_2$[7] prevented its electrochemical study in common organic solvents, we turned our attention to the dicationic complex $[Ru(bpy)(CO)_2(CH_3CN)]_2(PF_6)_2$ (**1**), which represents both a model of the polymer in its simplest form and an intermediate in its formation and oxidation. The synthesis, crystal structure, and physicochemical properties of **1** are reported here. The electrocatalytic activity of the polymer obtained by a two-electron reduction of **1** toward $CO_2$ reduction was demonstrated.

## Results and Discussion

**1. $[Ru(bpy)(CO)_2(CH_3CN)]_2(PF_6)_2$ (1). Synthesis and Characterization.** Reaction of $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$[8] with 2.5 equiv of bpy at room temperature for 2 h in acetonitrile, followed by precipitation of the product by the addition of diethyl ether, led to the diruthenium(I) complex **1** (Figure 1) in 65% yield.

The FT-IR absorption spectrum of **1**, recorded in the solid state, displays three strong absorption bands associated with shoulders in the terminal CO region. This pattern in the CO stretching region closely resembles that of a large number of diruthenium(I) compounds of the type $[Ru_2(CO)_4L_6]^{2+}$.[7,9] In these complexes the equatorial coordinated carbonyl ligands occupy *cis* positions at each octahedral ruthenium center and adopt either a *cis*- or *trans*-staggered conformation relative to one another about the Ru−Ru bond.

The molecular structure of **1** together with its atomic numbering scheme is depicted in Figure 2a, while

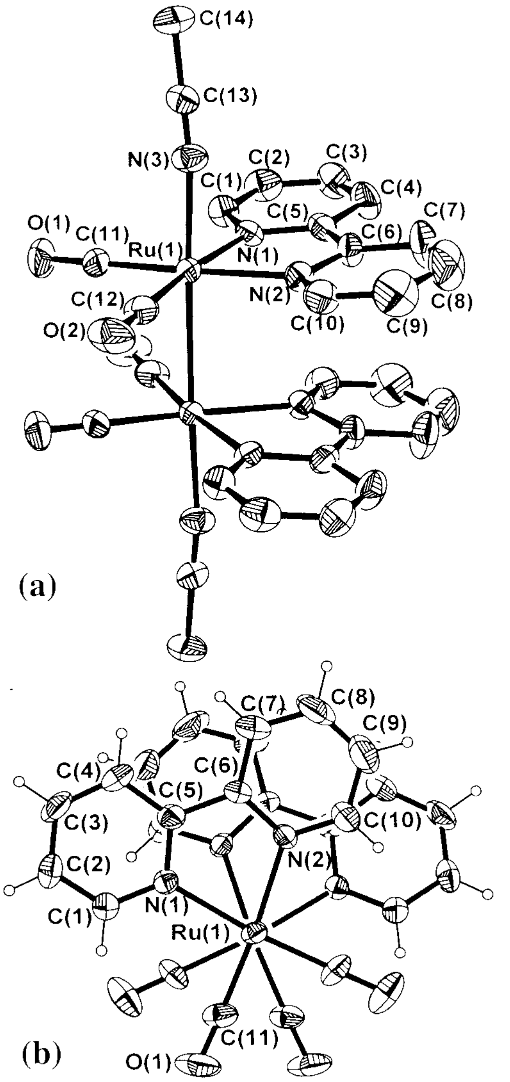

**Figure 2.** Molecular structure and atomic numbering scheme of the dication $\mathbf{1}\cdot 2CH_3CN$: (a) perspective showing the equatorial substituents; (b) view down the Ru−Ru bond axis. The atoms are represented by their thermal ellipsoids at the 25% probability level.

**Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $\mathbf{1\cdot 2CH_3CN}$[a]**

| | | | |
|---|---|---|---|
| Ru(1)−Ru(1)[b] | 2.829(2) | Ru(1)−N(2) | 2.110(8) |
| Ru(1)−C(11) | 1.860(13) | Ru(1)−N(3) | 2.145(9) |
| Ru(1)−C(12) | 1.858(11) | O(1)−C(11) | 1.132(14) |
| Ru(1)−N(1) | 2.107(8) | O(2)−C(12) | 1.149(12) |
| C(11)−Ru(1)−Ru(1)[b] | 87.2(4) | N(1)−Ru(1)−N(2) | 77.0(3) |
| C(12)−Ru(1)−Ru(1)[b] | 85.9(3) | N(1)−Ru(1)−N(3) | 85.7(3) |
| N(1)−Ru(1)−Ru(1)[b] | 92.1(2) | N(2)−Ru(1)−N(3) | 86.0(3) |
| N(2)−Ru(1)−Ru(1)[b] | 92.9(2) | C(12)−Ru(1)−C(11) | 87.3(6) |
| N(3)−Ru(1)−Ru(1)[b] | 177.7(2) | C(13)−N(3)−Ru(1) | 172.4(10) |
| C(11)−Ru(1)−N(1) | 98.2(4) | C(1)−N(1)−Ru(1) | 127.2(7) |
| C(12)−Ru(1)−N(1) | 174.0(4) | C(5)−N(1)−Ru(1) | 115.7(6) |
| C(11)−Ru(1)−N(2) | 175.2(4) | C(6)−N(2)−Ru(1) | 116.3(6) |
| C(12)−Ru(1)−N(2) | 97.5(5) | C(10)−N(2)−Ru(1) | 125.4(8) |
| C(11)−Ru(1)−N(3) | 93.7(5) | O(1)−C(11)−Ru(1) | 177.9(14) |
| C(12)−Ru(1)−N(3) | 96.2(4) | O(2)−C(12)−Ru(1) | 179.7(13) |

[a] The esd's of the least significant digits are given in parentheses. [b] Symmetry transformation used to generate equivalent atoms: $-x + 1, y, -z + {}^{3}/_{2}$.

selected bond distances and angles are given in Table 1.

The compound exists as discrete cations and hexafluorophosphate anions, together with acetonitrile sol-

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[7] Haukka, M.; Kiviaho, J.; Ahlgrén, M.; Pakkanen, T. A. *Organometallics* **1995**, *14*, 825.

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**Table 2. Comparison between the Proton Chemical Shifts of bpy in 1 and Related Ruthenium(II) Mononuclear Analogues**[a]

| | δ/ppm[b] | | | |
|---|---|---|---|---|
| | $H_{3,3'}$ | $H_{4,4'}$ | $H_{5,5'}$ | $H_{6,6'}$ |
| **1** | 8.00 | 8.11 | 7.49 | 8.42 |
| **3** | 8.39 (0.39) | 8.23 (0.12) | 7.70 (0.21) | 8.92 (0.50) |
| *trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$][c] | 8.47 (0.47) | 8.24 (0.13) | 7.74 (0.25) | 9.17 (0.75) |
| *cis*(CO)-[Ru(bpy)(CO)$_2$(C(O)OCH$_3$)Cl][c] | 8.40 (0.40) | 8.18 (0.07) | 7.64 (0.15) | 8.96 (0.54) |

[a] Recorded in CD$_3$CN at room temperature. [b] The change in chemical shift relative to that of **1** is given in parentheses. [c] Given in ref 5c.

vates, in the crystal, there being no unusual intermolecular contact distances between them. An approximately octahedral geometry is described about each ruthenium atom by a formal metal−metal bond, the donor atoms of the axial acetonitrile, and the equatorial carbonyl and bpy ligands. **1**·2CH$_3$CN possesses a crystallographically imposed center of symmetry midway between the Ru atoms. In comparison to the 2.829 Å Ru−Ru bond length observed for **1**·2CH$_3$CN, those measured for [Ru(bpy)(CO)$_2$Cl]$_2$ (2.860 Å)[7] and [Ru(dmbpy)(CO)$_2$Cl]$_2$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) (2.854 Å)[10] are noticeably longer. This is as a consequence of the effect on the metal−metal bond of the relatively high *trans* influence of the chloride ligand present in the latter examples.

Figure 2b illustrates the conformation of the cation of **1**·2CH$_3$CN, wherein the equatorial ligands adopt what can be described as a *syn*-staggered conformation[11] relative to one another about the Ru−Ru bond. This is in contrast to the molecular structure of the closely related complex [Ru(bpy)(CO)$_2$Cl]$_2$ reported by Pakkanen et al.[7] In this complex two rotamers are observed, with the equatorial bpy and CO ligands describing either "staggered" (with an *anti* arrangement of the bpy ligands) or "*anti*-eclipsed" positions about the Ru−Ru bond. In a diruthenium complex axially substituted by triphenylphosphine, [Ru(CO)$_2$(CH$_3$CN)$_2$(PPh$_3$)]$_2$(PF$_6$)$_2$, described by Klemperer et al.,[8] the equatorial acetonitrile and CO groups occupy *cis* positions at each ruthenium center and adopt a symmetrical *anti*-staggered conformation relative to one another about the Ru−Ru bond. That this strong precedent of an *anti* arrangement of the equatorial ligands is not preserved in the conformation of **1** is attributable to an intramolecular $\pi-\pi$ interaction between the two bpy groups. This stacking of the bpy rings, given the cylindrical symmetry of the M−M bond, may be the dominant electronic factor in the formation of this geometry. Indeed, such an interaction would favor the *syn* arrangement of the equatorial ligands, where the orientation of the bpy ligands relative to one another will allow a favorable overlap of their molecular orbitals. Clearly this argument does not appear to apply to the conformation of [Ru(bpy)(CO)$_2$Cl]$_2$. However, as Pakkanen et al.[7] have noted, this complex is barely soluble, in contrast to **1**, crystals of which can be grown by slow vapor diffusion of diethyl ether into an acetonitrile solution of the dimer **1**. This difference in the method of crystallization would permit the most energetically favorable conformation to be attained, viz. that of [Ru(bpy)(CO)$_2$(CH$_3$CN)]$_2$$^{2+}$. Significantly, the conformation assumed by [Ru(dmbpy)(CO)$_2$Cl]$_2$[10] is the same as that observed for **1**. The exclusive formation of a staggered rotamer in the former complex was attributed to steric and electronic interactions between the bulky methyl substituents of the bpy rings and the opposing carbonyl ligands.

Evidence for the conformation of **1** in solution is provided by $^1$H NMR spectral data. $^1$H NMR spectra of **1** recorded in CD$_2$Cl$_2$ or in CD$_3$CN at room temperature exhibit the same pattern of a single resonance for the acetonitrile ligand methyl protons. The bpy signals, displayed in the $^1$H spectra of **1**, show that bpy ligands chelate in a symmetrical environment with only four sets of aromatic proton resonances being observed.[2d] In addition the $^{13}$C NMR spectrum recorded at −80 °C in CD$_2$Cl$_2$ exhibits single resonances for the acetonitrile methyl and nitrile carbons at 3.05 and 119.26 ppm, respectively. The carbons of the carbonyl ligands are evident in this spectrum as a single resonance at 201.25 ppm.

A comparison between the chemical shifts of the bpy protons in **1** and three ruthenium(II) mononuclear analogues,[12] all of which pocess the same geometrical arrangement of bpy and carbonyl ligands about the metal center, is made in Table 2.

While protons $H_{4,4'}$ and $H_{5,5'}$ (Figure 1) do not exhibit a large difference in chemical shift across the series of complexes, $H_{3,3'}$ and $H_{6,6'}$ display noticably higher field resonances in the dinuclear complex. The crystal structure (Figure 2b) clearly shows that in a *syn*-staggered conformation these latter protons will be in closest proximity to the anisotropic magnetic field of the second bpy ligand. Protons $H_{5,5'}$ and, to the greatest extent, $H_{4,4'}$ will be located more to the periphery of the bpy shielding cone. The pattern observed with respect to the extent to which the individual proton resonances of **1** are shifted upfield relative to those of the mononuclear complexes is thus in keeping with a *syn*-staggered conformation of **1** in solution and with the oxidation state of the metal. One would anticipate that at lower temperatures rotation about the Ru−Ru bond would become more restricted and the anisotropic effect more pronounced. The chemical shifts of $H_{3,3'}$ and $H_{6,6'}$ in the spectrum of **1** recorded in CD$_2$Cl$_2$ at −80 °C thus display a slightly more marked upfield shift, with these resonances being observed at 7.91 and 8.27 ppm, respectively, in comparison to those in the spectrum recorded

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(10) Homanen, P.; Haukka, M.; Ahlgrén, M.; Pakkanen, T. A.; Baxter, P. N. W.; Benfield, R. E.; Connor, J. A. *J. Organomet. Chem.* **1998**, *552*, 205.

(11) The *syn*/*anti* notation is adopted to differentiate between the further two possible conformations of each staggered or eclipsed rotamer. *syn* describes the conformation in which equatorial ligands are on the same side of the molecule when it is viewed down the Ru−Ru axis.

(12) To our knowledge no NMR spectra of Ru(I) dinuclear anologues have been published yet, probably owing to the poor solubility of these compounds.

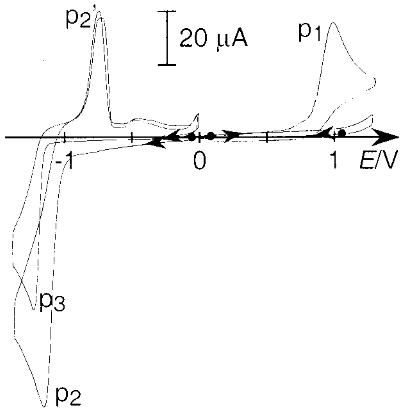

**Figure 3.** Cyclic voltammograms of 1.0 mM **1** in $CH_3CN$ + 0.1 M TBAP at a Pt electrode (diameter 5 mm; scan rate 100 mV $s^{-1}$) between 0 and 1.3 V and between 0 and −1.4 V, before ($p_1$ and $p_3$) and after ($p_2$ and $p_{2'}$) exhaustive oxidation at 1.1 V.

at room temperature, while those of $H_{5,5'}$ and $H_{4,4'}$ are effected to a lesser extent.

It should be noted that the complexation of the metal centers, by the bpy ligands during the synthesis of the dimer **1** in $CH_3CN$ starting from $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ precursor, can be easily followed by cyclic voltammetry and FT-IR, UV−vis, and $^1H$ NMR spectroscopy. The complexation (reaction 2) appears as fast, clean, and

$$[Ru^I(CO)_2(CH_3CN)_3]_2{}^{2+} + 2bpy \rightarrow [Ru^I(bpy)(CO)_2(CH_3CN)]_2{}^{2+} + 4CH_3CN \quad (2)$$

quantitative at room temperature. Thus, this in situ preparation provides the opportunity to quickly establish preliminary electrochemical and spectroscopic data for new Ru(I) binuclear complexes. The utilization of this procedure to generate and study $[Ru(L)(CO)_2(CH_3CN)]_2{}^{2+}$ binuclear complex, with a variety of α-diimine ligand (L), is currently under way.

On the other hand, as expected, **1** can be used as a precursor for the synthesis of $[Ru(bpy)(CO)_2Cl]_2$ dimer by the replacement of the two axial neutral $CH_3CN$ ligands in **1** by chloride anions. During this substitution, the initial ligand stereochemistry is preserved ($^1H$ NMR proof). A quantitative transformation into the dichloride dimer is achieved when the ratio of $Cl^-$ to dimer is 3:1 and after 3 h of stirring of the reagents in acetonitrile solution. However, when 1 molar equiv of a solution of chloride in $CH_3CN$ was added to a solution of **1** in $CH_3CN$, only one acetonitrile was displaced and the new monosubstituted $[Ru_2(bpy)_2(CO)_4(CH_3CN)Cl]^+$ dimer was obtained.

**2. Electrochemical Behavior of $[Ru(bpy)(CO)_2(CH_3CN)]_2{}^{2+}$ (1). 2.1. Oxidation.** On a platinum electrode, the cyclic voltammogram of a solution of 1.0 mM of **1** in $CH_3CN$ + 0.1 M TBAP (tetrabutylammonium perchlorate) reveals that the complex is irreversibly oxidized at $E_{p_1} = 0.98$ V[13] (Figure 3).

In fact, exhaustive oxidation conducted at 1.10 V requires the exchange of two electrons per mole of dimer. This reaction produces the Ru(II) monomer complex **2**, which results from the oxidatively induced breakage of the metal−metal bond and coordination of $CH_3CN$ with an approximatively 80% electrical yield (reaction 3).

$$[Ru^I(bpy)(CO)_2(CH_3CN)]_2{}^{2+} + 2CH_3CN \rightarrow 2[Ru^{II}(bpy)(CO)_2(CH_3CN)_2]^{2+} + 2e^- \quad (3)$$

The identity of this new complex **2** was determined by in situ physicochemical characterizations (cyclic voltammetry, FT-IR, UV−vis, $^1H$ NMR) and by the comparison of its physicochemical properties to those of similar monomers, such as the Ru(II) bpy dicarbonyl complexes previously described.[2] All characterizations of this bis(acetonitrile) Ru(II) complex are consistent with the unexpected *cis*(CO),*cis*($CH_3CN$) structural isomers schematically represented as for compound **2** in Figure 1. This indicates that a structural rearrangement occurs during associated Ru−Ru bond breaking and acetonitrile coordination.

To the best of our knowledge only one publication makes mention of this mononuclear *cis*($CH_3CN$) complex,[14] even when the *trans*($CH_3CN$) equivalent complex **3** was described and well-characterized.[2b,14] Unfortunately, our attempts to isolate this complex, either by extraction of the oxidation product of **1** from the electrolyte or through classical chemical synthesis, have failed. Therefore, we were not able to compare the properties of the electrochemically synthesized bis-$CH_3CN$ complex **2** with those of an original chemically prepared sample.

An absorption spectrum recorded after oxidation of **1** exhibits no absorption bands in the visible region. The FT-IR absorption spectrum exhibits two intense carbonyl absorption bands with frequencies similar to the C−O stretching frequencies recorded for the *trans*($CH_3CN$) isomer **3**. The breakage of the metal−metal bond of **1** and the concomitant oxidation of the ruthenium causes a simplification of the shape of the IR absorption spectrum and a shift of the $\nu$(CO) frequencies toward higher wavenumbers compared to those of the initial dimer **1**. This shift is attributed to a decrease of the electronic density on the metal and is in accordance with the shift observed previously between the $\nu$(CO) frequencies of the chloro dimer and monomer. No striking difference is observed for the FT-IR properties of isomers **2** and **3**, which is in agreement with what is observed for both $[Ru(bpy)(CO)_2Cl_2]$ isomers.[2d]

When the oxidation of **1** is carried out in a deuterated electrolyte ($CD_3CN$ + $LiClO_4$), an in situ $^1H$ NMR characterization of the oxidized dimer becomes possible. The aromatic part of the $^1H$ NMR spectrum of **2** is noticably different from that recorded for the starting binuclear **1** and the mononuclear *trans*($CH_3CN$) isomer **3** (Figure 4; Figure 1 shows the assigment of aromatic patterns for complexes **1**−**3**).

The resonances of the bpy ligand protons between 7.2 and 9.2 ppm change from four (**1** and **3**) to eight (**2**) well-resolved signals, each integrated for one proton. This pattern reflects a nonsymmetrical arrangement of ligands

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[13] All elecrode potentials are referenced to $Ag/AgNO_3$ 10 mM in $CH_3CN$ containing 0.1 M TBAP. They can be easily converted to other reference systems; see for instance: Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97.

[14] Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Aust. J. Chem.* **1982**, *35*, 2445.

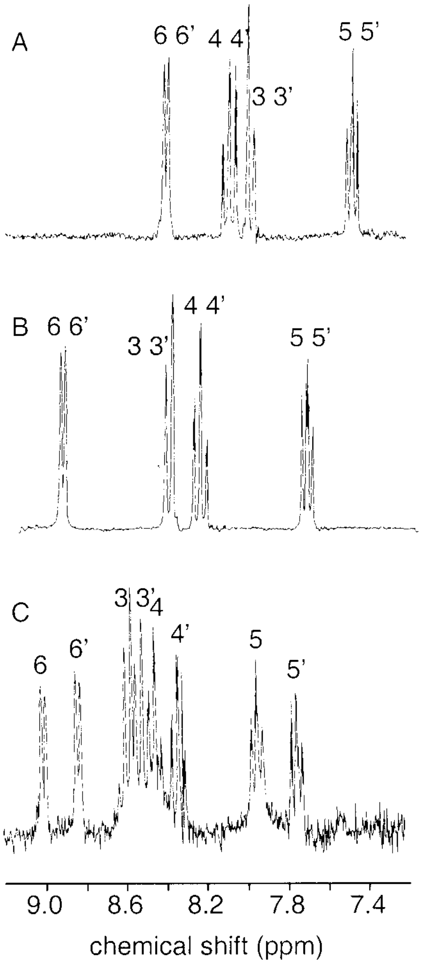

**Figure 4.** Aromatic area of $^{1}H$ NMR spectra in $CD_3CN$ of **1** (A), **3** (B), and **2** (C) in the presence of electrolyte.

about the Ru(II) center and is furthermore typical of asymmetry in the equatorial plane of the bpy ligand.[2d]

As we mentioned above, the synthesis of an original sample of **2** starting from *cis*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] and using a procedure similar to that published previously by Deacon et al.[14] or Klemperer et al.[8] was unsuccessful. However, during the process of these fruitless synthetic attempts it was possible to characterize the monosubstituted $CH_3CN$ complex [Ru(bpy)$(CO)_2(CH_3CN)Cl$]-$(PF_6)$ intermediate **4**, as well as a mixture of it with the expected compound **2** (details of the synthetic conditions and characterizations are given in the Experimental Section). The FT-IR, $^{1}H$ NMR, and electrochemical properties of **2** in the crude product agree very well with those of the complex resulting from the electrochemical oxidation of **1**.

One other indirect proof of the nature of **2** involved adding a small excess of $Cl^-$ anions (2.2 equiv per Ru(II)) to the electrolyte solution until the corresponding *cis*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] complex was obtained. The complete coordination of chloride was achieved after 15 h of stirring at room temperature (FT-IR, $\nu$(CO) 2067, 2001 $cm^{-1}$; $E_p$(Ru(II)/Ru(0)) = − 1.54 V, $E_{1/2}$(Ru(III)/Ru(II)) = 1.56 V) with a 90% yield. It should be noted that a monochloride complex is formed intermediately during this chemical reaction ($\nu$(CO) 2093 and 2035 $cm^{-1}$; $E_p$(Ru(II)/Ru(0)) = −1.30 V).

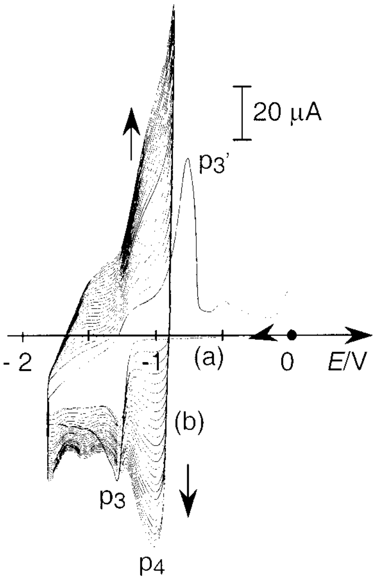

**Figure 5.** Cyclic voltammograms in $CH_3CN$ + 0.1 M TBAP of 1 mM **1** at a Pt electrode (diameter 5 mm; scan rate 100 mV $s^{-1}$): (a) 1st scan; (b) from the 2nd to the 26th successive scans between −0.9 and −1.8 V.

The electrochemical behavior of **2** (Figure 3) is essentially the same as that of the isomer *trans*$(CH_3CN)$-[Ru(bpy)$(CO)_2(CH_3CN)_2]^{2+}$.[2b] The cyclic voltammogram reveals that this Ru(II) monomer is not electroactive between 0 and 1.30 V. It is irreversibly reduced at the first reduction peak ($E_{p_2}$ = − 1.18 V; Ru(II)/Ru(0)). This redox system ($p_2$ and $p_{2'}$) exhibits the same shape as that obtained for **3**. The comparison of the height of the reduction peak ($p_2$; Figure 3) with that of the dimer **1** ($p_3$; Figure 3) is in agreement with a mononuclear structure. This irreversible system, corresponding to a Ru(II)/Ru(0) redox couple, is shifted positively (+0.04 V) compared with that of the *trans*$(CH_3CN)$ monomer complex **3**. This small change in $E_{pc}$ values is in agreement with that observed between the isomers of the corresponding dichloride complexes.[2d] This confirms that the reduction process is located on the bpy ligand and is not significantly influenced by the stereochemistry of the complex, as for all corresponding complexes containing two leaving ligands.

Formation of electroactive [Ru(bpy)$(CO)_2]_n$ polymer films was obtained by cycling the potential or by potentiostating the working electrode in the electroprepared solution of **2**. We have checked that the resulting polymer posesses exactly the same electroactivity and physicochemical properties as those obtained from other bpy dicarbonyl Ru(II) precursor complexes.

Thus, as for both [Ru(bpy)$(CO)_2Cl_2$] isomers,[2d] irrespective of the stereochemistry of the bis(acetonitrile) Ru(II) monomer complexes **2** and **3**, their two-electron reduction leads to the formation of the same organometallic polymer.

**2.2. Reduction.** In the negative potential area (Figure 5a) an irreversible reduction occurs at −1.24 V ($p_3$). The cyclic voltammogram exhibits a shape typical of an electroprecipitation−redissolution phenomenon ($p_3$ and $p_{3'}$) due to the polymer film formation in accordance with the overall reaction (4).

$$(n/2)[Ru^{I}(bpy)(CO)_2(CH_3CN)]_2^{2+} + ne^- \rightarrow [Ru^{0}(bpy)(CO)_2]_n + nCH_3CN \quad (4)$$

It should be noted that the potential of this cathodic peak is exactly the same as the one obtained for **3** and is shifted positively (+0.22 V) compared to that of the corresponding dichloride dimer recorded in DMSO + 0.1 M TBAP[3] in agreement with the electronic properties of acetonitrile ligands.

The electropolymerization can be accomplished by continuously cycling the potential or by applying a constant potential (−1.30 V). Both techniques caused a strongly adherent polymer film to deposit on the working electrode. Figure 5b shows the growth of the electroactive polymer film, as the potential is repeatedly scanned from −0.90 V to −1.80 V in a solution of **1**. Two clear systems appear at $E_{p_4} = -0.98$ V and $E_{1/2} = -1.51$ V and increase in size continuously. If, after a period of scanning, the resulting modified electrode is transferred to a clean electrolyte, both systems persist. The electrochemical stability of the film is excellent. By analogy with the mechanism of the polymerization process previously proposed and in part demonstrated for *trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$],[3] we suggest that the electropolymerization of **1** could proceed via propagation reactions which are initiated by the one-electron bpy ligand reduction and CH$_3$CN ligand decoordination.

The complete two-electron oxidation of the organometallic polymer can be achieved via either a direct two-electron oxidation or via two successive one-electron ruthenium-centered oxidations (reactions 5 and 6). Both

$$[\mathrm{Ru^0(bpy)(CO)_2}]_n + n\mathrm{CH_3CN} \rightarrow (n/2)[\mathrm{Ru^I(bpy)(CO)_2(CH_3CN)}]_2^{2+} + n\mathrm{e^-} \quad (5)$$

$$[\mathrm{Ru^I(bpy)(CO)_2(CH_3CN)}]_2^{2+} + 2\mathrm{CH_3CN} \rightarrow 2[\mathrm{Ru^{II}(bpy)(CO)_2(CH_3CN)_2}]^{2+} + 2\mathrm{e^-} \quad (6)$$

exhaustive oxidations induce the breakage of all Ru−Ru bonds in the polymer and lead quasi-quantitatively to the formation of the soluble bis-CH$_3$CN mononuclear complex **2**.

In practice, the first exhaustive one-electron oxidation of the polymer was carried out at 0.6 V and leads to the quantitative formation of the soluble dimer **1**. This indicates that there is no structural rearrangement during the partial Ru−Ru polymer bond breaking. As expected, a subsequent one-electron exhaustive oxidation at 1.1 V induces the cleavage of the metal−metal bond of the dimer and leads to the ruthenium(II) monomer **2** as reported before (section 2.1).

[Ru(bpy)(CO)$_2$]$_n$ films, deposited on optical transparent electrodes, can be characterized by UV−vis spectroelectrochemical experiments. The shape of the absorption spectra of the films agrees well with the presence of Ru−Ru bonds in the polymeric matrix, as previously reported.[15]

**3. Electrocatalytic Properties of 1 and Resulting [Ru(bpy)(CO)$_2$]$_n$ Polymer.** We have previously shown that Ru(II) monomer complexes such as [Ru(L)(CO)$_2$Cl$_2$] (L = diversely substituted α-diimine ligand) and electrodes modified by the corresponding [Ru(L)(CO)$_2$]$_n$ polymers are highly active catalytic systems (homogeneous and heterogeneous, respectively) for the selective electroreduction of CO$_2$ in hydro-organic and pure aqueous electrolytes.[4b] To examine the electrocatalytic properties of **1** and the polymer formed from it, a number of analytical studies and preparative electrolysis were performed in the presence of CO$_2$.

Two observations can be made. First, the bubbling of CO$_2$ into a homogeneous organic solution of **1** (CH$_3$CN + 0.1 M TBAP) causes an important modification of the voltammogram. In particular a strong catalytic current appears after −1.90 V, in close proximity to that observed for the direct reduction of CO$_2$ without catalysis.[16] The progressive addition of H$_2$O amounts induces an increase in the intensity of this CO$_2$ reduction peak, while its foot potential becomes less and less negative, reaching an optimum value (around −1.40 V) at a 5% concentration of H$_2$O. Second, when a glassy-carbon modified electrode (GC|[Ru(bpy)(CO)$_2$]$_n$), prepared by reduction of **1** as described in section 2.2, is transferred in a clean electrolyte solution (either CH$_3$CN + 5% H$_2$O or pure H$_2$O containing the appropriate electrolyte), a typical catalytic current is observed. This catalytic activity shows that the polymer derived from **1** is also an electrocatalyst for CO$_2$ reduction, in keeping with the properties of the polymer previously published.

Controlled-potential electrolysis of CO$_2$ saturated hydro-organic or aqueous electrolytes using the polymer-modified electrodes as cathodes confirm their high efficiency as electrocatalysts for CO$_2$ conversion. In these experiments, CO is formed in near-quantitative electrical yields at a low potential (−1.30 V vs SCE) while the production of formate is less than 2%. Moreover, the catalytic current is very stable. Similarly, the reduction of CO$_2$ catalyzed by the dimer **1** in homogeneous solution (CH$_3$CN + 0.1 M TBAP + 10% H$_2$O), gives CO in a 99% yield, the production of HCOO$^-$ being negligible (∼1%). All of these results are in accordance with those obtained during our previous electrocatalytic studies concerning Ru(II) monomer and Ru(0) polymers.[2a,d]

## Conclusion

In the present study we have confirmed that the binuclear Ru(I) complex [Ru(CO)$_2$(CH$_3$CN)$_3$]$_2$(PF$_6$)$_2$ is a very convenient precursor to synthesize, under mild conditions, several new dimers containing a metal−metal bond. Specifically, we have described the selective synthesis and X-ray characterization of the new compound [Ru(bpy)(CO)$_2$(CH$_3$CN)]$_2$(PF$_6$)$_2$.

It has been demonstrated that the breakage of the metal−metal bond during the one-electron oxidation of both metal centers of this ruthenium(I) bpy dimer affords the new mononuclear *cis*(CH$_3$CN)-[Ru(bpy)(CO)$_2$(CH$_3$CN)$_2$]$^{2+}$ complex. This electrochemical process could become a simple way to synthesize original Ru(II) bis(acetonitrile) monomers such as [Ru(L)(CO)$_2$(CH$_3$CN)$_2$]$^{2+}$ having a *cis*(CO),*cis*(CH$_3$CN) geometry.

On the other hand, the electroreduction of the dimer **1** leads to the formation of the organometallic polymer [Ru(bpy)(CO)$_2$]$_n$. All physicochemical data and electrochemical properties of the polymer produced in this way are identical with those of [Ru(bpy)(CO)$_2$]$_n$ electrogen-

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erated by the reduction of the mononuclear complex *trans*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] or *trans*($CH_3CN$)-[Ru(bpy)-$(CO)_2(CH_3CN)_2$]$^{2+}$. The results reported in this paper constitue additional proof that the Ru(0)−bpy polymers derived from mono- and binuclear complexes of ruthenium containing two leaving ligands have closely related structures and that the electrogeneration and oxidation of the Ru(0) organometallic polymer proceed through the formation of a dimeric intermediate.

## Experimental Section

**1. General Comments.** $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ was synthesized as described in the literature.[8] Reaction vessels were covered with aluminum foil during the synthetic preparations in order to minimize exposure to light. All solvents were freshly distilled and dried using standard procedures.[17] The solvents were degassed immediately prior to use using a freeze/thaw cycle. Infrared spectra were recorded with a Perkin-Elmer Spectrum GX FT-IR spectrometer as pellets or in solution. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity Inova or Bruker AC-250 apparatus; $\delta$(H) values in ppm are relative to the solvent $CD_3CN$ (1.96 ppm) or $CD_2Cl_2$ (5.32 ppm).

Electrochemical measurements were made using an EG & Princeton Applied Research Model 273 or 173 potentiostat−galvanostat equipped with a Sefram TGM 164 X−Y recorder. Voltammograms were obtained in a conventional three-electrode cell under an argon atmosphere in a drybox (Jaram). Working electrodes for cyclic voltammetry were platinum disks (0.19 $cm^2$) polished with a 2 $\mu$m diamond paste (Mecaprex Presi). All potentials reported are relative to Ag|10 mM $Ag^+$ in $CH_3CN$ + 0.1 M TBAP.[13] The supporting electrolyte was tetrabutylammonium perchlorate (TBAP) from Fluka and acetonitrile from Rathburn (HPLC grade); both were used as received without further purification.

Electrocatalysis experiments were run under a $CO_2$ atmosphere in a conventional three-electrode cell made airtight with vacuum grease (M. Apiezon). The total volume occupied by the gas in the electrolysis cell was 172 $cm^3$. Exhaustive electrolyses were carried out with a 10 × 10 × 4 mm carbon felt electrode (RVC 2000, 65 mg $cm^{-3}$, from Le Carbon Lorraine). The solution was degassed with $CO_2$ for 20 min with stirring. Films were grown under an argon atmosphere by potentiostating the carbon felt electrode dipped in $CH_3CN$ solution of the appropriate complex (1 mM). The solution was removed, and the electrodes were rinsed with a pure $CH_3CN$ solution under argon. The latter solution was substituted with the appropriate electrolyte solution purged with $CO_2$. All experiments were stopped after a known amount of coulombs had been passed. The gas was sampled through a septum. CO was analyzed on a Delsi Model 30 gas chromatograph equipped with an FID detector and a 120 cm 5 Å molecular sieve column. Hydrogen was used as the carrier gas. Formate ions were analyzed on a Perkin-Elmer Series 200 pump equipped with a Perkin-Elmer 785A UV/vis detector ($\lambda$ 210 nm) and a Bio-Rad 87H cation-exchange resin column eluted with a $10^{-2}$ M $H_2SO_4$ solution.

Electronic absorption spectra were recorded with a Hewlett-Packard HP 8452 A diode array spectrometer controlled with a Compaq 286 computer equipped with a Citizen 120 D printer. Absorption spectroelectrochemical experiments were conducted in a drybox under an argon atmosphere. The cuvettes were inserted into an optical translator connected to the spectrophotometer via an optical fiber system (Photonetics Spectrofip system). The optical fibers pass through the wall of the drybox by means of seals. Spectroelectrochemical measurements on films were made by using a conventional sandwich-type cell.[18] The optically transparent conductive electrode (OTE) (diameter 1.1 cm) was doped with indium tin oxide (ITO; Balthracon Z 20 from Balzers).

**2. Preparation of $[Ru(bpy)(CO)_2(CH_3CN)]_2(PF_6)_2$ (1).** This reaction was performed under an atmosphere of dry nitrogen gas using standard Schlenk techniques. A solution of $[Ru(CO)_2(CH_3CN)_3]_2(PF_6)_2$ (170 mg, 0.2 mmol) and bpy (78 mg, 0.5 mmol) in $CH_3CN$ (8 mL) was maintained at room temperature for 2 h. The resulting red solution was reduced in volume to ca. 3 mL under vacuum, and an excess of $Et_2O$ (20 mL) slowly added with stirring. When it stood for 12 h at −25 °C, the solution yielded orange needle-shaped crystals. The mother liquor was decanted and the crystals washed with $Et_2O$ (2 × 5 mL). The product was recrystallized from $CH_3CN/Et_2O$ a second time in the same manner described above. The material obtained was dried in vacuo for 30 min and then dissolved in $CH_3CN$ (5 mL). The solvent was completely removed under reduced pressure and the solid product dried under vacuum for 36 h to afford the pure diruthenium complex **1** as an orange-red powder (130 mg, 65%). $^1H$ NMR in $CD_3CN$: $\delta$ 8.42 (d, 4 $H_{6,6'}$), 8.11 (td, 4 $H_{4,4'}$), 8.00 (d, 4 $H_{3,3'}$), 7.49 (td, 4 $H_{5,5'}$), 1.98 (s, 6 $H_{CH_3CN}$). $^1H$ NMR in $CD_2Cl_2$ at room temperature: $\delta$ 8.38 (d, 4 $H_{6,6'}$), 8.17 (t, 4 $H_{4,4'}$), 8.05 (d, 4 $H_{3,3'}$), 7.52 (t, 4 $H_{5,5'}$), 1.92 (s, 6 $H_{CH_3CN}$). $^1H$ NMR in $CD_2Cl_2$ at −80 °C: $\delta$ 8.27 (s, 4 $H_{6,6'}$), 8.10 (t, 4 $H_{4,4'}$), 7.91 (d, 4 $H_{3,3'}$), 7.45 (t, 4 $H_{5,5'}$), 1.92 (s, 6 $H_{CH_3CN}$). $^{13}C$ NMR in $CD_2Cl_2$ at −80 °C: $\delta$ 201.25 (CO), 151.72 (C-6), 150.59 (C-2), 139.07 (C-4), 127.00 (C-5), 123.07 (C-3), 119.26 ($CH_3CN$), 3.05 ($CH_3CN$). FT-IR ($cm^{-1}$) as a KBr disk: 2313 (w, $\nu_{CN}$), 2285 (w, $\nu_{CN}$), 2044 (s, $\nu_{CO}$), 2003 (m, $\nu_{CO}$), 1969 (s, $\nu_{CO}$), 1948 (sh), 839 (vs, $\nu_{PF}$) 558 (m, $\nu_{PF}$); in $CH_3CN$: 2021 (s, $\nu_{CO}$), 1985 (sh), 1978 (w, $\nu_{CO}$), 1944 (s, $\nu_{CO}$), 1927 (sh). UV−vis ($\lambda_{max}$ nm ($\epsilon$, $M^{-1}cm^{-1}$) in $CH_3CN$: 244 (30 800), 297 (26 100), 312 (sh), 425 (sh). $ES^+MS$, mobile phase $CH_3CN$ ($z = 2$): $m/z$ 326.8 with the calculated isotopic patterns for $[M - 2\ CO]^{2+}$; 313.7 $[M - 2\ CH_3CN]^{2+}$ ; 285.8 $[M - 2\ CH_3CN - 2CO]^{2+}$. Anal. Found (calcd) for $Ru_2C_{28}H_{22}O_4N_6P_2F_{12}\cdot CH_3CN$: C, 34.66 (34.42): H, 2.42 (2.34); N, 9.24 (9.43); Ru, 19.44 (19.19).

**3. Attempted Chemical Preparation of *cis*(CO)*cis*-($CH_3CN$)-$[Ru(bpy)(CO)_2(CH_3CN)_2](PF_6)_2$ (2).** (a) *cis*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] (32 mg, 0.08 mmol) prepared as previously described[2d] and 2 molar equiv of $TlPF_6$ (62.6 mg, 0.18 mmol) were refluxed together in $CH_3CN$ (10 mL) for 2 h 15 min. The fine white precipitate that formed was removed by filtration and the solvent evaporated from the filtrate under vacuum with gentle heating, yielding the crude light green powder **4** containing $TlPF_6$ salt. $^1H$ NMR in $CD_3CN$: $\delta$ 9.49 (d, 1 $H_6$), 8.87 (d, 1 $H_{6'}$), 8.50 (2 d, 2 $H_{3,3'}$), 8.38 (t, 1 $H_4$), 8.27 (t, 1 $H_{4'}$), 7.92 (t, 1 $H_5$), 7.68 (t, 1 $H_{5'}$). FT-IR ($cm^{-1}$) as a CsI disk: 2094 (s, $\nu_{CO}$), 2037 (s, $\nu_{CO}$), 839 (vs, $\nu_{PF}$), 323 (w, $\nu_{RuCl}$). FT-IR ($cm^{-1}$) in $CH_3CN$: 2091 (s, $\nu_{CO}$), 2035 (s, $\nu_{CO}$). $FAB^+$ ($m/z$): 390 [M − $PF_6$], 349 [M − $PF_6$ − $CH_3CN$], 321 [M − $PF_6$ − $CH_3CN$ − CO]. To decoordinate the remaining complex **4**, the sample was then redissolved in $CH_3CN$ (20 mL) and the solution refluxed in the presence of the residual $TlFF_6$ for a further 72 h. IR absorption spectra recorded of the reaction solution show no marked change in the carbonyl region. Therefore, in an attempt to obtain the bis(acetonitrile) monomer **2**, the experimental conditions were changed.

(b) *cis*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] (32 mg, 0.083 mmol) and 4 molar equiv of $TlPF_6$ (116.5 mg, 0.33 mmol) were refluxed together in $CH_3CN$ (20 mL) continuously for 72 h under a nitrogen atmosphere. The resulting pale yellow solution was filtered from the white precipitate which formed, and the solvent was removed under vacuum to give a light tan residue consisting of a mixture of 45% of *cis*(CO)-$[Ru(bpy)(CO)_2(CH_3CN)Cl](PF_6)$ (**4**) and 65% of *cis*(CO),*cis*($CH_3CN$)-$[Ru(bpy)(CO)_2(CH_3CN)_2](PF_6)_2$ (**2**; the yields were estimated by using the

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**Table 3. Summary of the Crystal Data of $1 \cdot 2CH_3CN$**

| | |
|---|---|
| formula | $Ru_2C_{32}H_{28}F_{12}N_8O_4P_2$ |
| fw | 1080.70 |
| cryst syst, space group | monoclinic, *C*2/*c* |
| $a$/Å | 15.259(4) |
| $b$/Å | 17.754(4) |
| $c$/Å | 15.937(3) |
| α/deg | 90 |
| $\beta$/deg | 104.15(2) |
| $\gamma$/deg | 90 |
| $V$/Å$^3$ | 4187(2) |
| $Z$ | 4 |
| $D_c$/g cm$^3$ | 1.715 |
| $F$(000) | 2136 |
| $\mu$/mm$^{-1}$ | 0.897 |
| cryst dimens/mm | 0.70 × 0.34 × 0.15 |
| $\lambda$(Mo Kα)/Å | 0.710 69 |
| temp/K | 293(3) |
| $\theta$ range for collected data/deg | 2.01−22.98 |
| index ranges | $-16 \le h \le 16$<br>$-1 \le k \le 19$<br>$-1 \le l \le 17$ |
| total no. of rflns collected | 3170 |
| abs cor | empirical |
| rel transmissn coeff ($I$) | 0.9973, 0.7696 |
| no. of unique data | 2897 ($R_{int} = 0.0272$) |
| no. of unique obsd data ($I > 4\sigma(I)$) | 1964 |
| refinement method | full-matrix least squares on $F^2$ |
| no. of data/restraints/params | 2897/0/273 |
| goodness of fit (based on $F^2$) | 1.036 |
| extinction coeff | none |
| max $\Delta\rho$/e Å$^{-3}$ | 0.865 |
| min $\Delta\rho$/e Å$^{-3}$ | −0.643 |
| final $R$ indices ($I > 2\sigma(I)$) | R1 = 0.0587, wR$^2$ = 0.1430 |
| $R$ indices (all data) | R1 = 0.0967, wR2 = 0.1831 |

integrations of the proton signals in the $^1$H NMR spectrum of the crude product). The $^1$H NMR and FT-IR spectra of *cis*(CO),*cis*($CH_3CN$)-[Ru(bpy)$(CO)_2(CH_3CN)_2$]$(PF_6)_2$ listed here have been extracted from the crude product spectrum. $^1$H NMR in $CD_3CN$: $\delta$ 9.01 (d, 1 $H_6$), 8.82 (d, 1 $H_{6'}$), 8.56 (t, 1 $H_3$), 8.51 (t, 2 $H_{3'}$), 8.45 (td, 1 $H_4$), 8.33 (td, 1 $H_{4'}$), 7.94 (t, 1 $H_5$), 7.74 (td, 1$H_{5'}$). FT-IR (cm$^{-1}$) in $CH_3CN$: 2117 (s, $\nu_{CO}$), 2063 (s, $\nu_{CO}$).

**5. X-ray Data Collection and Structure Solution for 1.** Suitable crystals of **1** were grown by the slow vapor diffusion of diethyl ether into an acetonitrile solution of the complex. The intensities of the reflections were measured using the variable-speed $\omega - 2\theta$ scan method on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. The crystal exhibited a rapid falloff of scattering power above 23°. Thus, as only a very small percentage of the data would be observed at higher $\theta$ values, the collection of these data was not justified. Three standard reflections were measured every 1 h to check any possible decomposition of the crystal. Data were corrected for absorption by the $\psi$-scan method.[19] The loss of occluded solvent from the crystal during data collection necessitated the application of a linear decay correction using the mean value linear curves fitted through three intensity control reflections, measured at regular time intervals. The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling and full-matrix least-squares refinement based on $F^2$. The residuals and weighting schemes are defined as follows: $R1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$, $wR2 = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2F + 0.0005F^2)$. Non-hydrogen atoms were assigned anisotropic thermal factors and the hydrogen atoms a single common thermal factor; the latter were placed in calculated positions. For the structure solution SHELX-97[20] was employed, while ORTEP-III was used to produce the diagrams.[21] Crystallographic data are summarized in Table 3.

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**Supporting Information Available:** Further details of the crystal structure determination, including tables of bond lengths, bond angles, and anisotropic and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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