

## Contrasting Reactivity of [NO]BF<sub>4</sub> with CpRu(PPh<sub>3</sub>)(L)SR, L = PPh<sub>3</sub> or CO

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### Introduction

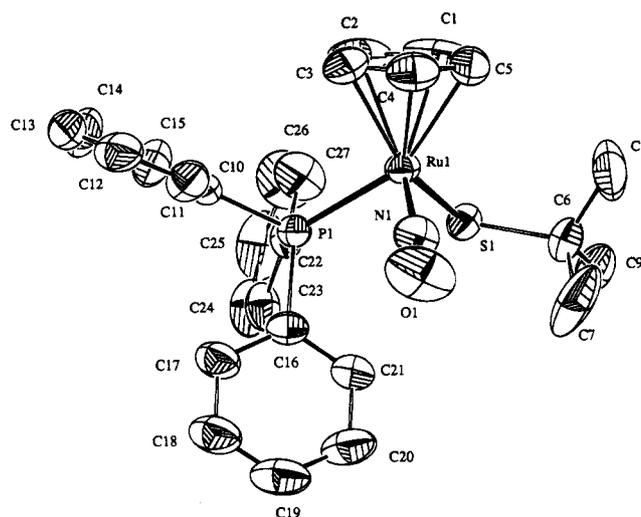
The significance of metal thiolate complexes in biological electron transfer processes<sup>1</sup> and nitrogen fixation<sup>1,2</sup> has long been recognized. Metal thiolato species are also implicated<sup>3</sup> in the hydrodesulfurization of fossil fuels. Thus the bonding properties of thiolate ligands are of continuing interest.

The stability of the electron-deficient complexes CpMo(NO)(SPh)<sub>2</sub><sup>4</sup> and Ru(SC<sub>10</sub>H<sub>13</sub>)<sub>4</sub>(NCCH<sub>3</sub>)<sup>5</sup> has been attributed to pπ–dπ donation from the thiolato ligands to the metal atoms. Molecular orbital calculations on CpFe(CO)<sub>2</sub>SH suggest<sup>6</sup> that the HOMO is an antibonding orbital involving the sulfur p and metal d orbitals whereas calculations on CpFe(CO)SH indicate<sup>6</sup> that the sulfur lone pair can stabilize this 16-electron species. Therefore one might expect 18-electron complexes containing a thiolato ligand to be chemically activated.

During the preparation of the complexes CpRu(PPh<sub>3</sub>)<sub>2</sub>SR, we noted reactivity consistent with the activation of the complexes via π donation from the thiolate ligands.<sup>7</sup> The compounds were prone to loss of PPh<sub>3</sub> leading to (1) ligand substitution in the presence of CO to give CpRu(PPh<sub>3</sub>)(CO)SR, (2) insertion of CS<sub>2</sub> into the Ru–SR bond to give CpRu(PPh<sub>3</sub>)S<sub>2</sub>CSR, (3) and aggregation in the absence of ligands to give the trimers [CpRuSR]<sub>3</sub>.<sup>8</sup> These observations raised the possibility that the relatively electron-rich compounds CpRu(PPh<sub>3</sub>)<sub>2</sub>SR might be susceptible to electrophilic attack. The complex CpRu(PMe<sub>3</sub>)<sub>2</sub>Cl reacted with NOPF<sub>6</sub> to give the stable ruthenium nitrosyl [CpRu(PMe<sub>3</sub>)<sub>2</sub>NO][PF<sub>6</sub>]<sub>2</sub> while the corresponding PPh<sub>3</sub> complex was too unstable to be isolated.<sup>9</sup> This is possibly a consequence of the lower electron density at the ruthenium atom of the latter system. The dicarbonyl thiolato complex CpRu(CO)<sub>2</sub>SPh reacted with NOPF<sub>6</sub> to give a dimer [(CpRu(CO)<sub>2</sub>)<sub>2</sub>S<sub>2</sub>Ph<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>

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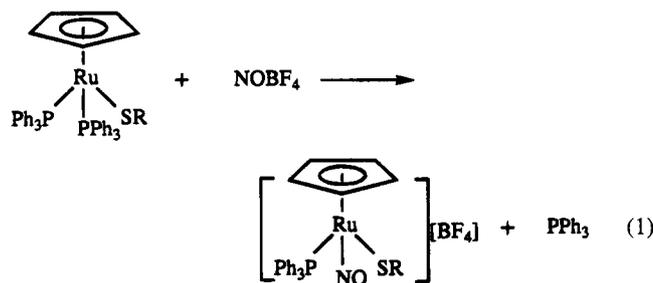


**Figure 1.** ORTEP drawing (50% probability level) of the cation [CpRu(PPh<sub>3</sub>)(NO)SR]<sup>+</sup>. Selected bond lengths (Å) and angles (deg): Ru–S, 2.386(2); Ru–P, 2.369(2); Ru–N, 1.753(6); Ru–C(1), 2.27(1); Ru–C(2), 2.22(1); Ru–C(3), 2.22(1); Ru–C(4), 2.235(9); Ru–C(5), 2.23(2); N–O, 1.148(9); S–Ru–N, 102.6(2); N–Ru–P, 93.1(2); P–Ru–S, 82.79(7); Ru–N–O, 170.7(7).

wherein the thiolato ligands had been oxidatively coupled.<sup>10</sup> Oxidation of CpRu(PPh<sub>3</sub>)<sub>2</sub>SR with dimethyldioxirane gave CpRu(PPh<sub>3</sub>)<sub>2</sub>SO<sub>2</sub>R, where R = Me, Ph, and CH<sub>2</sub>Ph.<sup>11</sup> In the last two cases the site of attack was the sulfur atom of the thiolato ligand. We report that treatment of CpRu(PPh<sub>3</sub>)(CO)SR with NOBF<sub>4</sub> gave disulfide-bridged dimeric dications analogous to those observed for the dicarbonyl complexes. However, treatment of CpRu(PPh<sub>3</sub>)<sub>2</sub>SR with NOBF<sub>4</sub> resulted in attack at the ruthenium atom to give ruthenium nitrosyl salts of the type [CpRu(PPh<sub>3</sub>)(NO)SR]BF<sub>4</sub>, where R = CMe<sub>3</sub>, CHMe<sub>2</sub>, and 4-C<sub>6</sub>H<sub>4</sub>Me.

### Results

Treatment of CpRu(PPh<sub>3</sub>)<sub>2</sub>SR with NOBF<sub>4</sub> in THF at room temperature gave [CpRu(PPh<sub>3</sub>)(NO)SR]BF<sub>4</sub>, where R = CMe<sub>3</sub>, CHMe<sub>2</sub>, and 4-C<sub>6</sub>H<sub>4</sub>Me, in isolated yields ranging from 58% to 90% (eq 1). These salts were air sensitive in solution and in



the solid state. They were soluble in acetone and in chlorinated solvents. They were characterized by IR and <sup>1</sup>H NMR spectroscopy and by elemental analyses. The structure of [CpRu(PPh<sub>3</sub>)(NO)SCMe<sub>3</sub>]BF<sub>4</sub> was determined and is depicted in Figure 1. Crystal data and selected positional parameters are given in Tables 1 and 2, respectively.

The infrared spectrum of each of the complexes displayed a strong band in the range 1817–1822 cm<sup>-1</sup> characteristic of the

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**Table 1.** Crystallographic Data for [CpRu(PPh<sub>3</sub>)(NO)SCMe<sub>3</sub>]BF<sub>4</sub>

chem formula: C <sub>27</sub> H <sub>29</sub> BF <sub>4</sub> NOPSRu	Z = 4
fw 634.44	$\rho_{\text{calc}} = 1.481 \text{ cm}^3$
space group: <i>P</i> 2 <sub>1</sub> / <i>c</i>	$\mu(\text{Mo K}\alpha) = 7.11 \text{ cm}^{-1}$
<i>a</i> = 16.380(2) Å	$\lambda = 0.71069 \text{ \AA}$
<i>b</i> = 17.135(3) Å	<i>T</i> = 22 °C
<i>c</i> = 10.137(2) Å	<i>R</i> <sup>a</sup> = 0.043
$\beta = 91.06(2)^\circ$	<i>R</i> <sub>w</sub> <sup>b</sup> = 0.047
<i>V</i> = 2937.5(1) Å <sup>3</sup>	

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}.$$

**Table 2.** Positional Parameters for [CpRu(PPh<sub>3</sub>)(NO)SCMe<sub>3</sub>]BF<sub>4</sub> Excluding Those of the Counterion, the Carbon Atoms of the PPh<sub>3</sub> Ligand, and the Hydrogen Atoms

atom	x	y	z
Ru(1)	0.18827(03)	0.04526(04)	0.23761(06)
S(1)	0.31672(11)	0.10904(11)	0.2148(02)
P(1)	0.25327(10)	-0.05445(11)	0.1163(02)
O(1)	0.1984(04)	-0.0404(04)	0.4831(06)
N(1)	0.2008(04)	-0.0044(04)	0.3878(06)
C(1)	0.1271(05)	0.1491(06)	0.1384(14)
C(2)	0.1079(07)	0.0802(09)	0.0684(09)
C(3)	0.0623(06)	0.0344(06)	0.1543(12)
C(4)	0.0566(05)	0.0715(06)	0.2708(10)
C(5)	0.0970(05)	0.1405(06)	0.2632(11)
C(6)	0.3399(05)	0.1760(05)	0.3532(07)
C(7)	0.3532(08)	0.1309(07)	0.4802(09)
C(8)	0.2757(06)	0.2384(06)	0.3708(11)
C(9)	0.4200(05)	0.2150(05)	0.3136(09)

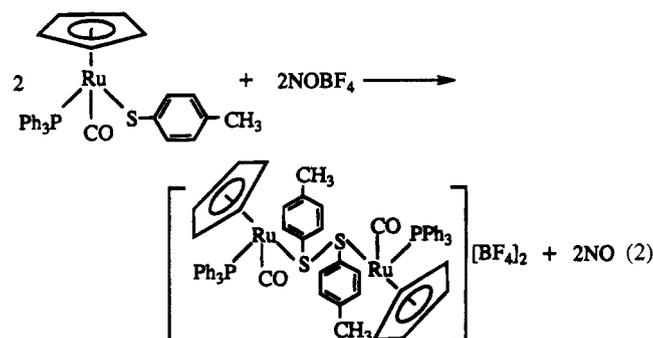
linear nitrosyl group.<sup>12</sup> In the <sup>1</sup>H NMR spectrum (acetone-*d*<sub>6</sub>) the peak due to the Cp ligand of each complex appeared in the range 6.10–6.30 ppm, whereas that for the starting complexes appeared in the range 3.93–4.26 ppm. The shift to lower field is consistent with reduction of electron density at the ruthenium atom. In the NMR spectrum of [CpRu(PPh<sub>3</sub>)(NO)SCHMe<sub>2</sub>]<sub>2</sub>BF<sub>4</sub> an overlapping doublet of doublets was observed for the diastereotopic methyl groups, which indicates that the chiral ruthenium center is configurationally stable on the NMR time scale at room temperature.

The RuNO moiety in [CpRu(PPh<sub>3</sub>)(NO)SCMe<sub>3</sub>]BF<sub>4</sub> is reasonably linear (Ru–N–O = 170.7(7)°) and the Ru–N distance (1.753(6) Å) is in the range observed for such systems (average = 1.743(27) Å).<sup>13</sup> The S–Ru–N angle (102.6(2)°) is comparable to the Cl–Ru–N angle (102.0(2)°) in [CpRu(PPh<sub>3</sub>)(NO)Cl]PF<sub>6</sub>.<sup>13</sup> The Ru–S bond distance (2.386(2) Å) is similar to that observed in complexes of the type CpRu(PPh<sub>3</sub>)(CO)E where E = SSCHMe<sub>2</sub><sup>14</sup> (2.393(3) Å), SSSC<sub>3</sub>H<sub>7</sub> (2.370(2) Å),<sup>14</sup> SS(O)CHMe<sub>2</sub> (2.379(2) Å),<sup>15</sup> SS(O)CH<sub>2</sub>Ph (2.377(3) Å)<sup>16</sup> and SS(O)<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Me (2.383(2) Å).<sup>15</sup>

The thiol complex CpRu(PPh<sub>3</sub>)<sub>2</sub>SH gave the known<sup>17</sup> S<sub>2</sub>-bridged dication [(CpRu(PPh<sub>3</sub>)<sub>2</sub>)<sub>2</sub>S<sub>2</sub>]<sup>2+</sup> upon treatment with NOBF<sub>4</sub>. The complex was isolated as the BF<sub>4</sub> salt and identified by its <sup>1</sup>H NMR spectrum.

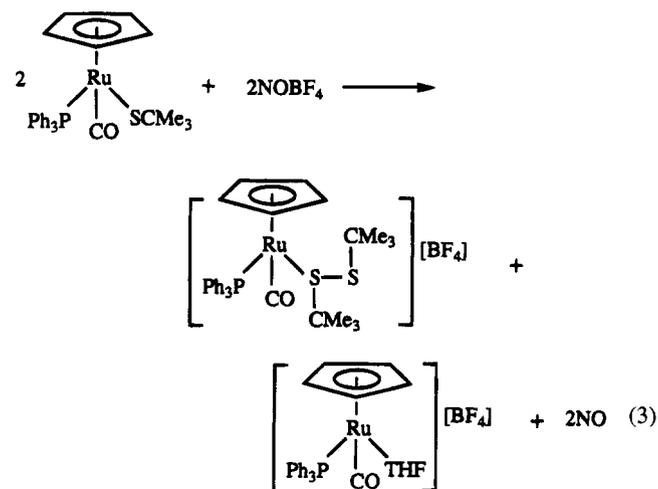
Treatment of CpRu(PPh<sub>3</sub>)(CO)S-4-C<sub>6</sub>H<sub>4</sub>Me with NOBF<sub>4</sub> in THF at room temperature gave the disulfide-bridged dicationic dimer [(CpRu(PPh<sub>3</sub>)(CO))<sub>2</sub>S<sub>2</sub>(4-C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in good yield. The infrared spectrum, the NMR spectrum, and the elemental analysis were consistent with the absence of the NO ligand and the presence of the PPh<sub>3</sub>, CO, and S-4-C<sub>6</sub>H<sub>4</sub>Me groups. In

addition the NMR spectrum (Figure 2 (supporting information)) revealed two Cp peaks in the ratio 4:1 (which varies somewhat depending on the history of the sample) each accompanied by a Me peak in the same ratio. There were also two CO stretching bands in roughly a 4:1 ratio in the infrared spectrum. These observations are consistent with the proposed formulation (eq 2) since the presence of the two chiral ruthenium centers would



be expected to generate diastereomerism and lead to the multiplicity of peaks and bands observed.

When CpRu(PPh<sub>3</sub>)(CO)SCMe<sub>3</sub> was treated with NOBF<sub>4</sub> in THF, the disulfide complex [CpRu(PPh<sub>3</sub>)(CO)S<sub>2</sub>(CMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>BF<sub>4</sub> precipitated (eq 3). Samples of the solution were taken at early



stages of the reaction, stripped to dryness and dissolved in acetone-*d*<sub>6</sub>. The NMR spectra of these samples revealed the presence of peaks due to the cation<sup>18</sup> [CpRu(PPh<sub>3</sub>)(CO)(acetone)]<sup>+</sup> in addition to those due to the disulfide complex which precipitated. Thus the monomeric disulfide product probably arises via cleavage of the corresponding dimeric dication [(CpRu(PPh<sub>3</sub>)(CO))<sub>2</sub>S<sub>2</sub>(CMe<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> as observed for the analogous reactions of CpFe(CO)<sub>2</sub>SR.<sup>19</sup>

## Discussion

Complexes of the type CpRu(CO)<sub>2</sub>SR were reported<sup>10</sup> to react with NO<sup>+</sup> to give the disulfide-bridged dication [(CpRu(CO)<sub>2</sub>)<sub>2</sub>S<sub>2</sub>R<sub>2</sub>]<sup>2+</sup>. We have observed that replacing one of the CO groups in the starting material with PPh<sub>3</sub> gave similar complexes containing disulfide ligands. However, if both CO groups were replaced by PPh<sub>3</sub> ligands, the site of attack of the NO<sup>+</sup> shifted from the sulfur atom to the ruthenium atom to give

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cations of the type  $[\text{CpRu}(\text{PPh}_3)(\text{NO})\text{SR}]^+$ . These reactions illustrate nicely the effects of the electronic and steric environment of the Cp–ruthenium thiolate moiety on its chemical reactivity.

### Experimental Section

All experiments were performed under nitrogen using standard techniques.<sup>20</sup> Tetrahydrofuran and hexanes were refluxed over sodium/benzophenone and distilled under nitrogen just prior to use. Methylene chloride was refluxed over  $\text{P}_2\text{O}_5$  and distilled under nitrogen. Absolute ethanol and spectrograde acetone were degassed by pumping followed by purging with nitrogen. Deuterated solvents (Isotec) were used as purchased. The ruthenium thiolates  $\text{CpRu}(\text{PPh}_3)(\text{L})\text{SR}$  ( $\text{L} = \text{PPh}_3, \text{CO}$ ) were prepared according to the published procedures.<sup>1</sup> The salt  $\text{NOBF}_4$  (Aldrich) was used as received.

Nuclear magnetic resonance spectra were recorded under nitrogen on a Varian XL-200 spectrometer. Chemical shifts are in ppm relative to TMS at 0 ppm. Infrared spectra were recorded on an Analect AQS-20 Fourier-transform infrared (FT-IR) spectrophotometer. Elemental analysis were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected.

**$[\text{CpRu}(\text{PPh}_3)(\text{NO})\text{SCMe}_3]\text{BF}_4$ .** In a 100-mL Schlenk flask  $\text{CpRu}(\text{PPh}_3)_2\text{SCMe}_3$  (0.51 g, 0.66 mmol) was dissolved in THF (20.0 mL),  $\text{NOBF}_4$  (0.093 g, 0.80 mmol) was added, and the solution was stirred overnight. During this time, the color became dark orange-brown and a dark red precipitate formed. The supernatant was removed with a syringe, and the precipitate was washed with diethyl ether ( $3 \times 5$  mL) and hexanes ( $3 \times 5$  mL). The resulting solid was recrystallized from acetone/hexanes to give dark red crystals (0.43 g, 84%). Mp: 198–199 °C dec. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{NO})$  1822 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ): 1.39 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 6.30 (s, 5H, Cp), 7.64 (m, 15H,  $\text{PPh}_3$ ). Anal. Calcd for  $\text{C}_{27}\text{H}_{29}\text{BF}_4\text{NOPRuS}$ : C, 51.12; H, 4.61; N, 2.21; S, 5.05. Found: C, 51.15; H, 4.65; N, 2.26; S, 5.28.

**$[\text{CpRu}(\text{PPh}_3)(\text{NO})\text{SCHMe}_2]\text{BF}_4$ .** Similarly,  $\text{CpRu}(\text{PPh}_3)_2\text{SCHMe}_2$  (0.38 g, 0.50 mmol) in THF (15.0 mL) and  $\text{NOBF}_4$  (0.070 g, 0.60 mmol) gave a brown precipitate. The supernatant was concentrated under vacuum to 3.0 mL volume, and diethyl ether (15 mL) was added to precipitate more solid. The combined solids were washed with diethyl ether ( $3 \times 5$  mL) and hexanes ( $3 \times 5$  mL) and pumped on overnight to give an orange-brown powder (0.18 g, 58%) which slowly decomposed in the solid state. This interfered with the elemental analysis. Mp: 184–186 °C dec. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{NO})$  1821 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 1.26 (d, 3H,  $\text{CHMe}_2$ ), 1.30 (d, 3H,  $\text{CHMe}_2$ ), 2.95 (septet, 1H,  $\text{CHMe}_2$ ,  $J(\text{H}-\text{H}) = 6.6$  Hz), 5.89 (s, 5H, Cp), 7.50 (m, 15H,  $\text{PPh}_3$ ).  $^1\text{H}$  NMR (acetone- $d_6$ ): 1.31 (d, 6H,  $\text{CHMe}_2$ ), 2.82 (septet, 1H,  $\text{CHMe}_2$ ,  $J(\text{H}-\text{H}) = 6.8$  Hz), 6.31 (s, 5H, Cp), 7.62 (m, 15H,  $\text{PPh}_3$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{27}\text{BF}_4\text{NOPRuS}$ : C, 50.34; H, 4.39; N, 2.26; S, 4.80. Found: C, 47.79; H, 3.82; N, 2.23; S, 5.01.

**$[\text{CpRu}(\text{PPh}_3)(\text{NO})\text{S-4-C}_6\text{H}_4\text{Me}]\text{BF}_4$ .** As above,  $\text{CpRu}(\text{PPh}_3)_2\text{S-4-C}_6\text{H}_4\text{Me}$  (0.40 g, 0.50 mmol) in THF (15.0 mL) and  $\text{NOBF}_4$  (0.070 g, 0.60 mmol) gave an orange precipitate, which was recrystallized from acetone/ethanol to give orange-red crystals (0.36 g, 90%). Mp: 218–220 °C dec. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{NO})$  1817  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ): 2.31 (s, 3H,  $\text{CH}_3$ ), 6.10 (s, 5H, Cp), 7.10 (d, 2H, 4- $\text{C}_6\text{H}_4\text{Me}$ ), 7.47 (d, 2H, 4- $\text{C}_6\text{H}_4\text{Me}$ ), 7.72 (m, 15H,  $\text{PPh}_3$ ). Anal. Calcd for  $\text{C}_{30}\text{H}_{27}$

$\text{BF}_4\text{NOPRuS}$ : C, 53.90; H, 4.07; N, 2.10; S, 4.80. Found: C, 53.66; H, 4.02; N, 2.07; S, 4.93.

**$[(\text{CpRu}(\text{PPh}_3)(\text{CO}))_2\text{S}_2(4\text{-C}_6\text{H}_4\text{Me})_2](\text{BF}_4)_2$ .** The compound  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{S-4-C}_6\text{H}_4\text{Me}$  (0.18 g, 0.31 mmol) in THF (15 mL) and  $\text{NOBF}_4$  (0.044 g, 0.37 mmol) after 3 h gave a yellow precipitate which was recrystallized from methylene chloride/hexanes to give yellow crystals (0.18 g, 87%). Mp: 185–187 °C dec. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2002 (s), 1980 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): isomer A, 2.48 (s, 3H, Me), 5.12 (s, 5H, Cp), 6.80 (m, 6H,  $\text{PPh}_3$ ), 7.40 (m, 13H, 4- $\text{C}_6\text{H}_4\text{Me}$ ,  $\text{PPh}_3$ ); isomer B, 2.33 (s, 3H, Me), 5.02 (s, 5H, Cp), 6.80 (m, 6H,  $\text{PPh}_3$ ), 7.40 (m, 13H, 4- $\text{C}_6\text{H}_4\text{Me}$ ,  $\text{PPh}_3$ ); A:B = 4:1. Anal. Calcd for  $\text{C}_{62}\text{H}_{54}\text{B}_2\text{F}_8\text{O}_2\text{P}_2\text{Ru}_2\text{S}_2$ : C, 55.86; H, 4.08; S, 4.81. Found: C, 56.15; H, 4.14; S, 4.98.

**$[\text{CpRu}(\text{PPh}_3)(\text{CO})\text{S}_2(\text{CMe}_3)_2]\text{BF}_4$ .** After 1 h,  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{-SCMe}_3$  (0.20 g, 0.37 mmol) in THF (20.0 mL) and  $\text{NOBF}_4$  (0.047 g, 0.40 mmol) gave a yellow precipitate which was recrystallized from methylene chloride/hexanes to give yellow crystals (0.082 g, 62%). Mp: 155–156 °C dec. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1984  $\text{cm}^{-1}$ .  $^1\text{H}$  HMR (acetone- $d_6$ ): 1.15 (s, 9H,  $\text{SCMe}_3$ ), 1.42 (s, 9H,  $\text{SCMe}_3$ ), 5.64 (s, 5H, Cp), 7.45 (m, 6H,  $\text{PPh}_3$ ), 7.63 (m, 9H,  $\text{PPh}_3$ ). Anal. Calcd for  $\text{C}_{32}\text{-H}_{38}\text{BF}_4\text{OPRuS}_2$ : C, 53.25; H, 5.31; S, 8.89. Found: C, 52.40; H, 5.11; S, 8.20.

**X-ray Structure Determination.** Table 1 contains the crystal parameters for  $[\text{CpRu}(\text{PPh}_3)(\text{NO})\text{SCMe}_3]\text{BF}_4$ . A red plate (0.470  $\times$  0.125  $\times$  0.500 mm) was sealed under  $\text{N}_2$  in a thin-walled glass capillary. All cell dimensions were obtained from 25 reflections with  $2\theta$  in the range 30.0–35.0°. Intensity measurements were made using a Rigaku AFC6S diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Data was initially collected on the reduced cell (triclinic), but refined coordinates indicated a possible conversion to monoclinic  $P2_1/c$  and the final solution is for this space group. A total of 8980 reflections were collected using the  $\omega/2\theta$  scan technique to a maximum  $2\theta$  value of 47.1°; of these, 4721 were unique (merging  $R = 6.4\%$ ). The intensities of three representative reflections remained constant throughout data collection. All calculations were performed using the TEXSAN system of crystallographic computer programs.<sup>21</sup> The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added in calculated positions. The  $\text{BF}_4^-$  anion was disordered over two orientations of related occupancies 0.67 and 0.33, and the fluorine atoms for each orientation were refined as a group. The disordered atoms and the boron atom, which is common to both orientations, were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 2626 observed reflections ( $I > 3.00\sigma(I)$ ).

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**Supporting Information Available:** The  $^1\text{H}$  NMR spectrum of  $[(\text{CpRu}(\text{PPh}_3)(\text{CO}))_2\text{S}_2(4\text{-C}_6\text{H}_4\text{Me})_2](\text{BF}_4)_2$  (Figure 2), a full table of positional parameters and isotopic temperature factors (Table 3), a table of anisotropic temperature parameters (Table 4), a complete table of bond lengths and angles (Table 5), and a table of hydrogen atom coordinates (Table 6) (7 pages). Ordering information is given on any current masthead page.

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