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Electron Exchange Involving a Sulfur-Stabilized Ruthenium Radical Cation

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Half-sandwich Ru(II) amine, thiol, and thiolate complexes were prepared and characterized by X-ray crystallography. The thiol and amine complexes react slowly with acetonitrile to give free thiol or amine and the acetonitrile complex. With the thiol complex, the reaction is dissociative. The thiolate complex has been oxidized to its Ru(III) radical cation and the solution EPR spectrum of that radical cation recorded. Cobaltocene reduces the thiol complex to the thiolate complex. The ^{1}H and ^{31}P NMR signals of the thiolate complex in acetonitrile become very broad whenever the thiolate and thiol complexes are present simultaneously. The line broadening is primarily due to electron exchange between the thiolate complex and its radical cation; the latter is generated by an unfavorable redox equilibrium between the thiol and thiolate complexes. Pyramidal inversion of sulfur in the thiol complex is fast at room temperature but slow at lower temperatures; major and minor conformers of the thiol complex were observed by ^{31}P NMR at –98 °C in CD_2Cl_2.

Introduction

Chiral nitrogen and sulfur ligands are potential resolving agents for chiral-at-metal transition-metal complexes, and ligand lability is important in catalytic ionic hydrogenations.[1] We set out to assess the differences in structure and reactivity of Ru(II) complexes with amine, thiol, and thiolate ligands (Figure 1) and to study their substitution kinetics and redox chemistry.

Transition-metal thiol complexes are often unstable because coordinated thiols can be acidic, and some of their complexes are easily oxidized.[2] Treichel found the iron thiol complex $[CpFe(CO)_2SHPh]BF_4$ to be a strong acid,[3] while Puerta found that electron rich half-sandwich Ru(II) thiol complexes are easily oxidized.[4]

We have observed line broadening in the NMR spectra of mixtures of the thiolate and thiol complexes. By conducting low-temperature NMR experiments and studying the redox chemistry of the thiol and thiolate complexes **1** and **3**, we have determined that the line broadening is largely due to electron exchange between the thiolate complex and its radical cation.

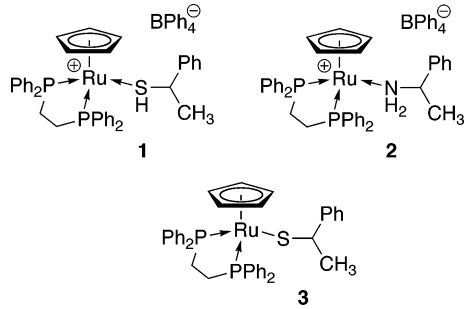

Figure 1.

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Hexanes were deoxygenated and dried by two successive activated alumina columns under argon. Benzene, toluene, ether, and THF were distilled from Na and benzophenone under a nitrogen atmosphere. HPLC grade acetonitrile (J. T. Baker) was sparged with N_2 and dried over 4 Å molecular sieves. Water was deionized with a Barnstead NANOpure water system. CD_2Cl_2 was dried over CaH_2, degassed by three freeze−pump−thaw cycles, and then purified by vacuum transfer at room temperature. $CDCl_3$ was degassed by three freeze−pump−thaw cycles and dried over 4 Å molecular sieves. UV−visible spectra were obtained on a HP 8453 spectrophotometer with a 1 cm quartz cell.

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Cyclic voltammetry was performed with a BAS CV-50W potentiostat. The supporting electrolyte for all solutions was 0.10 M $[Bu_4N]PF_6$ in acetonitrile. The cell consisted of a platinum (1.6 mm diameter) or glassy carbon disk (5.0 mm diameter) working electrode, a silver wire reference electrode (0.01 M $AgNO_3$ + 0.10 M $[Bu_4N]PF_6$), and a platinum wire auxiliary electrode (0.10 M $[Bu_4N]PF_6$). Fc/Fc^+ (0.001 M) was used as an external reference and was found to be +87 mV with respect to our reference electrode. All samples were prepared under a N_2/Ar atmosphere and sparged with Ar before analysis. Analyte concentrations were 0.001 M, and all scans were recorded at 100 mV/s.

Variable Temperature NMR Studies. Probe temperatures below room temperature were calibrated with a Wilmad chemical shift thermometer (99.97% methanol + 0.03% HCl).[5] Temperatures above room temperature were calibrated with an ethylene glycol chemical shift thermometer.[6]

Ligand Substitution Kinetics in CD_3CN. The ruthenium thiol or amine complex (0.005 mmol) and the internal standard anisole (1.0 μL) were added to 0.75 mL of CD_3CN in an NMR tube under an inert atmosphere. The tube was sealed and inserted into a preheated NMR probe calibrated at 341 K. The disappearance of the amine complex was monitored via the height of the Cp singlet (δ 4.51). The disappearance of the thiol complex was monitored via the height of the coordinated thiol methyl doublet (δ 1.06).

Ligand Substitution Kinetics in CD_3NO_2. The ruthenium thiol complex (0.012 mmol) and 4 equiv of CH_3CN were dissolved in 1.0 mL of CD_3NO_2. The tube was sealed and inserted into a preheated NMR probe calibrated at 341 K. The reaction was monitored via the ratio of the height of the free thiol doublet (δ 1.66) to that of the tetraphenylborate resonance (δ 6.84). The reaction was repeated with 16 equiv of CH_3CN.

$RuCl_2(PPh_3)_3$ was prepared in high yield on a large scale by a procedure derived from published methods.[7] $RuCl_3 \cdot 3H_2O$ (15.0 g, 57.0 mmol) was refluxed with PPh_3 (90.0 g, 343.5 mmol) in 3.25 L of deoxygenated anhydrous methanol for 2 h and 30 min. The liquid was decanted, and the remaining black solid loaded on a Schlenk frit, washed with ether (3 × 100 mL), and dried under vacuum overnight to give the product (52.0 g, 54.2 mmol) in 95% yield. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ −3.96 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 127.47 (m), 128.68 (m), 129.37 (s), 132.17 (m), 133.92 (m), 135.36 (m).

CpRu(dppe)Cl[8] was prepared by boiling a solution of $RuCl_2(PPh_3)_3$ (6.0 g, 6.27 mmol) and sodium cyclopentadienide[9] (0.59 g, 6.69 mmol) in 100 mL of dry THF for 3 h. An orange precipitate formed after evaporation of $^3/_4$ of the solvent and addition of 100 mL of hexanes, which was washed with hexanes and dried under vacuum. The resulting solid was boiled with 1,2-bis(diphenylphosphino)ethane (2.50 g, 6.28 mmol) in 85 mL of toluene for 15 h. The reaction mixture was filtered, and the filtrate was loaded onto the top of a silica column (8 cm × 2 cm diameter). Excess phosphines were eluted with benzene, and the product was eluted with a 1:1 benzene−ether mixture. Evaporation of the solvent gave the yellow product (2.16 g, 3.60 mmol) in 57% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 2.33−2.47 (m, $Ph_2PCH_2CH_2PPh_2$, 2H), 2.55−2.70 (m, $Ph_2PCH_2CH_2PPh_2$, 2H), 4.54 (s, *Cp*, 5H), 7.10−7.19 (m, *Ar*, 4H), 7.24−7.43 (m, *Ar*, 12H), 7.82−7.91 (m, *Ar*, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 79.90 (s).

[CpRu(dppe)(α-methylbenzylthiol)][BPh_4] (1). Sodium tetraphenylborate (445 mg, 1.30 mmol) and racemic α-methylbenzylthiol[10] (180 μL, 1.30 mmol) were refluxed with CpRu(dppe)Cl (600 mg, 1.0 mmol) in 50 mL of methanol for 90 min. The precipitate was filtered, washed with water and methanol, and dried under vacuum to give the yellow-green product (910 mg, 0.89 mmol) in 89% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.06 (d, CH_3, J_{H-H} = 6.8 Hz, 3H), 1.85−1.92 (m, S*H*, 1H), 2.30−2.64 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 2.71−2.81 (m, C*H*, 1H), 4.59 (s, *Cp*, 5H), 6.82−6.90 (t, *Ar*, 6H), 6.97−7.04 (t, *Ar*, 8H), 7.15−7.22 (t, *Ar*, 2H), 7.26−7.36 (m, *Ar*, 12H), 7.37−7.67 (m, *Ar*, 17H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): AB pattern, δ 78.28 (d, J_{P-P} = 25.8 Hz), 79.29 (d, J_{P-P} = 25.8 Hz). Anal. Calcd for $C_{63}H_{59}BP_2SRu$: C, 74.04; H, 5.82; S, 3.14. Found: C, 74.06; H, 5.84; S, 3.04.

[CpRu(dppe)(α-methylbenzylamine)][BPh_4] (2). Sodium tetraphenylborate (161 mg, 0.47 mmol) and racemic α-methylbenzylamine (61 μL, 0.47 mmol) were refluxed with CpRu(dppe)Cl (235 mg, 0.39 mmol) in 20 mL of methanol for 60 min. The precipitate was filtered, washed with water and methanol, and dried under vacuum to give the yellow product (270 mg, 0.27 mmol) in 69% yield. ^1H NMR (400 MHz, CD_3CN): δ 0.61 (d, CH_3, J_{H-H} = 6.4 Hz, 3H), 1.48 (br, NH_2, 1H), 1.62 (br, NH_2, 1H), 2.21−2.65 (m, $Ph_2PCH_2CH_2PPh_2$, 3H), 2.72−2.90 (m, $Ph_2PCH_2CH_2PPh_2$, 1H), 3.20−3.30 (m, C*H*, 1H), 4.51 (s, *Cp*, 5H), 6.59−6.64 (m, *Ar*, 2H), 6.81−6.87 (m, *Ar*, 4H), 6.96−7.02 (m, *Ar*, 8H), 7.22−7.30 (m, *Ar*, 13H), 7.32−7.39 (m, *Ar*, 2H), 7.40−7.45 (m, *Ar*, 3H), 7.45−7.49 (m, *Ar*, 3H), 7.51−7.58 (m, *Ar*, 3H), 7.58−7.66 (m, *Ar*, 3H), 7.71−7.78 (m, *Ar*, 2H), 7.84−7.90 (m, *Ar*, 2H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_3CN): AB pattern, δ 81.96 (d, J_{P-P} = 25.4 Hz), 82.88 (d, J_{P-P} = 25.4 Hz). Anal. Calcd for $C_{63}H_{60}NBP_2Ru$: C, 75.29; H, 6.02; N, 1.39. Found: C, 75.34; H, 5.92; N, 1.49.

CpRu(dppe)(α-methylbenzylthiolate) (3). The thiol complex **1** (440 mg, 0.43 mmol) was stirred in 10 mL of CH_3CN, and NEt_3 (0.88 mL, 6.45 mmol) was added in one portion, giving a yellow solution which was placed in a refrigerator at −24 °C overnight. The solvent was carefully decanted from the orange crystals that formed. The crystals were washed with CH_3CN (2 × 0.5 mL) and dried under vacuum to give the analytically pure thiolate complex (285 mg, 0.41 mmol) in 94% yield. ^1H NMR (300 MHz, CD_3CN): δ 0.78 (d, CH_3, J_{H-H} = 6.6 Hz, 3H), 2.05−2.23 (m, $Ph_2PCH_2CH_2PPh_2$, 2H), 2.28−2.50 (m, $Ph_2PCH_2CH_2PPh_2$, 1H), 2.62−2.85 (m, $Ph_2PCH_2CH_2PPh_2$, 1H), 3.10 (q, br, C*H*, 1H), 4.43 (s, *Cp*, 5H), 7.00−7.34 (m, *Ar*, 15H), 7.39−7.51 (br, *Ar*, 6H), 7.78−7.91 (m, *Ar*, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): AB pattern, δ 81.53 (d, J_{P-P} = 26.8 Hz), 82.83 (d, J_{P-P} = 26.8 Hz). The NMR spectra are often broad but sharpened by the addition of a small amount of Cp_2Co. FAB^+ MS: *m/z* 702.13 $[M + 1]^+$. Anal. Calcd for $C_{39}H_{38}P_2SRu$: C, 66.74; H, 5.46; S, 4.57. Found: C, 66.59; H, 5.62; S, 4.40.

[CpRu(dppe)(α-methylbenzylthiolate)][PF_6] (5-PF_6) was prepared as a 0.05 M solution in CH_2Cl_2 by treating **3** with an equimolar quantity of $[NO]PF_6$. Gas evolution appeared to be complete within 1 h, but residual gas was removed by four freeze−pump−thaw cycles. The X-band EPR of a 5 × 10^{-4} M sample was performed on a Bruker EMX EPR spectrometer with a TE_{102} rectangular cavity: microwave frequency 9.731 GHz; microwave

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Table 1. Summary of Crystallographic Data

	1	2	3
empirical formula	$C_{63}H_{59}BP_2RuS$	$C_{63}H_{60}BNP_2Ru$	$C_{39}H_{38}P_2RuS$
formula weight	1021.98	1004.94	701.76
crystal shape	yellow plate	yellow needle	orange block
crystal size (mm)	0.30 × 0.10 × 0.03	0.30 × 0.15 × 0.15	0.20 × 0.20 × 0.20
temp (K)	125(2)	125(2)	243(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	11.4497(6)	11.5351(11)	12.1405(5)
b (Å)	23.7658(13)	23.674(2)	20.7461(8)
c (Å)	18.9148(10)	18.6041(17)	14.1678(5)
α (deg)	90	90	90
β (deg)	101.4350(10)	100.6360(10)	109.8180(10)
γ (deg)	90	90	90
V (Å^3)	5044.8(5)	4993.1(8)	3357.1(2)
Z	4	4	4
d_{calc} (g/cm^3)	1.346	1.337	1.388
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.457	0.420	0.651
data collected	81097	88343	23868
unique data	15473	18388	7888
data/restraints/params	15473/2/637	18388/3/648	7888/0/388
GOF on F^2	1.008	1.024	1.014
R1, wR2 [$I > 2\sigma(I)$]	0.0511, 0.1040	0.0337, 0.0796	0.0342, 0.0747
R1, wR2 (all data)	0.0983, 0.1235	0.0507, 0.0878	0.0590, 0.0828

power 63.616 mW; modulation amplitude 4.00 G; center field 3350 G. Simulation was performed with Bruker WINEPR SimFonia version 1.0 software.

[CpRu(dppe)CD$_3$CN][BPh$_4$]. The thiol complex **1** (0.01 mmol) was dissolved in 0.75 mL of CD_3CN and heated to 75 °C for 2 h and 30 min. The ^{1}H NMR spectrum showed free thiol and complete conversion to the CD_3CN complex. ^{1}H NMR (300 MHz, CD_3CN): δ 2.49−2.64 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 4.72 (s, *Cp*, 5H), 6.80−6.88 (m, *Ar*, 4H), 6.94−7.03 (m, *Ar*, 8H), 7.20−7.57 (m, *Ar*, 24H), 7.70−7.82 (m, *Ar*, 4H). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN): δ 79.33 (s). The addition of 1 equiv of Cp_2Co left the spectra unchanged.

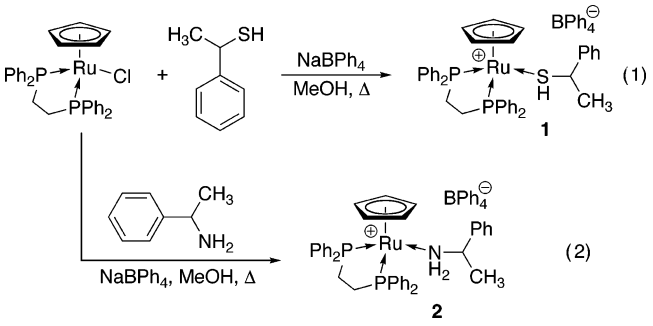
X-ray Structure Determinations. Crystals of **1** and **2** were grown by slow diffusion of a layer of methanol into concentrated CH_2Cl_2 solutions. Crystals of **3** were grown by slow evaporation of a concentrated CD_3CN solution. The hydrogen atom on the sulfur of **1** was not found. The thiol ligand of **1** was disordered, and the minor component was refined isotropically. The amine ligand of **2** was also disordered. The minor component of the disordered amine group was refined isotropically, and the protons on nitrogen were placed in idealized positions; the protons on the nitrogen of the major component were located and refined.

For **1** and **2**, data were collected on a Bruker Apex II diffractometer; for **3**, data were collected on a Bruker P4 diffractometer. The structures were solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures using SHELXTL version 5.10 software. Hydrogen atoms on carbon were included in calculated positions.

Results and Discussion

Thiol and Amine Complexes. Halide dissociation from the complexes $CpRu(PR_3)_2Cl$ is known to occur readily in polar solvents (methanol, acetonitrile, and dimethylsulfoxide) and is promoted by the presence of a suitable halide acceptor (Na^+ or NH_4^+).[11,12] Cationic complexes $[CpRu(PR_3)_2L]^+$ form in the presence of a coordinating ligand or solvent.[8a]

We thus prepared compound **1** in high yield by treating CpRu(dppe)Cl with *rac*-α-methylbenzylthiol in the presence of $NaBPh_4$ in refluxing methanol (eq 1). Treichel has prepared cationic ruthenium *tert*-butyl thiol complexes under similar conditions.[2] The racemic amine complex **2** was obtained analogously (eq 2).



Compounds **1** and **2** are yellow-green and yellow, respectively. They may be handled in air when dry and are moderately soluble in CH_3CN and CH_2Cl_2. Complexes **1** and **2** both display an AB pattern in their ^{31}P NMR spectra; the two phosphorus atoms are diastereotopic because of the chiral thiol or amine ligand. X-ray analysis of crystals of **1** and **2** (Table 1, Figures 2 and 3) showed that, in both structures, the phenyl group of the thiol or amine ligand is oriented toward the Cp ring and away from the phosphine phenyl groups. The Ru−S bond length of 2.3412(13) Å in **1** is comparable to that of 2.369(2) Å in $[CpRu(PPh_3)_2(C_6H_5CH_2CH_2SH)][BF_4]$[13] and 2.377(2) Å in $[CpRu(PPh_3)_2(n\text{-PrSH})][BF_4]$[14]

Ligand Substitution Kinetics. The thiol compex **1** and the amine complex **2** form [CpRu(dppe)CD$_3$CN][BPh$_4$] over the course of several days at room temperature in CD_3CN.

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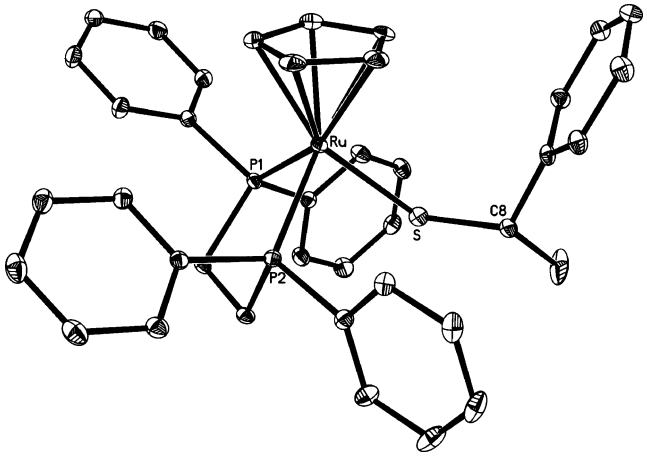


Figure 2. Molecular structure of **1** (20% probability level). Counterion and hydrogen atoms omitted for clarity. The hydrogen atom on sulfur was not found. Selected distances (Å) and angles (deg): Ru−S 2.3412(13), Ru−P1 2.2911(7), Ru−P2 2.2842(7), Ru···C8 3.60, Ru−S−C8 118.79(14), P1−Ru−P2 83.79(3), P1−Ru−S 88.20(4), P2−Ru−S 86.22(4).

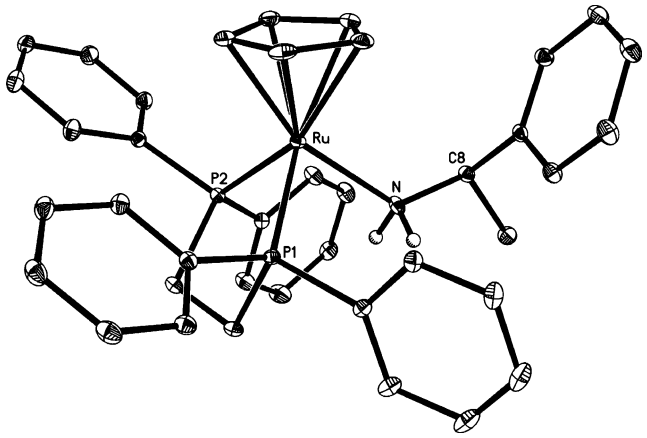
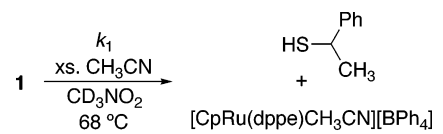


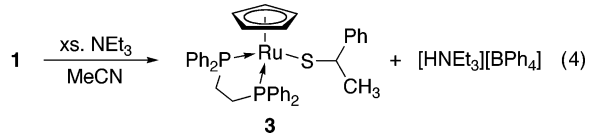
Figure 3. Molecular structure of **2** (20% probability level). Counterion and hydrogen atoms except those on nitrogen omitted for clarity. Selected distances (Å) and angles (deg): Ru−N 2.211(3), Ru−P1 2.2842(4), Ru−P2 2.2879(4), Ru···C8 3.34, Ru−N−C8 128.5(3), P1−Ru−P2 83.445(14), P1−Ru−N 85.7(2), P2−Ru−N 91.84(10).

Monitoring these reactions by ^{1}H NMR spectroscopy gave first-order rate constants (at 68 °C) of $5.2(2) \times 10^{-4}$ s^{-1} for **1** and $5.5(1) \times 10^{-4}$ s^{-1} for **2**—rate constants approximately 40 times greater than that determined by Treichel and Vincenti for the solvolysis of CpRu(dppe)Cl in CD_3CN under similar conditions.[12] In the polar but less coordinating solvent CD_3NO_2, the rate proved to be independent of [CH_3CN], so the reaction of the thiol complex with CH_3CN is a dissociative first-order process (eq 3). At 68 °C k_1 is $2.6(1) \times 10^{-4}$ s^{-1}.



$$-\frac{d[\mathbf{1}]}{dt} = k_1[\mathbf{1}] \qquad (3)$$

Deprotonation of the Thiol Complex 1 and Oxidation of the Resulting Thiolate Complex 3. Thiolate complexes $CpRu(PPh_3)_2SR$ (R = alkyl) are known; Shaver prepared several by treating $CpRu(PPh_3)_2Cl$ with thiolate anions in THF.[15] The orange thiolate complex **3** is obtained by treating **1** with excess NEt_3 in acetonitrile (eq 4). As with complexes **1** and **2**, the ^{31}P NMR spectrum of **3** displays an AB pattern. Crystals of **3** are readily formed by cooling or slowly evaporating concentrated acetonitrile solutions. Slow evaporation of a CD_3CN solution gave a crystal suitable for X-ray analysis (Table 1, Figure 4). Like the thiol and amine complexes, the phenyl group of the thiolate is oriented away from the phosphine phenyl groups. The Ru−S bond length of 2.4019(7) Å in **3** is similar to the 2.420(4) Å found in CpRu(dippe)SPh.[4]



Compound **3** is oxidized by $[NO]PF_6$ to the Ru(III) radical cation **5** (eq 5). Such half-sandwich 17-electron radical cations of iron[16,17] and ruthenium[18,19] are well-known. The EPR spectrum of **5**-PF_6 in CH_2Cl_2 (Figure 5) shows hyperfine coupling to two ^{31}P and $^{99/101}$Ru, although the spectrum is broad. Broad solution EPR spectra have been observed by Díaz for sulfur-stabilized iron radical cations, albeit without hyperfine splitting.[17a]

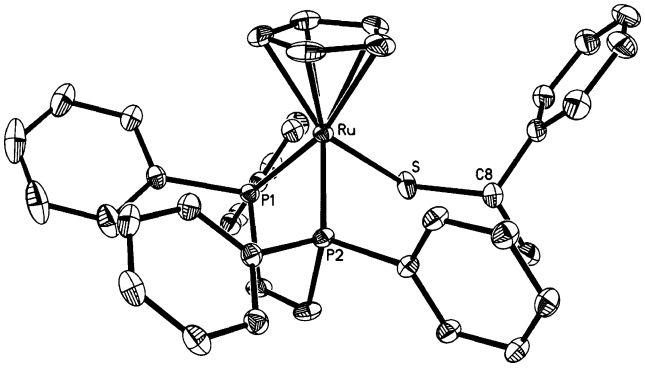


Figure 4. Molecular structure of **3** (20% probability level). Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): Ru−S 2.4019(7), Ru−P1 2.2613(6), Ru−P2 2.2483(6), Ru···C8 3.50, Ru−S−C8 110.80(9), P1−Ru−P2 82.65(2), P1−Ru−S 82.87(2), P2−Ru−S 87.86-(3).

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(16) Iron radical cations: (a) Tilset, M.; Fjeldahl, I.; Hamon, J.-R.; Hamon, P.; Toupet, L.; Saillard, J.-Y.; Costuas, K.; Haynes, A. *J. Am. Chem. Soc.* **2001**, *123*, 9984−10000. (b) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429−1431. (c) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77−88.

(17) Sulfur-stabilized iron radical cations: (a) Díaz, C. *Bol. Soc. Chil. Quím.* **1999**, *44*, 315−320. (b) Díaz, C.; Leal, C.; Yutronic, N. *J. Organomet. Chem.* **1996**, *516*, 59−64. (c) Treichel, P. M.; Rosenhein, L. D.; Schmidt, M. S. *Inorg. Chem.* **1983**, *22*, 3960−3965. (d) Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191−197.

(18) Ruthenium radical cations: (a) Guan, H.; Saddoughi, S. A.; Shaw, A. P.; Norton, J. R. *Organometallics* **2005**, *24*, 6358−6364. (b) Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed., Engl.* **1997**, *36*, 65−67. (c) Hembre, R. T.; McQueen, J. S.; Day, V. W. *J. Am. Chem. Soc.* **1996**, *118*, 798−803. (d) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−8689.

(19) Sulfur-stabilized ruthenium radical cations: See refs 2 and 4, also: Treichel, P. M.; Schmidt, M. S.; Crane, R. A. *Inorg. Chem.* **1991**, *30*, 379−381.

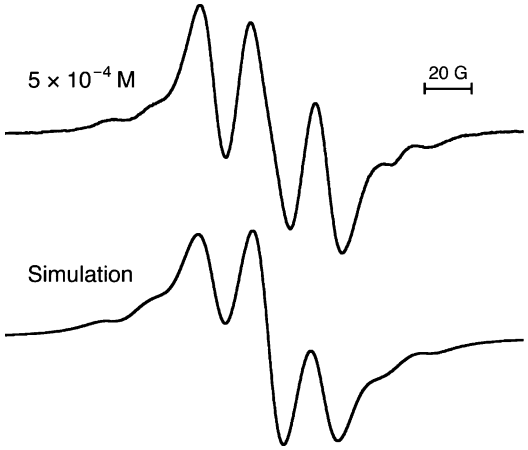


Figure 5. EPR spectrum (9.731 GHz, $g = 2.075$) of **5**-PF_6 in CH_2Cl_2 at room temperature (top). Simulation (bottom) used $a_{Ru} = 16.0$ G; $a_P = 21.4$ G; $a_S = 15.0$ G; line broadening 13.70 G.

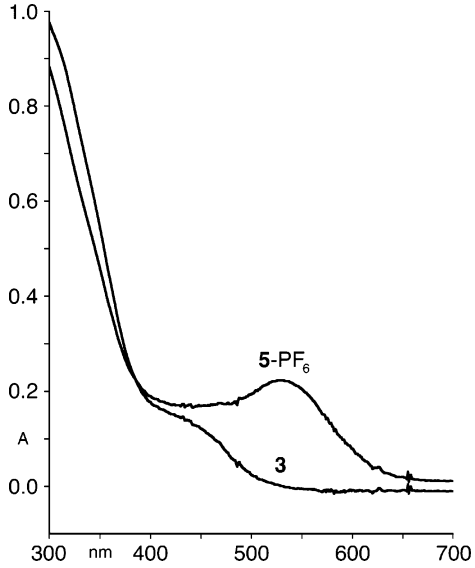
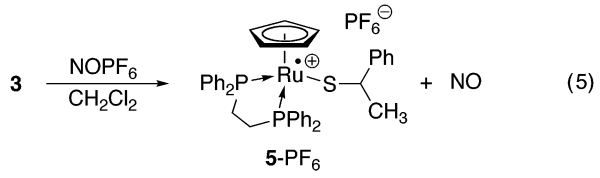


Figure 6. Overlaid UV-visible spectra of **3** (2×10^{-4} M) and **5**-PF_6 (2×10^{-4} M) in CH_2Cl_2.

Concentrated deep purple CH_2Cl_2 solutions of **5**-PF_6 stored under an inert atmosphere in ambient light gradually decompose (turning brown) over the course of several days at room temperature.



(5)

Dilute solutions of **3** and **5**-PF_6 are yellow and purple, respectively, and may be distinguished by their UV-visible spectra (Figure 6).

Cyclic Voltammetry Studies of 3 and 1. In CH_3CN the thiolate complex **3** is reversibly oxidized by one electron, presumably to the same radical cation **5** (the cyclic voltammogram is shown in Figure 7). From the **3**/**5** potential

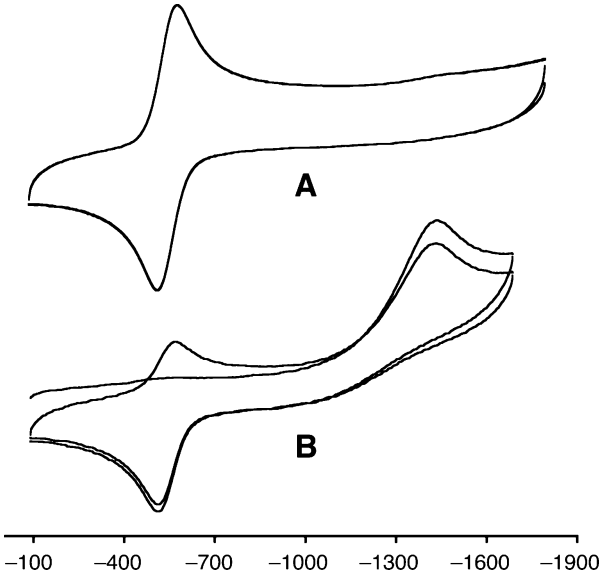


Figure 7. Cyclic voltammograms (platinum disk working electrode) of **3** (A) and **1** (B) in CH_3CN at 100 mV/s. Potentials (mV) vs Fc/Fc^+ in CH_3CN.

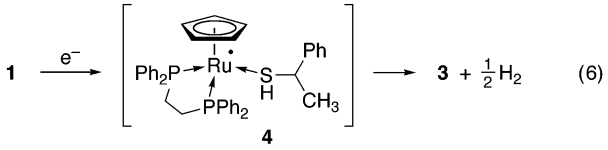
Table 2. Redox Potentials[a]

compound	potential	process
1	[−1429]	reduction
3	−544	oxidation
Cp_2Co	(−1334, Δ73)	oxidation
Cp^*_2Co	(−1912, Δ90)	oxidation

[a] All potentials (mV) in CH_3CN at 100 mV/s vs Fc/Fc^+. A platinum disk working electrode was used. Brackets indicate an irreversible peak. Parentheses enclose $E_{1/2}$ and $E_{pa} - E_{pc}$ for quasireversible processes. Plain text indicates $E_{1/2}$ for a reversible process where $E_{pa} - E_{pc} = 59$ mV and $I_a/I_c = 1$.

(Table 2), Cp_2Co should reduce the radical cation **5**, and that prediction has been confirmed experimentally.

In contrast, the thiol complex **1** is *irreversibly* reduced (Figure 7). Subsequent scans show peaks for the **3**/**5** couple, implying that **3** and presumably H_2 are the products of the irreversible reduction of **1**. A 19-electron complex **4** is drawn in eq 6 as an intermediate in a stepwise mechanism, although there is no evidence precluding a ring slip to η^3 or the dissociation of one arm of the chelating diphosphine.[20]



(6)

(20) Several half-sandwich cyclopentadienyl complexes of group 8 metals have been reported that are ostensibly 19-electron, but in no case has their structure been determined by X-ray crystallography; it is possible that they are really 17-electron complexes. (a) Hamon, P.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1602−1603. (b) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471−5483. (c) Aase, T.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4974−4975. (d) Ruiz, J.; Guerchais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 812−813. (e) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817−819.

Scheme 1

$$Cp_2Co + H^+ \rightleftharpoons Cp_2CoH^+$$

$$Cp_2CoH^+ + Cp_2Co \rightleftharpoons Cp_2CoH + Cp_2Co^+$$

$$Cp_2CoH + H^+ \longrightarrow Cp_2Co^+ + H_2$$

Organic thiols are known to undergo S−H bond cleavage upon reduction at transition-metal electrodes.[21] At a platinum electrode, it is likely that **1** proceeds directly to **3** as shown in eq 7.

$$\mathbf{1} \xrightarrow[-H^\bullet]{+e^-} \mathbf{3} + [H]_{ads} \longrightarrow \tfrac{1}{2}H_2 \qquad (7)$$

We reduced **1** at a glassy carbon electrode (as a reviewer suggested) in an attempt to observe a return oxidation peak (**4** → **1**). Except for a shift in the irreversible cathodic peak to −2110 mV (vs Fc/Fc^+), the voltammogram was the same as that obtained with a platinum electrode, and the thiolate complex **3** was observed on subsequent scans as in Figure 7.

Díaz has observed complexity in the electrochemistry of [CpFe(dppe)SR][PF_6] arising from the involvement of disulfides.[22] We have not observed any analogous complications in our ruthenium system; the **3**/**5** couple is straightforwardly reversible.

Chemical Reduction of the Thiol Complex 1. Although the irreversible cathodic peak for **1** (Table 2) occurs at a more negative potential than the Cp_2Co/Cp_2Co^+ couple, Cp_2Co cleanly reduces **1** to **3** (eq 8). Only **3** and Cp_2Co^+ are observed by the time the ^1H NMR spectrum of a **1**/Cp_2Co solution can be recorded (5−10 min).

$$\mathbf{1} \xrightarrow[CD_3CN]{Cp_2Co} \mathbf{3} + [Cp_2Co][BPh_4] + \tfrac{1}{2}H_2 \qquad (8)$$

An analogous reaction of Cp_2Co is that with strong acids, giving Cp_2Co^+ and hydrogen. Koelle has shown that Cp_2CoH^+ is involved.[23,24] The most plausible mechanism consistent with his pulse radiolysis experiments is shown in Scheme 1.

The reduction in eq 8 may proceed by electron transfer from Cp_2Co to **1**, followed by disproportionation of **4** (Scheme 2). It is also possible that Cp_2CoH^+ is generated by $H^\bullet$ transfer from **4** to Cp_2Co^+ after or concurrent with the initial reduction and then evolves hydrogen via the last two equations in Scheme 1.

Scheme 2

$$\mathbf{1} + Cp_2Co \longrightarrow \mathbf{4} + [Cp_2Co][BPh_4]$$

$$\mathbf{4} \longrightarrow \tfrac{1}{2}H_2 + \mathbf{3}$$

Attempted Deprotonation and Reduction of the Amine Complex 2. We have not been able to deprotonate the amine complex **2** in acetonitrile, even with strong bases such as DBN (1,5-diazabicyclo[4.3.0]non-5-ene) or TMG (1,1,3,3-tetramethylguanidine). This is not surprising given that amide complexes comparable to the one that would result are extremely basic.[25] Complex **2** is not reduced by Cp_2Co, but is by Cp^*_2Co, giving unidentified products and free amine.

NMR Line Broadening of the Thiolate Complex 3. We attempted (unsuccessfully) to estimate the pK_a of the thiol complex **1** in CD_3CN by treating it with various amines and monitoring the resulting **1**/**3** equilibria by ^1H NMR. We expected both NEt_3 and DBN to deprotonate **1** (eq 9), given that NEt_3 was used for the synthesis of **3** in high yield from **1**.

$$\underset{\mathbf{1}}{Ru^+{-}SHR} \xrightleftharpoons[CD_3CN]{NEt_3 \text{ or DBN}} \underset{\mathbf{3}}{Ru{-}SR} \qquad (9)$$

However, when **1** was treated with a single equiv of NEt_3 or DBN in an NMR tube, the ^1H NMR peaks of the resulting **3** were broad, while the peaks of the resulting Et_3NH^+ or $DBNH^+$ were sharp. In a ^{31}P NMR spectrum, **3** appeared only as a broad featureless bump, although cooling the tube to −51 °C resulted in the appearance of the two doublets (J_{P-P} = 26.4 Hz, δ 82.9 and 80.1) of **3**.[26]

We suspected this line broadening arose from traces of **1**. The addition of 6 equiv of DBN to **1** (ensuring that essentially no **1** remained) resulted in a sharp spectrum of **3**. The addition of a small amount of Cp_2Co to an equimolar mixture of **1** and NEt_3 eliminated broadening of the peaks of **3** in the ^1H NMR and ^{31}P NMR spectra, causing us to suspect electron exchange between **3** and its radical cation **5**. (We have experience with the effects of Ru(II)/Ru(III) electron exchange on NMR spectra.[18a])

To generate a mixture of **3** and **5** uncomplicated by the presence of **1**, we added a small (substoichiometric) amount of [NO]PF_6 to a saturated solution of **3** in CD_3CN; its Cp ^1H NMR singlet and thiolate doublet broadened into the baseline. The addition of Cp_2Co made the spectra of **3** sharp again, presumably by reducing the **5**. Thus *the broadening above is caused by fast electron exchange between **3** and **5***.

Electron Transfer from the Thiolate Complex 3 to the Thiol Complex 1. Treating **1** with *half* an equivalent of NEt_3 gave a mixture of **1** and **3** that we used for a variable temperature NMR study (eq 10).

At room temperature, the ^{31}P NMR signal of the thiolate complex appeared as a broad featureless lump in the baseline,

(21) Bukhtiarov, A. V.; Mikheev, V. V.; Lebedev, A. V.; Tomilov, A. P.; Kuz'min, O. V. *Zh. Obshch Khim.* **1988**, *58*, 684−692. English translation: *J. Gen. Chem. USSR.* **1988**, *58*, 605−612.

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(23) Koelle, U.; Infelta, P. P.; Grätzel, M. *Inorg. Chem.* **1988**, *27*, 879−883.

(24) The third equation in Scheme 1 reflects the ease with which a hydride ligand can serve as the kinetic site for protonation of a hydride complex: Papish, E. T.; Magee, M. P.; Norton, J. R. Protonation of Transition Metal Hydrides to Give Dihydrogen Complexes: Mechanistic Implications and Catalytic Applications. In *Recent Advances in Hydride Chemistry;* Poli, R., Ed.; Elsevier: New York, 2001; pp 39−74.

(25) (a) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781−2794. (b) Kaplan, A. W.; Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6828−6829.

(26) At room temperature in CD_3CN, **3** appears as an AB pattern centered about δ 82.2 ($\Delta\nu$ = 1.3 ppm, J_{P-P} = 26.8 Hz). The temperature dependence of the ^{31}P NMR spectrum was confirmed by obtaining low-temperature spectra of a genuine sample.

$$\underset{\mathbf{1}}{\overset{+}{\text{Ru}}\text{—SHR}} \xrightarrow[\text{CD}_3\text{CN}]{\frac{1}{2}\,\text{NEt}_3} \frac{1}{2}\,\underset{\mathbf{1}}{\overset{+}{\text{Ru}}\text{—SHR}} + \frac{1}{2}\,\underset{\mathbf{3}}{\text{Ru—SR}} \qquad (10)$$

while the AB pattern of the thiol complex was broadened but still clearly visible. As the temperature was lowered, the peaks of the thiolate complex sharpened (Figure 8). This indicated the operation of a process that selectively broadened the peaks of the thiolate complex.

We believe that **4** and **5** are generated by the following redox reaction (eq 11).

$$\underset{\mathbf{1}}{\overset{+}{\text{Ru}}\text{—SHR}} + \underset{\mathbf{3}}{\text{Ru—SR}} \rightleftharpoons \underset{\mathbf{4}}{\overset{\bullet}{\text{Ru}}\text{—SHR}} + \underset{\mathbf{5}}{\overset{\bullet+}{\text{Ru}}\text{—SR}} \qquad (11)$$

$$\overset{\bullet}{\text{Ru}}\text{—SHR} \xrightarrow{\textit{slow}} \mathbf{3} + \frac{1}{2}\,\text{H}_2$$

We also believe that eq 11 is an equilibrium, albeit an unfavorable one, that is established more rapidly than the disproportionation of **4**, as the extent of line broadening of **3** does not change appreciably over several days.[27] Our electrochemical studies imply that this equilibrium in eq 11 lies substantially to the left. Even though the amount of radical cation **5** produced must be exceedingly small, the resulting electron exchange (eq 12) is extremely fast,[28] and very little **5** is required to substantially broaden the NMR peaks of **3**.

$$\underset{\mathbf{3}}{\text{Ru—SR}} + \underset{\mathbf{5}}{\overset{\bullet+}{\mathbf{Ru}}\mathbf{—SR}} \rightleftharpoons \underset{\mathbf{5}}{\overset{\bullet+}{\text{Ru}}\text{—SR}} + \underset{\mathbf{3}}{\mathbf{Ru—SR}} \qquad (12)$$

The electron exchange in eq 12 is expected to be rapid. Low-spin octahedral Ru(II) and Ru(III) differ by a nonbonding t_{2g} electron, so the electron transfer is accompanied by minimal changes in metal−ligand distances. The electron transfer in eq 11 is expected to be much slower because it requires movement of an antibonding e_g electron and thus significant changes in metal−ligand distances.

Are Any Other Electron-Transfer Reactions Involved in 1/3 Systems? A CD_3CN solution of **1** and **3** slowly produces [CpRu(dppe)CD_3CN][BPh_4] and free thiol (from the reaction of **1** with the solvent), so we have considered the possibility that the acetonitrile complex and the free thiol are involved in redox chemistry. The acetonitrile complex is not reduced by Cp_2Co, which means it must be a poorer oxidizing agent than the thiol complex **1**. The free thiol does not reduce **1** or **5**, as evidenced by the unchanged NMR line broadening of **1**/**3** mixtures over time as free thiol appears. Both [CpRu(dppe)CD_3CN][BPh_4] and free thiol retain sharp NMR peaks in mixtures of **1** and **3**. Thus neither [CpRu(dppe)CD_3CN][BPh_4] nor free thiol are participating in redox chemistry in **1**/**3** systems.

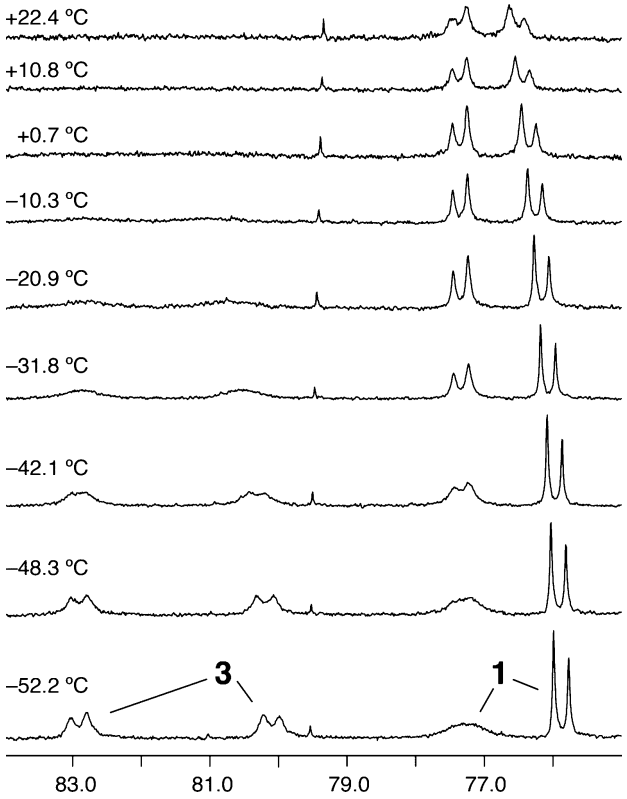


Figure 8. Variable temperature ^{31}P NMR spectra (121.5 MHz) of the mixture in eq 10. The small singlet at δ 79.33 is due to a small amount of [CpRu(dppe)CD_3CN][BPh_4].

Our NMR experiments are consistent with eq 12 as the primary reason for the line broadening of the NMR signals of **3** and with slower exchange processes[29] broadening **1** to a much lesser degree.

Can We Stop Electron Exchange in 1/3 Systems? The addition of *excess* DBN to **1** generates **3** quantitatively, with sharp ^{1}H and ^{31}P NMR spectra. The absence of **1** prevents the generation of **5** by eq 11 and thus suppresses line broadening by the electron exchange in eq 12.

The addition of Cp_2Co to a mixture of **1** and **3** produces a similar result, the quantitative generation of **3** with sharp ^{1}H and ^{31}P NMR spectra. The Cp_2Co converts the **1** into **3**, preventing the generation of **5** by eq 11; furthermore, the Cp_2Co reduces any **5** that is present. Again, line broadening by the electron exchange in eq 12 is suppressed. The relevant processes are shown in Scheme 3.

Inversion of Coordinated Sulfur. When the temperature of a solution of **1** and **3** in acetonitrile was lowered, the downfield ^{31}P resonance of the thiol complex **1** broadened (Figure 8). Because of the freezing point of acetonitrile, we examined the thiol complex **1** alone in CD_2Cl_2. As the temperature was lowered (Figure 9), the downfield ^{31}P NMR resonance first broadened and then split into two signals. The upfield phosphorus resonance broadened at lower temperatures and then split into two signals. At −98 °C, the ^{31}P NMR spectra reveal major and minor conformers, surely

(27) Mixtures of **1** and **3** in CD_3CN are unchanged over time except for the slow reaction of **1** with solvent. Over the course of four days, the thiolate complex resonances remain broad with no discernible changes, but sharp peaks for free thiol and [CpRu(dppe)CD_3CN][BPh_4] appear in the ^{1}H and ^{31}P NMR spectra. We conclude that **4** (eq 11) must not disproportionate rapidly when it is present in such low concentrations.

(28) This system is in the "large hyperfine" or "slow exchange" limit of the de Boer−MacLean equation for NMR line broadening due to e^- exchange. See ref 18a and de Boer, E.; MacLean, C. *J. Chem. Phys.* **1966**, *44*, 1334−1342.

(29) This could be due to the electron transfer equilibrium in eq 11 (most likely), slow electron exchange between **1** and **4**, or proton exchange between **1** and **3**.

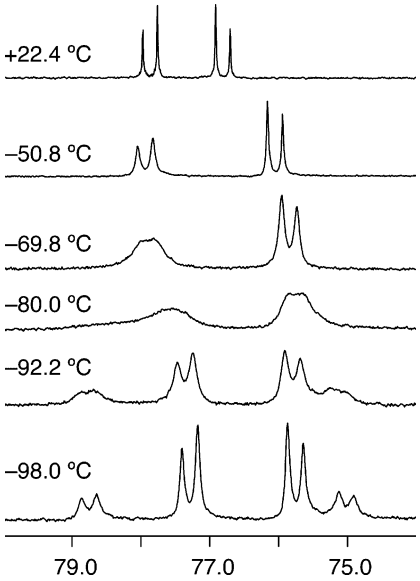
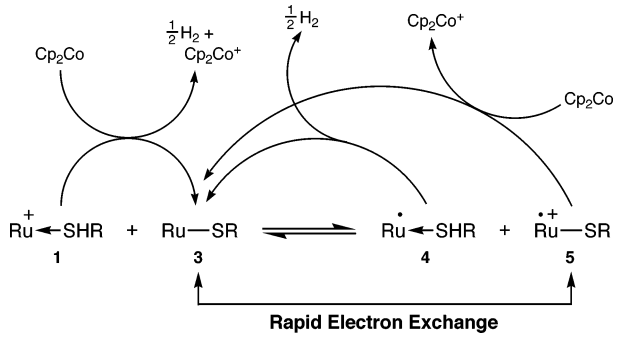


Figure 9. Variable temperature ^{31}P NMR spectra (121.5 MHz) of **1** in CH_2Cl_2.

Scheme 3



the result of slowing pyramidal inversion of the sulfur of the thiol ligand.

Inversion of sulfur in transition-metal complexes typically occurs rapidly at room temperature. Low inversion barriers in electron-deficient complexes are due to stabilization of the planar transition state by empty metal d orbitals.[30] In 18-electron complexes the low inversion barriers must be due to destabilization of the pyramidal ground state.[31]

Conclusions

The NMR spectra in acetonitrile of the thiolate complex **3** become broad whenever **3** and its conjugate acid, the cationic thiol complex **1**, are present simultaneously. Oxidation of **3** by **1** generates a small amount of the radical cation **5**, which then undergoes rapid electron exchange with **3**.

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Supporting Information Available: Complete details of the crystallographic study. This material is available free of charge via the Internet at http://pubs.acs.org.

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