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Article

Diruthenium Dithiolato Cyanides: Basic Reactivity Studies and a Post Hoc Examination of Nature's Choice of Fe versus Ru for Hydrogenogenesis

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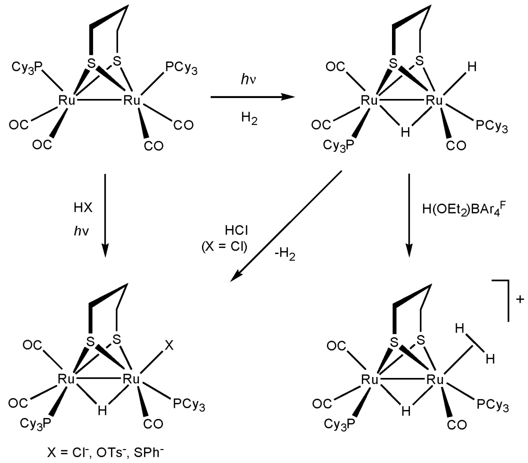
The reaction of $Ru_2(S_2C_3H_6)(CO)_6$ (**1**) with 2 equiv of Et_4NCN yielded $(Et_4N)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]$, $(Et_4N)_2$[**3**], which was shown crystallographically to consist of a face-sharing bioctahedron with the cyanide ligands in the axial positions, trans to the Ru–Ru bond. Competition experiments showed that **1** underwent cyanation >100× more rapidly than the analogous $Fe_2(S_2C_3H_6)(CO)_6$. Furthermore, $Ru_2(S_2C_3H_6)(CO)_6$ underwent dicyanation faster than $[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-$, implicating a highly electrophilic intermediate $[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)(CO)_5]^-$. $Ru_2(S_2C_3H_6)(CO)_6$ (**1**) is noticeably more basic than the diiron compound, as demonstrated by the generation of $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_6]^+$, [**1**H]$^+$. In contrast to **1**, the complex [**1**H]$^+$ is unstable in MeCN solution and converts to $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_5(MeCN)]^+$. $(Et_4N)_2$[**3**] was shown to protonate with HOAc ($pK_a = 22.3$, MeCN) and, slowly, with MeOH and H_2O. Dicyanide [**3**]$^{2-}$ is stable toward excess acid, unlike the diiron complex; it slowly forms the coordination polymer $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)(CNH)(CO)_4]_n$, which can be deprotonated with Et_3N to regenerate [H**3**]$^-$. Electrochemical experiments demonstrate that [**3**H]$^-$ catalyzes proton reduction at –1.8 V vs Ag/AgCl. In contrast to [**3**]$^{2-}$, the CO ligands in [**3**H]$^-$ undergo displacement. For example, PMe_3 and [**3**H]$^-$ react to produce $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_3(PMe_3)]^-$. Oxidation of $(Et_4N)_2$[**3**] with 1 equiv of Cp_2Fe^+ gave a mixture of $[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)_3(CO)_3]^-$ and $[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-$, via a proposed $[Ru_2]_2(\mu\text{-}CN)$ intermediate. Overall, the ruthenium analogues of the diiron dithiolates exhibit reactivity highly reminiscent of the diiron species, but the products are more robust and the catalytic properties appear to be less promising.

Introduction

In examining diruthenium dithiolato carbonyls, we sought new insights into the reactivity of $M_2(SR)_2(CO)_{6-x}L_x$ complexes.[1,2] This family of butterfly structures resembles the active sites of the Fe-only hydrogenase (Fe H_2-ase) enzymes.[3] We recently described the use of diruthenium dithiolates to generate the first $M_2(SR)_n$ species bearing a terminal hydride, which in turn was converted to an H_2 adduct (Scheme 1).[4]

We now report the substitution, redox, and acid–base behavior of $Ru_2(S_2C_3H_6)(CO)_6$ and its derivatives. We focus on the propanedithiolate complexes because they sterically resembles the dithiolate cofactor in the enzyme.[5]

Scheme 1



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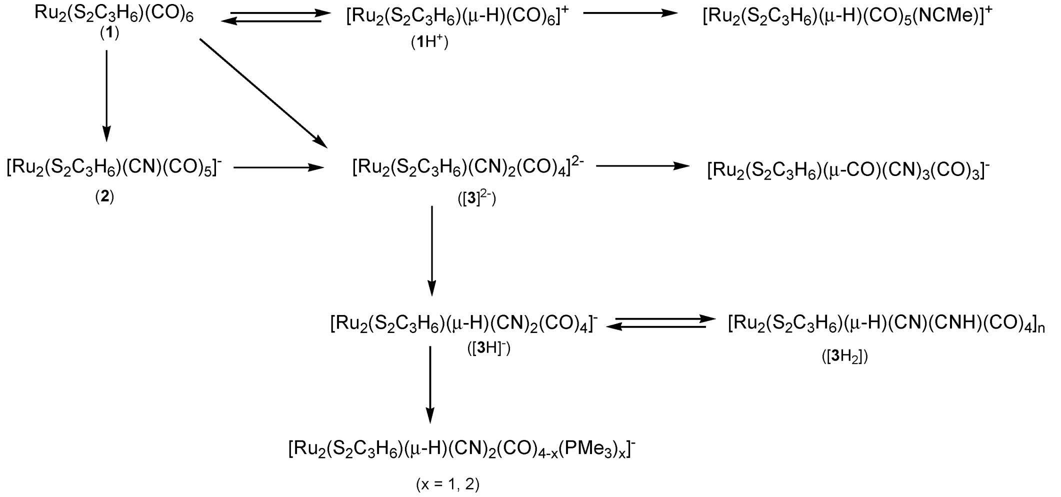
Scheme 2



Using diruthenium dithiolates, we have addressed certain anomalies arising from our studies on the corresponding diiron dithiolates. We previously reported that the dicyanation of $Fe_2(SR)_2(CO)_6$ proceeds more rapidly than the cyanation of $[Fe_2(SR)_2(CN)(CO)_5]^-$,[6] and questions arose about the generality of this highly unusual behavior. The instability of $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$ upon treatment with excess acid is well-known,[7,8] but the decomposition pathway has remained unexplained. Finally, the diiron complexes are unstable toward oxidation,[7] at least in the absence of trapping ligands[9] and we sought insights into the relevant redox events, including the possible isolation of a mixed-valence intermediate. Studies on the ruthenium analogues provide insights relevant to all of these questions. Mononuclear Ru−SR−CN compounds have been previously described by Liaw and co-workers.[10] The preparative results are summarized in Scheme 2.

Results

$Ru_2(S_2C_3H_6)(CO)_6$. Cabeza and co-workers prepared the dithiolato complex $Ru_2(S_2C_6H_4)(CO)_6$ via the Zn reduction of carbonylated solutions of ruthenium chloride in the presence of the benzene-1,2-dithiol.[11] Key to their methodology is the reductive carbonylation of Ru(III) to produce Ru(II) chloro-carbonyls.[12] We found that Cabeza's method could be applied to the synthesis of the 1,3-propanedithiolate, $Ru_2(S_2C_3H_6)(CO)_6$ (**1**). Yields are 30−40% based on hydrated ruthenium trichloride.

Cyanation of $M_2(S_2C_3H_6)(CO)_6$ (M = Fe, Ru). Slow addition of 1 equiv of Et_4NCN to a dilute MeCN solution of **1** efficiently gave $Et_4N[Ru_2(S_2C_3H_6)(CN)(CO)_5]$, Et_4N[**2**]. We obtained substantial amounts of the corresponding dicyanide $(Et_4N)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]$ ($(Et_4N)_2$[**3**]) when the Et_4NCN was added rapidly or when concentrated solutions of **1** were used. With two or more equivalents of Et_4NCN, **1** converted cleanly to the dicyanide $(Et_4N)_2$[**3**]; no evidence was ever obtained for formation of the tricyanide $[Ru_2(S_2C_3H_6)(CN)_3(CO)_3]^{3-}$. The tendency of **1** to give the dicyanide [**3**]$^{2-}$ even upon treatment with substoichiometric amounts of cyanide is reminiscent of the behavior of related diiron dithiolato complexes.[6,13]

The mechanism for dicyanation does not entail two consecutive CN^- for CO substitutions,[6] i.e., Et_4N[**2**] is not an intermediate in the formation of dicyanide $(Et_4N)_2$[**3**] under preparative conditions. This point was proven by treatment of an equimolar mixture of **1** and Et_4N[**2**] with 2 equiv of Et_4NCN to give $(Et_4N)_2$[**3**], leaving unreacted Et_4N[**2**]. Complete conversion of **1** occurred. The same result was obtained using ^{13}CN-labeled Et_4N[**2**], the ^{13}C-labeled species remained unreacted (eq 1).

$$\begin{array}{l} [Ru_2(S_2C_3H_6)(^{13}CN)(CO)_5]^- \\ \quad Ru_2(S_2C_3H_6)(CO)_6 \end{array} \overset{+2CN^-}{\underset{-2CO}{\Longrightarrow}} \begin{array}{c} [Ru_2(S_2C_3H_6)(^{13}CN)(CO)_5]^- \\ [Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-} \\ (100\%) \end{array} \qquad (1)$$

Of course, Et_4N[**2**] *does* react with Et_4NCN to give $(Et_4N)_2$[**3**], but this reaction is clearly slower than the conversion **1** + 2 Et_4NCN → $(Et_4N)_2$[**3**].

Comparative Cyanation of 1 and its Diiron Analogue. We probed the relative reactivity of the diiron and diruthe-

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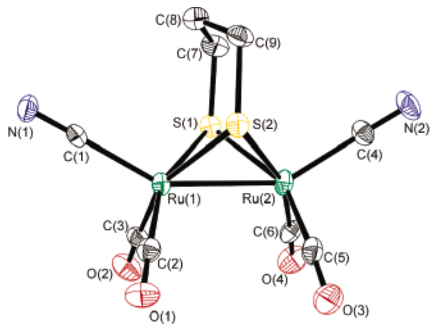

Figure 1. Molecular structure of the dianion of (PPN)$_2$[Ru$_2$(S$_2$C$_3$H$_6$)(CN)$_2$(CO)$_4$]·MeCN with the thermal ellipsoids at the 35% probability level. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ru$_2$(S$_2$C$_3$H$_6$)(Co)$_6$ (**1**) the anion in (PPN)$_2$[Ru$_2$(S$_2$C$_3$H$_6$)(CN)$_2$(CO)$_4$], (PPN)$_2$[**3**]

(PPN)$_2$[**3**]		(**1**)	
Ru(1)−Ru(2)	2.6667(7)	Ru−Ru	2.6743(13)
Ru(1)−S(1)	2.4205(11)	Ru−S$_{(av)}$	2.396
Ru(1)−S(2)	2.4206(11)	Ru−CO$_{(axial,av)}$	1.941
Ru(2)−S(1)	2.4195(12)	Ru−CO$_{(basal,av)}$	1.912
Ru(2)−S(2)	2.4142(12)		
Ru(1)−C(2)	1.861(4)		
Ru(1)−C(3)	1.879(4)		
Ru(2)−C(5)	1.857(5)		
Ru(2)−C(6)	1.894(4)		
Ru(1)−C(1)	2.048(4)		
Ru(2)−C(4)	2.032(4)		
Ru(1)−S(1)−Ru(2)	66.87(3)	Ru−S−Ru	67.84(3)
Ru(1)−S(2)−Ru(2)	66.95(3)	Ru−Ru−CO(1)	154.80(11)
Ru(2)−Ru(1)−C(1)	149.87(11)	Ru−Ru−CO(5)	151.78(11)
Ru(1)−Ru(2)−C(4)	147.47(12)	Ru−Ru−CO$_{(basal,av.)}$	101.25
Ru(1)−Ru(2)−C(5)	99.10(12)		
Ru(1)−Ru(2)−C(6)	104.93(13)		
Ru(2)−Ru(1)−C(2)	102.79(13)		
Ru(2)−Ru(1)−C(3)	101.25(12)		

nium complexes toward cyanide through competition experiments. Treatment of a 1:1 mixture of Fe$_2$(S$_2$C$_3$H$_6$)(CO)$_6$ and **1** with 2 equiv Et$_4$NCN produced exclusively [**3**]$^{2-}$, leaving unreacted Fe$_2$(S$_2$C$_3$H$_6$)(CO)$_6$ (Scheme 2). In a more stringent competition experiment, 2 equiv of Et$_4$NCN was added to a solution of 5 equiv of Fe$_2$(S$_2$C$_3$H$_6$)(CO)$_6$ and 1 equiv of **1**. Again, IR spectroscopic and extractive workup indicated complete conversion of **1** to [**3**]$^{2-}$, leaving Fe$_2$(S$_2$C$_3$H$_6$)(CO)$_6$ unaffected (eq 2).

$$\begin{matrix} 5\mathrm{Fe_2(S_2C_3H_6)(CO)_6} \\ \mathrm{Ru_2(S_2C_3H_6)(CO)_6} \end{matrix} \underset{-2\mathrm{CO}}{\overset{+2\mathrm{CN}^-}{\Longrightarrow}} \begin{matrix} 5\mathrm{Fe_2(S_2C_3H_6)(CO)_6} \\ [\mathrm{Ru_2(S_2C_3H_6)(CN)_2(CO)_4}]^{2-} \\ (100\%) \end{matrix} \qquad (2)$$

As a control experiment, we confirmed that (Et$_4$N)$_2$[Fe$_2$(S$_2$C$_3$H$_6$)(CN)$_2$(CO)$_4$] did not react with **1**, i.e., the product ratio from the competition experiment reflects relative rates of the cyanation.

Characterization of [Ru$_2$(S$_2$C$_3$H$_6$)(CN)$_2$(CO)$_4$]$^{2-}$. The (Et$_4$N)$_2$[**3**] salt is soluble in polar organic solvents, as well as water, producing air-sensitive yellow solutions. The solid-state structure of (PPN)$_2$[**3**] (PPN = N(PPh$_3$)$_2$) was determined via single-crystal X-ray diffraction (Figure 1, Table 1). A conventional butterfly structure is evident; both cyanide ligands are trans to the Ru−Ru bond as seen for (Et$_4$N)$_2$[Fe$_2$[(SCH$_2$)$_2$NR](CN)$_2$(CO)$_4$] for R = Me[14] and H.[15] The Ru−Ru bond distance (2.67 Å) and the average Ru−S distance (2.42 Å) are similar to those distances in **1**, which was also characterized crystallographically (Table 1). The Ru−CN distances are 2.04 Å, ca. 0.2 Å longer than the Ru−CO distances of 1.87 Å. Analogous to the corresponding diiron system, the Ru−CO distances are ~0.05 Å shorter in (PPN)$_2$[**3**] than in **1**.

[Ru$_2$(S$_2$C$_3$H$_6$)(μ-H)(CO)$_6$]$^+$. Compound **1** was found to protonate to give a stable hydride, in contrast to the corresponding diiron hexacarbonyl.[16] Thus, the addition of HOTf to a CH$_2$Cl$_2$ solution of **1** caused the νCO bands to shift by ~50 cm^{-1} toward higher energy, as seen for the substituted diiron systems.[16] The ^{1}H NMR spectrum of the resulting solution exhibited a hydride signal at δ −12.66. The addition of hexanes to such solutions precipitated [**1**H]OTf. [**1**H]$^+$ was easily deprotonated by weak bases such as THF. The related hydride [Ru$_2$(S$_2$C$_6$H$_4$)(μ-H)(CO)$_6$]$^+$ is apparently[11] less stable than the propanedithiolato derivative described above.

Treatment of [**1**H]$^+$ with 1 equiv of Et$_4$NCN and PMe$_3$ resulted in the deprotonation of [**1**H]$^+$. After it stood in a MeCN solution, [**1**H]OTf underwent monosubstitution to give [Ru$_2$(S$_2$C$_3$H$_6$)(μ-H)(CO)$_5$(NCMe)]OTf. An in situ ^{1}H NMR experiment showed the formation of a kinetic isomer (δ −12.8) followed over the course of several hours by the appearance of a second isomer (δ −17.64). In the absence of acids, MeCN solutions of **1** are stable.

[Ru$_2$(S$_2$C$_3$H$_6$)(μ-H)(CN)$_2$(CO)$_4$]$^-$. The increased basicity of the Ru−Ru versus Fe−Fe bonds is particularly evident for dianion [**3**]$^{2-}$, which has a pK_a greater than 22 indicated by its ability to deprotonate HOAc in MeCN solution.[17] Water and MeOH are also sufficiently acidic to protonate the dicyanide, although this conversion required several minutes at ambient temperatures.

The addition of 1 equiv of TsOH (p-MeC$_6$H$_4$SO$_3$H, pK_a = 8.0 in MeCN) to aqueous or MeCN solutions of (Et$_4$N)$_2$[**3**], followed by the addition of large organic cations, yielded crystalline salts (e.g., A[**3**H] where A = PPN$^+$, PPh$_4$$^+$, and Et$_4N^+$). The ν_{CO} bands for [**3**H]$^-$ occur at ca. 50 cm^{-1} higher energy than its conjugate base, as is typical.[8,18] The ^{1}H NMR spectrum indicates the presence of two isomers in the ratio 1.0:0.75. This isomer ratio remains unchanged over the course of several hours at room temperature in MeCN solution. Two major isomers were previously observed in the ^{1}H NMR spectrum of [Fe$_2$(S$_2$C$_3$H$_6$)(μ-H)(CN)$_2$(CO)$_4$]$^-$.[8] Given its greater basicity, [**3**]$^{2-}$ was tested for its ability to deprotonate [Fe$_2$(S$_2$C$_3$H$_6$)(μ-H)(CN)$_2$(CO)$_4$]$^-$. No reaction was observed for an equimolar solution of [**3**]$^{2-}$ and [Fe$_2$-

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$(S_2C_3H_6)(\mu\text{-H})(CN)_2(CO)_4]^-$. When an equimolar solution of $[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ and $[\mathbf{3}]^{2-}$ was treated with 1 equiv of HOTs, the two dimetallic complexes protonated to the same extent, despite the extreme difference in their basicity. The slow rate of proton transfer between metal hydrides is well-known,[19] so product distribution is a result of the rate of protonation, not the basicity of the metal−metal bond.

$[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)(CNH)(CO)_4]_n$. The addition of two or more equivalents of HOTs to solutions of $(Et_4N)_2[\mathbf{3}]$ resulted in rapid formation of $Et_4N[\mathbf{3}H]$, followed by the slower precipitation of a yellow solid. The IR spectrum of this precipitate is consistent with $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)(CNH)(CO)_4]_n$, $(\mathbf{3}H_2)_n$. Relative to $Et_4N[\mathbf{3}H]$, the ν_{CO} and ν_{CN} bands of $(\mathbf{3}H_2)_n$ are shifted toward higher energy by 10 and 35 cm^{-1}, respectively. The fact that protonation induces a greater shift in ν_{CN} than ν_{CO} is consistent with protonation at cyanide. The addition of Et_3N converted $(\mathbf{3}H_2)_n$ back into $[\mathbf{3}H]^-$, signaled by the formation of a homogeneous solution and the appearance of IR bands at the appropriate positions. We propose that $(\mathbf{3}H_2)_n$ is a hydrogen-bonded polymer consisting of RuCNH···NCRu linkages. Consistent with this proposal, the presence of NEt_4Cl, a source of the hydrogen-bond acceptor Cl^-, prevents precipitation. The IR spectrum of the resulting solution matches well that for solid $(\mathbf{3}H_2)_n$.

Treatment of $[\mathbf{3}H]^-$ with a 1.0 M solution of DCl produced the corresponding solid $(\mathbf{3}HD)_n$, $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)(CND)(CO)_4]$. Neutralization of this solid with Et_3N regenerated $[\mathbf{3}H]^-$, with no evidence of H−D exchange between the Ru−H−Ru and RuCN−D sites (eq 3), and there is no evidence for exchange between $[\mathbf{3}H]^-$ and free Et_3ND^+ in MeCN.

$$Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)(CND)(CO)_4 \nrightarrow Ru_2(S_2C_3H_6)(\mu\text{-D})(CN)(CNH)(CO)_4 \quad (3)$$

Treatment of MeCN solutions of $[\mathbf{3}H]^-$ with $ONMe_3$ and PMe_3 smoothly yielded $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)_2(CO)_{4-x}(PMe_3)_x]^-$ (x = 1, 2). On the basis of ^{31}P and ^1H NMR measurements, we determined that the monophosphine complex, $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)_2(CO)_3(PMe_3)]^-$, formed as a single isomer.

Redox Properties of Substituted Diruthenium Dithiolates. Cyclic voltammetry indicates that compared to $Fe_2(S_2C_3H_6)(CO)_6$, **1** is both more difficult to oxidize and more difficult to reduce. The compound exhibits an irreversible oxidation at +1.3 V and an irreversible reduction at −1.5 V (vs Ag/AgCl, MeCN solution). For comparison, $Fe_2(S_2C_3H_6)(CO)_6$ oxidizes at +1.2 V and reduces at −1.16 V. Upon treatment of a solution of **1** with excess HOTf, the current increases dramatically and the reduction potential shifts by −0.10 to −1.60 V. We attribute these changes to the effect of protonation and catalytic proton reduction catalyzed by $[\mathbf{1}H]^+$.

CV experiments showed that MeCN solutions of $(Et_4N)_2[\mathbf{3}]$ oxidized irreversibly at the mild potential of 19 mV. In a preparative scale experiment, treatment of $(Et_4N)_2[\mathbf{3}]$ with 1 equiv Cp_2FePF_6 resulted in complete consumption of the starting materials. ESI-MS and IR analysis indicates that the major CN-containing products are $[\mathbf{2}]^-$ and $[Ru_2(S_2C_3H_6)(\mu\text{-CO})(CN)_3(CO)_3]^-$, resulting from disproportionation (eq 4).

$$\underbrace{[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}}_{([\mathbf{3}]^{2-})} + Cp_2Fe^+ \rightarrow 0.5[Ru_2(S_2C_3H_6)(\mu\text{-CO})(CN)_3(CO)_3]^- + 0.5\underbrace{[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-}_{([\mathbf{2}]^-)} + Cp_2Fe \quad (4)$$

The tricyanide was independently generated utilizing a protocol recently published for $[Fe_2(S_2C_2H_4)(\mu\text{-CO})(CN)_3(CO)_3]^-$.[9] Thus $[\mathbf{3}]^{2-}$ was oxidized by the simultaneous addition of 2 equiv of Cp_2Fe^+ and 1 equiv of Et_4NCN. The product distribution in eq 4 is consistent with an initially formed radical, $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^-$, which suffers nucleophilic attack by $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ to form a μ-CN-linked Ru_4 species.

Cyclic voltammetry revealed $[\mathbf{3}]^{2-}$ an irreversible oxidation wave at 19 mV, and protonation of the Ru−Ru bond causes a loss of the oxidation wave and the appearance of an irreversible wave at approximately −1.8 V. Upon addition of 5 and 10 equiv HOTs, the reduction current increases, indicative of the catalytic reduction of protons.[1] The electrode became coated during the course of the electrolysis experiments, probably because of the formation of $(\mathbf{3}H)_n$.

Discussion

Compared to the analogous diiron dithiolates, $Ru_2(S_2C_3H_6)(CO)_6$ is more susceptible to attack by both nucleophilic and electrophilic reagents. Both features can be rationalized on the basis of electronic and molecular structures. The high basicity of the Ru−Ru bond conforms with the well-known trend that second-row metals are stronger Brønsted bases than analogous complexes of first-row metals.[20] The enhanced electrophilicity of $Ru_2(S_2C_3H_6)(CO)_6$ was demonstrated by competition experiments. Relative to the analogous diiron system, $Ru_2(S_2C_3H_6)(CO)_6$ reacts >100× faster with cyanide. We attribute this increased electrophilicity to the greater size of ruthenium, which facilitates associative reactions. As in the analogous diiron compound, only two cyanide ligands could be installed.

The cyanation is characterized by two unusual findings. First, the monocyanide $[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-$ is *not* an intermediate in the dicyanation. This result is understandable since this monocyanide is isoelectronic to the hexacarbonyl except that it is anionic, which would be expected to inhibit cyanation. The fact that dicyanation of the hexacarbonyl is faster than monocyanation requires a more complex explanation. It is known that ligand substitution is associative,[21] and the initial product could reasonably be $[Ru_2(S_2C_3H_6)(\mu\text{-CO})$-

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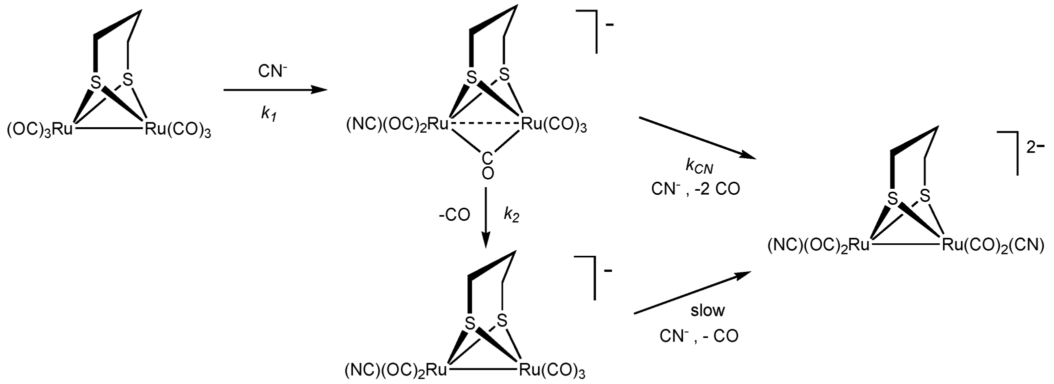
Scheme 3



$(CN)(CO)_6]^-$ (Scheme 3). An analogous intermediate has been detected in the cyanation of a diiron carbonyl containing a specially modified thioether ligand.[22] Pickett et al. showed that the attacking cyanide in effect pushes a CO from a terminal position into a bridging site, concomitant with loss of the Fe−Fe bond. Apparently, this μ-CO species is more electrophilic than either $[Ru_2(S_2C_3H_6)(CO)_6]$ or $[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-$. Pickett et al. rationalized the high electrophilicity of the $Fe_2(\mu\text{-CO})$ intermediate as resulting from the electron-withdrawing properties of the μ-carbonyl, which also labilizes the trans terminal carbonyl.

A mechanism that rationalizes these results is presented in Scheme 3.

Two isomers were observed for $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)_2(CO)_4]^-$, which presumably result from protonation of two rotamers of the dicyanide conjugate base, as seen in the protonation of the analogous diiron system.[23] The low rotational barriers in the $34e^-$ species, $Fe_2(S_2C_nH_{2n})(CO)_4L_2$, allow rapid isomerization at room temperature,[4,24] whereas the rotational barriers are higher in the confacial bioctahedral derivatives, $[Fe_2(S_2C_nH_{2n})(\mu\text{-X})(CO)_{6-x}L_x]^z$ (X = CO, SMe, H).[9,25] We obtained no evidence for protonation at a single metal, as is implied in the Fe-only H_2-ases. For related cyclopentadienyl complexes, Angelici had also found that protonation occurs at the Ru−Ru bond, not at a single metal site, even in electronically unsymmetrical species.[26]

In contrast to the substitutional inertness of dicyanide $[\mathbf{3}]^{2-}$, the carbonyl ligands in its conjugate acid $[\mathbf{3}H]^-$ are readily substituted by PMe_3. Protonation-induced labilization of carbonyl ligands has been observed previously in the case of $[Fe_2(S_2C_3H_6)(\mu\text{-H})(CO)_4(PMe_3)_2]^+$, wherein MeCN displaces one CO ligand.[27] Similarly, complexes of the type $[(C_5R_5)_2Ru^{II}_2(\mu\text{-H})(CO)_4]^+$ exhibit enhanced reactivity toward nucleophiles relative to its conjugate base.[28]

One-electron oxidation of $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ initiates a multistep process that entails a bis(bimetallic) intermediate, most likely containing a μ-CN linkage. Two-electron oxidation of $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ was demonstrated by the synthesis of $[Ru_2(S_2C_3H_6)(\mu\text{-CO})(CN)_3(CO)_4]^-$. In contrast, the active site of the Fe-only H_2-ase, which is buried near the center of globular proteins,[29] does form a stable $S = 1/2$ state. Our quest for related mixed-valence bimetallic dithiolates continues.

Because of a large overpotential, $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CN)_2(CO)_4]^-$ is a poorer catalyst for hydrogen evolution relative to the known diiron complexes. Despite the fact that $Ru_2(S_2C_3H_6)(CO)_6$ readily protonates and lacks donor ligands, this species is a poor catalyst for proton reduction, requiring −1.6 V, compared to ca. −1.0 V for $[Fe_2(S_2C_3H_6)(\mu\text{-H})(CN)(CO)_4(PMe_3)]$. Our evidence indicates that iron compounds are superior catalysts relative to the analogous ruthenium compounds.

Evolutionarily optimized bioorganometallic enzymes have evolved highly efficient mechanisms to accomplish some of nature's and synthetic chemistry's most important reactions. The conversion of protons and electrons to dihydrogen is an example of a reaction that nature has perfected using inexpensive, plentiful metals, such as iron. Using the more reactive platinum group metals, the chemical industry struggles to achieve such reactions with the same efficiency, environmental-friendliness, and gentleness as the natural systems. The results presented in this paper indicate that platinum-group metal mimics of the Fe-only hydrogenase active sites yield catalysts *less* effective for proton reduction, although many aspects of the associated reactivity are quite analogous.

Experimental

General. Previous reports describe the general methods used in this work.[30] Zinc powder, 2-ethoxyethanol, 1,3-propanedithiolate, Et_4NCN, Et_4NCl, and hydrated *p*-toluenesulfonic acid were obtained

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from Aldrich; $ONMe_3$ (Aldrich) was dried via benzene−water azeotropic distillation, followed by repeated vacuum-sublimation cycles; PMe_3 was obtained from Strem. $RuCl_3{\cdot}3H_2O$ was obtained from Pressure Chemical Co, and $FcPF_6$ was prepared by literature methods.[31]

$Ru_2(S_2C_3H_6)(CO)_6$, 1. A dark brown suspension of 5 g (20.54 mmol) of $RuCl_3{\cdot}3H_2O$ in 300 mL of 2-ethoxyethanol was warmed to reflux, while being purged with CO for 3.5 h. The light yellow solution was cooled to room temperature and treated with 1.15 mL (11.4 mmol) of 1,3-propanedithiol, followed by 10 g (150 mmol) of Zn powder. The mixture was warmed to reflux for 2 h, again under a CO purge. After it was cooled to room temperature, the mixture was poured into a beaker containing 1500 mL of H_2O. The resulting flocculent precipitate was collected by filtration on a pad of Celite, where it was washed with 3 × 100 mL of H_2O before being air-dried. The yellow-orange product was extracted from the Celite with 3 L of CH_2Cl_2, and the filtrate was evaporated under vacuum. An extract of the residue in 8 mL of CH_2Cl_2 was loaded onto a column of neutral alumina that was packed with hexane. After the column was washed with hexane, a yellow band was eluted with CH_2Cl_2. Crystals suitable for X-ray diffraction studies were grown from hexane solution at −20 °C. Yield: 1.5 g (35%). ^1H NMR ($CDCl_3$): δ 2.2 (bs, 4H), 1.9 (bs, 2H). IR (hexane): ν_{CO} 2085, 2054, 2012, 2003, 1993 cm^{-1}. Anal. Found (calcd): C, 22.82 (22.69); H, 1.19 (1.27).

The complex $Ru_2(S_2C_2H_4)(CO)_6$ was prepared analogously in a 28% yield. ^1H NMR (C_6D_6): δ 1.44 (bs, 4H). IR (hexane): ν_{CO} 2087, 2056, 2014, 2005, 1995, 1966 cm^{-1}. Anal. Found (calcd): C, 21.23 (20.78); H, 0.54 (0.87).

$[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_6]OTf$, [1H]OTf. A yellow solution of 0.10 g (0.21 mmol) of **1** in 5 mL of CH_2Cl_2 was treated with 1.80 mL of a 0.113 M solution of HOTf in CH_2Cl_2. The solution was concentrated to 2 mL, and the light-yellow product precipitated upon addition of 30 mL of hexane. The sample was washed with 30 mL of hexane and dried under vacuum. Yield: 0.125 g (96%). ^1H NMR (CD_2Cl_2): δ 2.78 (t, 4H, SCH_2), 2.29 (d, 2H, $SCH_2CH_2CH_2S$), −12.66 (s, Ru−H−Ru). IR (CH_2Cl_2): ν_{CO} 2143, 2126, 2078 cm^{-1}. When the same reaction was conducted in an MeCN solution, after 48 h the spectrum changed to indicate a new species assigned as $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_5(NCMe)]OTf$. ^1H NMR (MeCN-d_3): δ 2.2 (t, 4H, SCH_2), 1.95 (d, 2H, $SCH_2CH_2CH_2S$), −17.6 (s, 1H, Ru-*H*-Ru). IR (MeCN): ν_{CO} 2131, 2076, 2062, 2025 cm^{-1}. ESI-MS: *m/z* 490.9 ($[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_5(MeCN)]^+$).

$Et_4N[Ru_2(S_2C_3H_6)(CN)(CO)_5]$ Et_4N[2]. A solution of 0.10 g (0.21 mmol) of **1** in 6 mL of MeCN was treated dropwise with a solution of 0.036 g (0.23 mmol) of Et_4NCN in 4 mL of MeCN. The solvent was removed from the yellow-orange solution. The red-orange residue was extracted into 3 × 5 mL of THF, and this extract was filtered through a pad of Celite. The solvent was reduced to 1 mL; the mustard yellow product precipitated upon addition of 30 mL of hexane. The product was further washed with hexane and dried under vacuum. Yield: 0.060 g (47%). ^1H NMR (DMSO-d_6): δ 1.1 (t, 12H, NCH_2CH_3), 2.0 (bs, 2H, $SCH_2CH_2CH_2S$), 2.1 (bs, 4H, $SCH_2CH_2CH_2S$), 3.2 (q, 8H, NCH_2CH_3). IR (MeCN): ν_{CN} 2103, ν_{CO} 2046, 1988, 1965, 1925 cm^{-1}. Anal. Found (calcd): C, 47.29 (48.76); H, 3.06 (3.35); N, 3.56 (3.45).

$(Et_4N)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]$, $(Et_4N)_2$[3]. A solution of 0.20 g (0.42 mmol) of **1** in 5 mL of MeCN was treated with a solution of 0.14 g (0.90 mmol) of Et_4NCN in 5 mL of MeCN. The reaction mixture was concentrated to 2 mL, and a yellow-orange product precipitated upon the addition of 30 mL of Et_2O. The product was washed with 3 × 10 mL of Et_2O and vacuum-dried. Yield: 0.230 g (75%). ^1H NMR (acetone-d_6): δ 1.4 (t, 24H, NCH_2CH_3), 1.9 (bs, 2H, $SCH_2CH_2CH_2S$), 2.1 (bs, 4H, $SCH_2CH_2CH_2S$), 3.5 (q, 16H, NCH_2CH_3). ^{13}C NMR (CD3OD, 20OC): δ 7.8 (q, 8C, NCH_2CH_3), 24.2 (bs, 2C, $SCH_2CH_2CH_2S$), 35.5 (bs, 1C, $SCH_2CH_2CH_2S$), 53.3 (t, 8C, NCH_2CH_3), 150 (2, 2C, Ru*C*N), 207 (bs, 4C, Ru*C*O). IR (MeCN): ν_{CN} 2087, ν_{CO} 1978, 1938, 1899 cm^{-1}. Anal. Found (calcd): C, 40.58 (40.97); H, 6.11 (6.33); N, 7.43 (7.64).

$(PPN)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]$, $(PPN)_2$[3]. This species was prepared in a manner analogous to that for $(Et_4N)_2$[**3**], using PPNCN in place of Et_4NCN. Crystals suitable for X-ray diffraction analysis were grown from a mixture of MeCN−hexanes−Et_2O.

Competitive Cyanation of 1 and $Fe_2(S_2C_3H_6)(CO)_6$. A red-orange solution containing 0.081 g (0.210 mmol) of $Fe_2(S_2C_3H_6)(CO)_6$ and 0.020 g (0.042 mmol) of **1** in 10 mL of MeCN was treated with 0.013 g (0.084 mmol) of Et_4NCN in 3 mL of MeCN. IR (MeCN): ν_{CN} 2087, ν_{CO} 2074, 2034, 1994, 1979, 1939, 1900 cm^{-1}.

As a control experiment, a MeCN solution of $(Et_4N)[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$ and **1** was demonstrated to be stable for 12 h. A related competition experiment was also conducted on a 1:1 solution of **1** and $Fe_2(S_2C_3H_6)(CO)_6$ with similar results.

Dicyanation of 1 in the Presence of $Et_4N[Ru_2(S_2C_3H_5)(^{13}CN)(CO)_5]$. A solution of 0.032 g (0.0671 mmol) of 1 and 0.040 g (0.067 mmol) of $Et_4N[Ru_2(S_2C_3H_6)(^{13}CN)(CO)_5]$ in 10 mL of MeCN was shown to be stable by IR spectroscopy. To this solution was added 0.022 g (0.134 mmol) of Et_4NCN in 5 mL of MeCN. IR (MeCN): ν_{CN} 2100, 2087, ν_{CO} 2045, 1985, 1978, 1963, 1938, 1925, 1900 cm^{-1}. This corresponds to a mixture of unreacted $Et_4N[Ru_2(S_2C_3H_6)(^{13}CN)(CO)_5]$ and [**3**].

$PPh_4[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_4]$, PPh_4[3H]. An solution of 0.25 g (0.341 mmol) of $(Et_4N)_2$[**3**] in 35 mL H_2O was first treated with 0.34 mL (0.341 mmol) of 1 M HCl and then added slowly to a solution of 0.65 mg (1.71 mmol) of PPh_4Cl in 10 mL of H_2O. The pale yellow precipitate was collected by filtration on a pad of Celite and washed with 30 mL each of H_2O and Et_2O. The product was extracted from the Celite with 10 mL of MeCN, and the extract was concentrated to a volume of 1 mL. The product, which precipitated upon addition of 30 mL of Et_2O, was washed with 30 mL of Et_2O and dried under vacuum. Yield: 0.21 mg (65%). ^1H NMR (DMSO-d_6): δ 7.9 (m, 20H, PPh_4), 2.6 (m, 6H, $SCH_2CH_2CH_2S$), −12.8 (s, 1H, Ru-*H*-Ru), −14.2 (s, 1H, Ru-*H*-Ru). IR (MeCN): ν_{CN} 2120, ν_{CO} 2057, 2037, 1991 cm^{-1}. Anal. Found (calcd): C, 33.28 (33.77); H, 4.67 (4.33); N, 4.37 (4.6).

Reaction of $[3H]^-$ with DCl. A solution of 0.005 g (0.0068 mmol) of $(NEt_4)_2$[**3**] in ∼1.0 mL of MeCN-d_3 was treated with 0.26 mL (0.0068 mmol) of a 0.026 M solution of $HOTs{\cdot}H_2O$ in a sealable NMR tube, using standard vacuum-line techniques, followed by the addition of 140 μL (0.0136 mmol) of a 0.10 M solution of DCl. The yellow precipitate redissolved upon addition of 140 μL (0.0136 mmol) of 0.10 M NEt_3 with no evidence for deuteration of $[\mathbf{3}H]^-$.

$[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)(CNH)(CO)_4]_n$, $[3H_2]_n$. A solution of 0.050 g (0.0682 mmol) of Et_4N[**3**H] in 5 mL of MeCN was treated with 0.129 g (0.682 mmol) of $HOTs{\cdot}H_2O$ in 2 mL of MeCN. After the solution was stirred for 24 h, the solvent was removed, leaving a yellow solid. IR (KBr): ν_{CN} 2152, ν_{CO} 2064, 2045, 2003 cm^{-1}. When the reaction was conducted in the presence of 0.110 g (0.682 mmol, 10 fold excess) of NEt_4Cl, a homogeneous yellow solution was obtained. IR (MeCN): ν_{CN} 2146, ν_{CO} 2065, 2050, 2007 cm^{-1}.

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$Et_4N[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_3(PMe_3)]$. A yellow solution of 0.200 g (0.273 mmol) of $(Et_4N)_2[3]$ in 10 mL of MeCN was treated with 2.73 mL (0.273 mmol) of a 0.10 M HCl solution in MeCN, followed by a solution of 0.020 g (0.273 mmol) of $ONMe_3$ in 3 mL of MeCN, and then 0.55 mL (0.273 mmol) of a 0.5 M solution of PMe_3 was added. After the reaction was allowed to proceed overnight, the solvent was removed in a vacuum. After it was rinsed with ca. 30 mL of H_2O, the residue was extracted into 2 mL of MeCN, and a yellow solid precipitated upon further addition of Et_2O. Yield: 0.122 g (68%). ^1H NMR (MeCN-*d3*): δ 3.2 (q, 8H,NCH_2CH_3), 2.2 (bs, 4H, SCH_2), 2.0 (bs, 2H, SCH_2CH_2), 1.5 (d, 9H, Ru−P*Me*$_3$, J_{H-P} = 10 Hz), 1.2 (t, 12H, NCH_2CH_3), −13.7 (d, 1H, Ru-*H*-Ru, J_{H-P} = 11 Hz). ^{31}P NMR (MeCN-d_3): δ 9.54 (s). IR (MeCN): ν_{CN} 2116, 2100, ν_{CO} 2033, 1972, 1951 cm^{-1}. ESI-MS: *m*/*z* 522.0 ($[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_3(PMe_3)]^+$).

$Et_4N[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_2(PMe_3)_2]$. A yellow solution of 0.200 g (0.273 mmol) of $(Et_4N)_2[3]$ in 10 mL of MeCN was treated with 2.73 mL (0.273 mmol) of a 0.10 M HCl solution in MeCN, followed by a solution of 0.041 g (0.546 mmol) of $ONMe_3$ in 3 mL of MeCN and 2.2 mL (1.092 mmol) of a 0.50 M solution of PMe_3. After 24 h, the solvent was removed in a vacuum. After it was rinsed with 30 mL of H_2O, the residue was extracted into 2 mL of MeCN and diluted with Et_2O to give a yellow solid. Yield: 0.164 g (72%). ^1H NMR (MeCN-d_3): δ 3.2 (q, 8H,NCH_2CH_3), 2.2 (bs, 4H, SCH_2), 2.0 (bs, 2H, SCH_2CH_2), 1.5 (d, 9H, Ru−P*Me*$_3$, J_{H-P} = 11 Hz), 1.4 (d, 9H, Ru−P*Me*$_3$, J_{H-P} = 10 Hz), 1.2 (t, 12H, NCH_2CH_3), −13.1 (t, 1H, Ru-*H*-Ru, J_{H-P} = 11 Hz), −13.7 (t, 1H, Ru-*H*-Ru, J_{H-P} = 11 Hz), −15.1 (t, 1H, Ru-*H*-Ru, J_{H-P} = 11 Hz), −15.4 (t, 1H, Ru-*H*-Ru, J_{H-P} = 11 Hz). ^{31}P NMR (MeCN-d_3): δ 9.47 (s), 5.12 (s). IR (MeCN): ν_{CN} 2090, ν_{CO} 1938, 1922 cm^{-1}. ESI-MS: *m*/*z* 569.9 ($[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_2(PMe_3)_2]^+$).

Oxidation of $(Et_4N)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]$ with $FcPF_6$. A solution of 0.050 g (0.027 mmol) of $(Et_4N)_2$[**3**] in 5 mL of MeCN was cooled to −40 °C under a stream of CO and then treated with 0.009 g (0.027 mmol) of $FcPF_6$ in 5 mL of MeCN. After resulting solution was allowed to warm to room temperature, the solvent was removed in vacuo, and the residue was rinsed with 3 × 10 mL of hexanes. The residue was extracted with 2 mL of MeCN, and the addition of 35 mL of Et_2O precipitated a solid, identified spectroscopically as $Et_4N[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)_3(CO)_3]$ (see next preparation) and NEt_4[**2**]. IR (MeCN): ν_{CN} 2125, 2102, ν_{CO} 2057, 2046, 2017, 1988, 1980, 1964, 1926, 1902 cm^{-1}. ESI-MS: *m*/*z* 499.8 ($[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)_3(CO)_3]^-$), 475.8 ($[Ru_2(S_2C_3H_6)(CN)(CO)_5]^-$).

$(Et_4N)[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)_3(CO)_3]$. A solution of 0.050 g (0.027 mmol) of $(Et_4N)_2$[**3**] in 5 mL of MeCN was cooled to −40 °C under a stream of CO and then treated simultaneously with 0.018 g (0.054 mmol) of $FcPF_6$ in 5 mL of MeCN and 0.004 g (0.027 mmol) of Et_4NCN. The resulting dark yellow solution was then allowed to warm to room temperature, and the solvent was removed in vacuo. The residue was rinsed with 3 × 10 mL of hexanes. The residue was extracted into 2 mL of MeCN and precipitated upon addition of 35 mL of Et_2O. After a few hours at room temperature, the product mixture became insoluble in MeCN. IR (MeCN): ν_{CN} 2123, ν_{CO} 2059, 2016, 1979, 1902 cm^{-1}. ESI-MS: *m*/*z* 499.8 ($[Ru_2(S_2C_3H_6)(\mu\text{-}CO)(CN)_3(CO)_3]^-$).

Table 2. Crystallographic Data

	$Ru_2(S_2C_3H_6)(CO)_6$ (**1**)	$(PPN)_2[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]\cdot MeCN$ (**3**)
chemical formula	$C_9H_6O_6Ru_2S_2$	$C_{83}H_{69}N_5O_4P_4Ru_2S_2$
temp (K)	193 (2)	193(2)
cryst size (mm)	0.26 × 0.22 × 0.07	0.44 × 0.22 × 0.06
cryst syst	monoclinic	monoclinic
space group	*C*2/*m*	*P*21/*n*
a (Å)	16.643(9)	10.175(2)
b (Å)	9.798(6)	52.898(12)
c (Å)	9.177(5)	13.697(3)
α (deg)	90	90
β (deg)	91.127(10)	94.099(9)
γ (deg)	90	90
V (Å^3)	1496.1 (14)	7344 (3)
Z	4	4
density$_{calcd}$ (Mg m^{-3})	2.115	1.439
μ(Mo Kα) (mm^{-1})	0.71073	0.71073
max/min. transition	0.9931/0.6569	0.9652/0.8186
reflns measured/independent	4070/1450	46029/12954
data/restraints/params	1450/38/114	12954/85/930
GOF on F^2	1.063	0.884
R_{int}	0.0274	0.0932
R1 [$I > 2\sigma$] (all data)[a]	0.0180 (0.0219)	0.0431 (0.1035)
wR2 [$I > 2\sigma$] (all data)[b]	0.0451 (0.0463)	0.0653 (0.0753)
max peak/hole (e$^-$/Å^3)	0.313/−0.402	0.382/−0.489

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{[w(|F_o| - |F_c|)^2]/\sum[wF_o^2]\}^{1/2}$, where $w = 1/\sigma^2(F_o)$.

Crystallography. Crystals were mounted to a thin glass fiber using Paratone-N oil (Exxon). Data, collected at 198 K on a Siemens CCD diffractometer, were filtered to remove statistical outliers. The integration software (SAINT) was used to test for crystal decay as a bilinear function of X-ray exposure time and sin(Θ). The data were solved using SHELXTL by direct methods (Table 2); atomic positions were deduced from an E map or by an unweighted difference Fourier synthesis. H atom *U*’s were assigned as 1.2 U_{eq} for adjacent C atoms. Non-H atoms were refined anisotropically. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the final cycle.

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Supporting Information Available: X-ray crystallographic data for **1** and $(PPN)_2$[**3**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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