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Isolation of Chromium(0) Thiols: Molecular Structure of $(Bu^tSH)Cr(CO)_5$

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The synthesis and characterization of $(RSH)Cr(CO)_4L$ (L = CO, R = Bu^t, Pr^i, Et, Ph; L = PEt_3, R = Ph, Bu^t) are reported as the first examples of thiols bound to zerovalent d^6 metals. An X-ray crystal structure determination of $(Bu^tSH)Cr(CO)_5$ found minor distortions from octahedral geometry about the Cr; two carbonyls are bent below the equatorial plane by 6° in response to the bulky Bu^t group. The ∠Cr–S–C and ∠Cr–S–H angles are 121.3 (2) and 106°, respectively, and the Cr–S distance of 2.439 (2) Å is significantly shorter than that of the anion, $(Bu^tS)Cr(CO)_5^-$ (2.479 (1) Å). The complex crystallized in the monoclinic space group $P2_1/n$, with $a = 6.545$ (2) Å, $b = 10.918$ (2) Å, $c = 17.731$ (4) Å, $\beta = 97.58$ (2)°, $V = 1256.0$ Å^3, and $Z = 4$. Restricted force field calculations (Cotton–Kraihanzel approximation) of the CO stretching force constants are used to contrast the RSH ligands with amines and phosphines according to their ability as σ-donating ligands ($RSH < NR_3 < PR_3$) and as π-accepting ligands ($NR_3 < RSH < PR_3$). When RSH ligands bind to the $Cr(CO)_5$ moiety, the acidity of the thiols is moderately increased. There is no indication of S–H oxidative addition of isolated $(Bu^tSH)Cr(CO)_5$, $(PhSH)Cr(CO)_5$, or *cis*-$(Bu^tSH)Cr(CO)_4(PEt_3)$ in solution, under either photochemical or thermal conditions. The most easily accessible reaction path is RSH ligand loss.

Introduction

The activation of RS–H bonds by transition metals may take the form of promotion of heterolysis of the SH bond generating RSM^- and H^+ or, alternatively, homolysis resulting in H_2 and coupled metallo- or sulfur-based radicals. In the latter, a seminal question has been whether "formal" oxidative addition of RS–H to a low-valent metal is necessary or whether the RS–H bond may be homolytically activated through S coordination via lone-pair donation so that H transfer may occur directly from the metal-bound sulfur. Recently we examined an Fe d^8 system at which S–H oxidative addition may occur with great facility.[1] The low-temperature protonation of $RSFe(CO)_4^-$ and $RSFe(CO)_3(PEt_3)^-$ permitted spectroscopic detection of thermally unstable neutral products [$(RSH)Fe(CO)_4$ when R = Ph, Me, and Et; the thiolato hydride $(RS)(H)Fe(CO)_3(PEt_3)$ when R = Ph; and the η^2-RSH derivative $(\eta^2\text{-}RSH)Fe(CO)_3(PEt_3)$ when R = Me]. Upon being warmed to 22 °C, all complexes decomposed, yielding H_2 and μ-thiolato dimeric iron complexes, $(\mu\text{-}RS)_2[Fe(CO)_3]_2$ or $(\mu\text{-}RS)_2[Fe(CO)_2(PEt_3)]_2$. Such binuclear reductive elimination reactions result in an oxidation of the metal, in this case Fe(0) to Fe(I).

In order to examine the effect of the metal fragment on RSH stability, we have prepared a series of $(RSH)Cr(CO)_4L$ complexes (L = CO, R = Bu^t, Pr^i, Et, Ph; L = PEt_3, R = Ph, Bu^t). The series is particularly attractive since the structures and the oxidative chemistry of anionic and binuclear analogues, $RSCr(CO)_5^-$ and $(\mu\text{-}RS)[Cr(CO)_5]_2^-$, have recently been reported.[2] Herein are recorded comparative spectroscopic properties and Cotton–Kraihanzel[3] ν(CO) force constants for the series as well as the X-ray crystal structure of the $(Bu^tSH)Cr(CO)_5$ derivative. Although several thioether derivatives of $M(CO)_5$ (M = Cr, Mo, W) are known[4] and $(H_2S)W(CO)_5$ has been characterized in solution,[5] to our knowledge this report is the first of a thiol bound to Cr(0).

Experimental Section

Materials and Methods. All manipulations were performed with standard Schlenk and glovebox techniques. Tetrahydrofuran and hexane were distilled from Na/benzophenone under N_2. Diethyl ether was distilled from $LiAlH_4$ under N_2. Acetonitrile was distilled two times from CaH_2 and then two times from P_2O_5 under N_2. Unless noted below, reagents were purchased from standard vendors and used without further purification. Photolysis experiments were carried out with a Hanovia 450-W Hg lamp. Infrared spectra were recorded on an IBM FTIR/32 spectrometer using 0.10-mm CaF_2 solution cells or KBr pellets. ^1H and ^{13}C NMR spectra were obtained on an XL200 Varian spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

[PPN][RSCr(CO)$_5$] [R = Bu^t (1), Et (2), Pr^i (3)]. These complexes have been synthesized previously by numerous synthetic routes.[6] In our laboratories, the Cr thiolates were prepared as follows. A 1.5-g (2.0-mmol) amount of $[PPN][Cr(CO)_5Cl]$[7] was added to a N_2-filled 100-mL Schlenk flask along with 1 molar equiv (2.0 mmol) of NaSR. (The NaSR salts were prepared by reacting equimolar quantities of the appropriate RSH and Na metal in THF under N_2 and isolated by extraction of the dried white residue with CH_3CN.) The solid mixture was dissolved in 30 mL of CH_3CN. The resulting yellow solution was stirred for 2 h or until completion of the reaction as monitored by IR spectroscopy, at which time the solution was filtered through Celite to remove NaCl. The solvent was removed in vacuo. Recrystallization from THF/Et_2O/hexane (1:1:1) yielded the yellow-orange solid in 60–82% yields. Anal. Found (calcd) for **1** ($C_{45}CrH_{39}NO_5P_2S$): C, 66.35 (65.93); H, 4.83 (4.79); S, 3.57 (3.91). ^1H NMR (acetone-d_6): **1**, ∂ 1.35 (s, CH_3); **2**, ∂ 2.29 (q, CH_2), 1.18 (t, CH_3); **3**, ∂ 3.05 (m, CH), 1.43 (d, CH_3). ^{13}C NMR (acetone-d_6): **1**, ∂ 228.6 (1 CO), 223.6 (4 CO); **2**, ∂ 227.5 (1 CO), 222.4 (4 CO); **3**, ∂ 227.4 (1 CO), 222.4 (4 CO).

[Et$_4$N][C$_6$H$_5$SCr(CO)$_5$] (4). This salt was prepared according to literature procedures.[8]

[PPN][RSCr(CO)$_4$(PEt$_3$)] [R = Ph (5), Bu^t (6)]. In a typical preparation, 0.12 g (1.4 mmol) of **1** was dissolved in 20 mL of THF. Two molar equivalents (440 μL, 2.9 mmol) PEt_3 was added. The orange solution was stirred at room temperature for 2 h and then filtered through Celite. The solvent volume was reduced, and Et_2O/hexane was added to precipitate the crude yellow product, which was recrystallized three times from THF/Et_2O/hexane. Yields: 85–88%. Anal. Found (calcd) for **6** ($C_{50}H_{54}NO_4P_3SCr$): C, 64.65 (65.99); H, 6.00 (5.99); S 3.32 (3.52). ^1H NMR (acetone-d_6): **6**, ∂ 1.35 (s, CH_3), 1.71 (m, CH_2), 1.08 (m, CH_3).

(RSH)Cr(CO)$_5$ [R = Bu^t (7), Et (8), Pr^i (9), Ph (10)]. (a) THF Ligand Displacement. In a typical preparation, 70 mL of $Cr(CO)_5(THF)$ [ν(CO) (IR (THF)) at 2074 w, 1938 s, 1894 m cm^{-1}] generated from photolysis of 0.37 g (1.70 mmol) of $Cr(CO)_6$ in THF was transferred to a 100-mL Schlenk flask, and RSH was added (1 molar equiv for R = alkyl; 20 molar equiv was necessary for rapid reaction when R = Ph) via syringe. The solution was stirred for 1 h or until the reaction was complete. The residue was recrystallized (three times) from pentane at −20 °C and dried in vacuo to give a yellow solid in 55–70% yields. Anal.

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Table I. Crystallographic Data for $(Bu^tSH)Cr(CO)_5$

formula	$C_9CrH_{10}O_5S$	Z	4
fw	282.2	D(calc), g/mL	1.492
space grp	$P2_1/n$ (No. 14)	temp, °C	−70
a, Å	6.545 (2)	μ(Mo Kα), cm^{-1}	10.49
b, Å	10.918 (2)	wavelength, Å	0.71073
c, Å	17.731 (4)	$R(F)$, %	0.078
β, deg	97.58 (2)	$R_w(F)$, %	0.071
V, Å^3	1256.0		

Found (calcd) for **7** ($C_9H_{10}O_5SCr$): C, 37.69 (38.30); H, 3.62 (3.57); S, 11.61 (11.36).

(b) Protonation of [PPN][RSCr(CO)$_4$L] [L = CO, R = Bu^t, Et, Pr^i, Ph; L = PEt$_3$, R = Ph (11), Bu^t (12)]. In a Schlenk tube, 0.061 mmol of [PPN][RSCr(CO)$_4$L] was dissolved in 5 mL of THF and the solution was cooled to −78 °C. One molar equivalent (0.061 mmol) of $HBF_4\cdot Et_2O$ (85% solution) was added dropwise via syringe. The reaction was complete within the time of mixing. The solvent was removed in vacuo, and the resulting solid was extracted with hexane to yield a clear yellow solution. IR and NMR spectral parameters are listed in Tables IV and VI.

[PPN][Bu^{t}SCr(CO)$_5$] + MeI. In a Schlenk tube, 0.080 g (0.098 mmol) of **1** was dissolved in 5 mL of THF and cooled to −78 °C. One molar equivalent (6.1 μL, 0.098 mmol) of MeI was added to the solution via syringe. The solvent was removed in vacuo at 0 °C, and the residue was extracted with hexane. IR (hexane): 2068 w, 1946 s (sh), 1940 vs, 1932 s (sh) cm^{-1}. ^{1}H NMR (C_6D_6): ∂ 1.53 (s, CH_3), 0.82 (s, CH_3). These spectroscopic properties are consistent with the formulation $(Bu^tSMe)Cr(CO)_5$.

Deprotonation of (RSH)Cr(CO)$_5$. (a) Et$_3$N/CH$_3$CN. In a Schlenk tube, 0.052 g (0.18 mmol) of **8** was dissolved in 5 mL of CH$_3$CN. One molar equivalent of Et$_3$N was added, yielding a yellow-orange solution with ν(CO) (IR (CH$_3$CN)) at 2076 w, 1944 s, and 1908 m cm^{-1}, consistent with the formation of $(CH_3CN)Cr(CO)_5$.[9]

(b) Et$_3$N/THF. To a 10-mL aliquot of 0.023 M **8** in THF was added 1 molar equiv (0.023 g, 0.23 mmol) of Et$_3$N, resulting in a yellow solution with ν(CO) (IR (THF)) at 2053 w, 2037 w, 1960 m (sh), 1935 s, 1926 s, 1894 m, and 1869 m cm^{-1}, consistent with the formation of $(\mu\text{-}SBu^t)[Cr(CO)_5]_2^-$.[2] To a 0.030 M solution of **10** in the presence of a 20-fold excess of PhSH was added 1 molar equiv of Et$_3$N, yielding a yellow solution with ν(CO) (IR (THF)) at 2050 w, 1921 s, 1877 m cm^{-1}, consistent with formation of $PhSCr(CO)_5^-$.[8]

(c) [Et$_4$N][OH]/THF. To a 10-mL aliquot of 0.023 M **8** in THF was added 1 molar equiv (0.034 g, 0.23 mmol) of [Et$_4$N][OH], resulting in a yellow-orange solution with ν(CO) (IR (THF)) at 2035 w, 1906 s, and 1850 m cm^{-1}, consistent with the formation of $EtSCr(CO)_5^-$.

(Bu^{t}SH)Cr(CO)$_5$ + PPh$_3$. In a Schlenk tube, 0.035 g (0.12 mmol) of **7** was combined with 1 molar equiv (0.032 g, 0.12 mmol) of PPh$_3$ in 5 mL of THF. After 15 min the reaction was complete, yielding $(Ph_3P)Cr(CO)_5$,[10] ν(CO) (IR (THF)) at 2059 w and 1939 s cm^{-1}.

Photolysis of (PhSH)M(CO)$_5$ (M = Cr, W). These complexes were prepared in situ by addition of 20 molar equiv (1.2 mL, 11.4 mmol) of PhSH to a 0.031 M (0.57 mmol) THF solution of M(CO)$_5$(THF). For M = Cr, solutions photolyzed in a quartz reactor for 7 h showed no reaction as monitored by IR. For M = W, photolysis for 1.5 h yielded a green solution with ν(CO) bands consistent with formation of $(\mu\text{-}SPh)_2[W(CO)_4]_2$.[11]

Crystallographic Characterization of (Bu^{t}SH)Cr(CO)$_5$. Two independent crystallographic studies, one of which is reported below, yielded essentially the same results. Table I contains data relating to this structural study. A lime-colored irregular-plate crystal with dimensions 0.26 × 0.10 × 0.31 mm was mounted in a glass capillary under N$_2$ and placed on an Enraf-Nonius CAD4 diffractometer equipped with a gas-cooled low-temperature unit operating at −70 °C. The diffractometer routines and photographic work determined the cell to be monoclinic with the space group $P2_1/n$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $(Bu^tSH)Cr(CO)_5$[a]

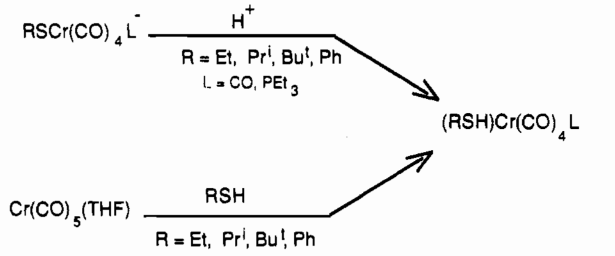
atom	x	y	z	U
Cr	4750.1 (19)	941.8 (10)	2287.8 (6)	1.7 (1)
S	3093 (3)	2586 (2)	1500 (1)	2.6 (1)
O(1)	6834 (9)	−918 (6)	3374 (3)	4.7 (2)
O(2)	1268 (10)	1032 (6)	3262 (4)	5.2 (2)
O(3)	7173 (10)	2858 (6)	3247 (3)	4.5 (2)
O(4)	8467 (9)	689 (5)	1460 (3)	4.4 (2)
O(5)	2603 (10)	−1191 (5)	1416 (4)	4.9 (2)
C(1)	5993 (12)	−208 (8)	2944 (4)	3.2 (2)
C(2)	2551 (12)	1037 (8)	2980 (4)	3.4 (2)
C(3)	6246 (12)	2175 (7)	2881 (4)	3.0 (2)
C(4)	7036 (12)	795 (7)	1734 (4)	3.4 (2)
C(5)	3366 (12)	−364 (7)	1733 (4)	2.9 (2)
C(6)	2883 (11)	2530 (7)	445 (3)	2.6 (2)
C(7)	1682 (28)	3606 (13)	153 (5)	11.5 (6)
C(8)	4918 (17)	2588 (18)	225 (5)	10.5 (6)
C(9)	1879 (28)	1398 (13)	170 (5)	11.9 (6)
H(1)	1275 (118)	2435 (75)	1492 (38)	4.6 (18)
H(7)	1503	3662	−383	5.1
H(7′)	2354	4366	351	5.1
H(7″)	329	3616	321	5.1
H(8)	4955	2574	−303	5.1
H(8′)	5798	1925	452	5.1
H(8″)	5645	3343	421	5.1
H(9)	1763	1324	−366	5.1
H(9′)	541	1317	326	5.1
H(9″)	2686	691	385	5.1

[a] Isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Bond Angles for $(Bu^tSH)Cr(CO)_5$

	(a) Bond Distances, Å		
Cr–S	2.439 (2)	C–O(2)	1.135 (8)
Cr–C(1)	1.828 (8)	C–O(3)	1.113 (8)
Cr–C(2)	1.904 (8)	C–O(4)	1.117 (8)
Cr–C(3)	1.900 (8)	C–O(5)	1.143 (8)
Cr–C(4)	1.902 (8)	S–C(6)	1.858 (6)
Cr–C(5)	1.984 (8)	S–H(1)	1.2 (1)
C–O(1)	1.173 (9)		
	(b) Bond Angles, deg		
S–Cr–C(1)	175.4 (3)	S–Cr–C(5)	96.4 (2)
S–Cr–C(2)	88.2 (2)	Cr–S–C(6)	121.3 (2)
S–Cr–C(3)	87.3 (2)	Cr–S–H(1)	106 (1)
S–Cr–C(4)	95.0 (2)		

Scheme I



The structure was solved via an automated Patterson analysis (PHASE), yielding one molecule in a position suggesting a pseudomirror plane at y = 0.25 through the sulfur and one of the methyl groups of the *tert*-butyl group. A difference Fourier map revealed a peak of 1.6 e approximately 2.3 Å from the sulfur, suggesting a mirror-related residual of the chromium atom. This orientation superimposes the oxygens of two CO groups as well as the thiol group. Refinement of the multiplicities of the extra peak as a chromium atom indicated a 92–8% distribution over the two sites. Additionally, a peak near the sulfur, 1.2 Å, was clearly reasonable for the SH hydrogen (∠Cr–S–H = 106°) and was satisfactorily refined. Hydrogen atom positions were idealized with d(C–H) = 0.95 Å. Atomic coordinates are given in Table II, and selected bond distances and angles, in Table III.

Results and Discussion

The two routes that may be used to produce (RSH)Cr(CO)$_5$ or *cis*-(RSH)Cr(CO)$_4$(PEt$_3$) are outlined in Scheme I. The RSH displacement of THF in THF solutions of photochemically generated Cr(CO)$_5$(THF) gives good yields, even at 1:1 ratios of

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(9) The identity of this product was confirmed by its independent preparation from equimolar quantities of Cr(CO)$_5$(THF) and CH$_3$CN in THF (ν(CO) 1975 w, 1945 s, 1908 m cm^{-1}). Mixing Cr(CO)$_5$(THF) and 20 molar equiv of Et$_3$N in THF did not yield (Et$_3$N)Cr(CO)$_5$. After 12 h, only Cr(CO)$_5$(THF) and Cr(CO)$_6$ were observed in the IR spectrum.

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Table IV. $\nu(CO)$ Stretching Frequencies for $(RSH)Cr(CO)_4L^a$

		freq, cm^{-1}		
	complex	$A_1^{(2)}$	$A_1^{(1)}$	E
1	$[PPN][Bu^tSCr(CO)_5]$	2034 (w)	1850 (m)	1918 (s), 1894 (s)
2	$[PPN][EtSCr(CO)_5]$	2034 (w)	1850 (m)	1905 (s)
3	$[PPN][Pr^iSCr(CO)_5]$	2033 (w)	1850 (m)	1907 (s)
4	$[Et_4N][PhSCr(CO)_5]$	2044 (w)	1869 (m)	1916 (s)
7	$(Bu^tSH)Cr(CO)_5$	2075 (w)	1926 (m)	1950 (s)^b
		2070 (w)	1917 (m)	1940 (s)
8	$(EtSH)Cr(CO)_5$	2072 (w)	1937 (m)	1948 (s)^b
		2070 (w)	1917 (m)	1941 (s)
9	$(Pr^iSH)Cr(CO)_5$	2072 (w)	1934 (m)	1951 (s)^b
		2070 (w)	1917 (m)	1943 (s)
10	$(PhSH)Cr(CO)_5$	2071 (w)	1931 (m)	1942 (s)^b
		2072 (w)	1915 (m)	1939 (s)

		freq, cm^{-1}			
	complex	A'	A''	A'	A'
5	$[PPN][cis\text{-}PhSCr(CO)_4(PEt_3)]$	1982 (m)	1871 (s)	1861 (s)	1810 (m)
6	$[PPN][cis\text{-}Bu^tSCr(CO)_4(PEt_3)]$	1975 (m)	1865 (s)	1854 (s)	1798 (m)
11	$cis\text{-}(PhSH)Cr(CO)_4(PEt_3)$	2007 (m)	1881 (s)	1871 (s)	1856 (m)
12	$cis\text{-}(Bu^tSH)Cr(CO)_4(PEt_3)$	2007 (m)	1893 (s)	1887 (s)	1859 (m)

[a] Measured in THF except where noted. [b] Measured in hexane.

Table V. $\nu(CO)$ Force Constants Derived by the Cotton–Kraihanzel[3] Method for $LCr(CO)_5{}^a$

L	force const,^{b} mdyn/Å	
	κ_1	κ_2
CO^c	16.49	
Bu^tSH	15.16	15.98
Pr^iSH	15.29	15.98
EtSH	15.35	15.94
PhSH	15.29	15.84
Bu^tSMe	15.27	15.87
$PPh_3{}^c$	15.51	15.85
$PMe_3{}^c$	15.54	15.75
$PBu_3{}^c$	15.43	15.68
piperdine^d	15.06	15.76
pyridine^d	15.08	15.82
Bu^tS^{-e}	13.97	15.31
Pr^iS^{-e}	13.99	15.30
EtS^{-e}	13.98	15.30
PhS^{-e}	14.27	15.46

[a] IR spectra measured in hexane unless noted. [b] κ_1 is defined as the force constant for the CO trans to L. κ_2 is the cis CO force constant. [c] Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919. [d] Dennenberg, R. J.; Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 72. [e] Measured in THF.

Table VI. ^1H NMR Data for RSH Resonances of $(RSH)Cr(CO)_4L^a$

complex	CH_3	CH_2	CH	SH
$(Bu^tSH)Cr(CO)_5$	0.85 (t)			1.32 (s)
$(Pr^iSH)Cr(CO)_5$			2.06 (m)	1.00 (d)
$(EtSH)Cr(CO)_5$	0.52 (t)	1.57 (m)		0.77 (t)
$cis\text{-}(Bu^tSH)Cr(CO)_4(PEt_3)$	0.82 (t)			1.20 (s)
$cis\text{-}(PhSH)Cr(CO)_4(PEt_3)$			7.20 (m)	2.80 (s)

[a] Recorded as ppm in benzene-d_6.

$RSH{:}Cr(CO)_5(THF)$, for R = alkyl; for R = Ph, a 20-fold excess of PhSH is necessary for rapid reactions. At either −78 °C or room temperature protonation of $RSCr(CO)_5^-$ occurred in the time of mixing and was clean and spectroscopically quantitative. In contrast, the analogous approach for the attempted synthesis of $(H_2S)W(CO)_5$ from $HSW(CO)_5^-$ led to facile displacement of H_2S by $HSW(CO)_5^-$, resulting in formation of $(\mu\text{-}HS)[W(CO)_5]_2^-$.[5] Binuclear species, $(\mu\text{-}RS)[Cr(CO)_5]_2^-$, were not observed in our preparations despite their known stability (vide infra). The PEt_3-substituted derivatives, $cis\text{-}(RSH)Cr(CO)_4(PEt_3)$, were also prepared in good yields by the low-temperature protonation of the corresponding anion, $cis\text{-}RSCr(CO)_4(PEt_3)^-$, with $HBF_4{\cdot}Et_2O$ in THF solution. A small amount of $(Et_3P)Cr(CO)_5$ was always present as a contaminant.

Characterization. In general, the RS–H stretching vibrations are of low intensity and are difficult to assign in the solution spectra of these and other known thiol complexes.[12] A band at 2555 cm^{-1} in the solid-state spectrum of $(Bu^tSH)Cr(CO)_5$ was assigned to $\nu(SH)$. As expected for local C_{4v} symmetry, a three-band pattern was observed in the $\nu(CO)$ IR solution spectra of the octahedral $(RSH)Cr(CO)_5$ complexes (Table IV). The $\nu(CO)$ IR bands were shifted approximately 30 cm^{-1} higher in energy relative to the anionic species $RSCr(CO)_5^-$, similar to those shifts observed for alkylation of $RSCr(CO)_5^-$, presumably yielding thioether complexes such as $(Bu^tSMe)Cr(CO)_5$ (see Experimental Section). Complexities in the $\nu(CO)$ IR band pattern for $Bu^tSCr(CO)_5^-$, i.e., a split E band and an unusually intense $A_1^{(2)}$ band, were indicative of lower symmetry about the Cr center for the bulky ligand. Upon protonation of the thiolato anion, the characteristic three-band pattern was observed for $(Bu^tSH)Cr(CO)_5$. These results are consistent with a greater distortion of the equatorial carbonyls in the anionic compound than [illegible] neutral $(Bu^tSH)Cr(CO)_5$.

Energy-factored CO stretching force constants, calculated by the Cotton–Kraihanzel[3] method, have been used to compare the ability of the RSH ligands to donate to $Cr(CO)_5$ with that of the more common phosphine and nitrogen donor ligands (Table V). Alkanethiol ligands are slightly poorer σ-donors (as reflected in κ_2) than amines and phosphines. Benzenethiol has σ-donating ability similar to that of PPh_3. As expected, the relative order of σ-donating ability for RSH ligands parallels the solution acidities of the free thiols. Due to the directionality of π-overlap in octahedral geometry, the F_{CO}, κ_1, for the CO trans to the donor ligand, better reflects the π-acceptor character of L. The π-accepting ability of the RSH ligands is better than that of amines but poorer than that of phosphines. The thiolato ligands are stronger than thiols in σ-donating ability, but poorer π-acceptors. It will be suggested below that the σ-donating ability is the dominating factor in ligand substitution chemistry; i.e., RSH is more readily displaced than RS^- by phosphine ligands.

The ^1H NMR spectra exhibit a slight upfield shift for the R substituent protons as well as the S*H* resonance relative to the free thiol (Table VI). The latter observation contrasts with all other examples of RSH coordination in the literature in which downfield shifts are noted.[4a,13,14] Herberhold and Suss[4a] have suggested S*H* chemical shifts may be used as a measure of relative

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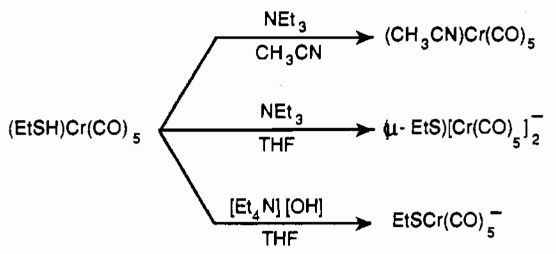
(12) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(13) Strohmeier, W.; Guttenberger, J. F.; Popp, G. *Chem. Ber.* **1965**, *98*, 2248.

(14) Treichel, P. M.; Rosenhein, L. D. *Inorg. Chem.* **1981**, *20*, 942.

Scheme II



acidity and that downfield shifts are consistent with increased acidity of metal-bound thiols. This generalization does not hold for RSH complexed to $Cr(CO)_4L$, as these thiols also exhibit increased acidity (vide infra), despite upfield shifts of the RS*H* upon complexation.

The neutral $(RSH)Cr(CO)_4L$ complexes were isolated as moderately air-sensitive yellow solids soluble in a variety of solvents, including hexane and THF. Hexane solutions of these complexes under N_2 are stable for 1 week while THF solutions under N_2 begin to decompose after 1 day. Decomposition is slower in nonpolar solvents than in polar solvents, e.g., THF or CH_3CN. The solution stability with respect to RSH loss and formation of $Cr(CO)_5L$ (along with decomposition products of the fragments from $Cr(CO)_4L$) depends both on the R substituent, decreasing in the order $Bu^t > Pr^i > Et \gg Ph$, and on L ($CO \gg PEt_3$). (For the $RSCr(CO)_5^-$ anions, the stability decreases in the order R = Ph > alkyl.)[2] Regardless of solvent or R substituent, the Cr–S bond in the thiol complexes is considerably more labile and *presumably* weaker than the Cr–S bond in the anions, $RSCr(CO)_5^-$. For example, the chromium thiolate anions reacted over several hours with phosphines at 22 °C to yield CO and the cis-substituted products *cis*-$RSCr(CO)_4(PR_3)^-$ (eq 1). In contrast,

$$RSCr(CO)_5^- + PR_3 \rightarrow \textit{cis}\text{-}RSCr(CO)_4(PR_3)^- + CO \quad (1)$$

$$(RSH)Cr(CO)_5 + PR_3 \rightarrow (R_3P)Cr(CO)_5 + RSH \quad (2)$$

$$(RSH)Cr(CO)_5 + RSCr(CO)_5^- \rightarrow \mu\text{-}RS[Cr(CO)_5]_2^- + RSH \quad (3)$$

the thiol complexes reacted within 15 min with phosphines and within the time of mixing with $RSCr(CO)_5^-$, yielding the RSH replacement products (eqs 2 and 3, respectively).

Deprotonation Studies. Results of these studies are summarized in Scheme II and eq 4. Clean deprotonation of $(EtSH)Cr(CO)_5$

$$(PhSH)Cr(CO)_5 + NEt_3 \rightarrow [HNEt_3][PhSCr(CO)_5^-] \quad (4)$$

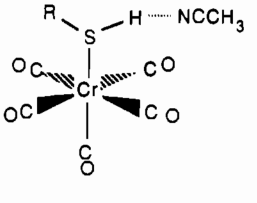
(**8**) in THF solution resulted in addition of 1 equiv of $[Et_4N][OH]$, yielding $[Et_4N][EtSCr(CO)_5]$. With CH_3CN as solvent, the thiol is rapidly displaced, yielding $(CH_3CN)Cr(CO)_5$ and EtSH with no observable deprotonation or formation of $(Et_3N)Cr(CO)_5$;[9] with the stronger acid, $(PhSH)Cr(CO)_5$, complete deprotonation was observed in the time of mixing with 1 equiv of Et_3N in THF (eq 4). The reaction of either 1 or 2 equiv of Et_3N with **8** in THF yielded the binuclear $(\mu\text{-}EtS)[Cr(CO)_5]_2^-$, quantitatively. That the last reaction is a result of slow deprotonation leading to a reactive mixture of $(EtSH)Cr(CO)_5$ and $EtSCr(CO)_5^-$ was confirmed by the independent reaction of isolated $[PPN][EtSCr(CO)_5]$ and $(EtSH)Cr(CO)_5$ at 22 °C in THF (eq 3); formation of $(\mu\text{-}EtS)[Cr(CO)_5]_2^-$ was instantaneous from these reagents.

Noteworthy points about these results are as follows:

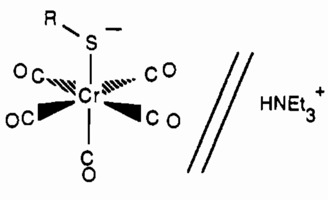
(1) Binding to $Cr(CO)_5$ increases the Brønsted acidity of EtSH, as free EtSH is only partially deprotonated by Et_3N under similar conditions.[15] The increased acidity of RSH when complexed to chromium is consistent with other reports of metal-bound thiols in the literature. The iron(II)-activated thiol $[CpFe(CO)_2(PhSH)][BF_4]$ is so acidic that it reacts with most solvents, suggesting that, relative to the pK_a of free PhSH (6.62 in aqueous methanol), the pK_a of complexed PhSH is many orders of magnitude greater.[14] The complex $(H_2S)W(CO)_5$ is deprotonated by the relatively weak base $[Et_4N][Br]$.[5] Although no quantitative studies have been carried out for RSH bound to Cr(0), the increased acidity observed here is not as great as in earlier studies.

(2) The protonation of $RSCr(CO)_5^-$ by 1 equiv of $HBF_4{\cdot}Et_2O$ in THF, a synthetic route to $(RSH)Cr(CO)_5$, is a faster reaction than deprotonation of $(RSH)Cr(CO)_5$ by Et_3N in THF. Otherwise the binuclear $(\mu\text{-}RS)[Cr(CO)_5]_2^-$ would have been observed during the protonation reactions.

(3) The solvent effect on the Et_3N reaction suggests CH_3CN enhances ligand loss over ion-pair separation, structures A and B, respectively. Were the latter the case, the more polar CH_3CN



(A)

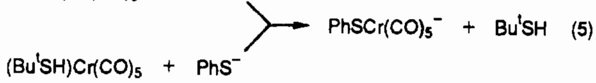


(B)

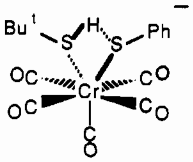
would be expected to promote formation of $HNEt_3^+$ and $RSCr(CO)_5^-$ rather than ligand displacement.

(4) Products obtained upon deprotonation depend both on the base ($[Et_4N][OH] > Et_3N$) and on the acidity of the metal-bound thiol (PhSH > EtSH).

A comparison of S–H and Cr–S bond reactivities (deprotonation vs ligand displacement) is shown in eq 5. Both reactions lead to identical products and are within the time of mixing. Kinetic



measurements have not been attempted. A simple D mechanism may possibly account for the reactions. However, in view of literature precedents for two S donors simultaneously interacting at $M(CO)_5$ centers[16] and the observation of hydrogen-bonding of the Cr-bound thiol proton with polar solvents as indicated in the $\nu(CO)$ IR results (Table IV), an I_a mechanism involving a common intermediate, structure C, is appealing. This intermediate



(C)

would proceed to products by cleaving the weaker S–H bond, PhS–H (BDE: PhSH, 75 kcal/mol < Bu^{t}SH, 90 kcal/mol),[17] and the (presumably) weaker Cr–SR bond, Cr–SBu^t.

(Bu^{t}SH)Cr(CO)$_5$ Solid-State Structure. Crystallization of $(Bu^tSH)Cr(CO)_5$ is complicated by the lability of the thiol ligand. Although crystals obtained from the evaporation of concentrated hexane solutions appear single, they are twinned and contaminated with a minor component in a second orientation. However, analyses carried out on two separate crystals yielded essentially the same results. Appropriate crystallographic data are found in Tables I–III. The geometry about Cr is almost a regular octahedron (Figure 1). The greatest deviation from O_h geometry is in the equatorial plane in which the two CO ligands closest to the bulky Bu^t group lie approximately 6° below the plane. The

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[15] (a) Oae, S., Ed. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977, p 157. (b) Barnett, J. *J. Chem. Soc.* **1944**, 5.

[16] Abel, E. W.; Moss, I.; Orrell, K. G.; Qureshi, K. B.; Sik, V.; Stephenson, D. *J. Chem. Soc., Dalton Trans.* **1988**, 1489.

[17] (a) Oae, S., Ed. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977, p 367. (b) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

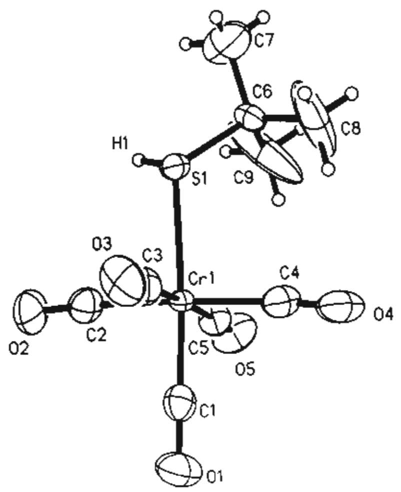
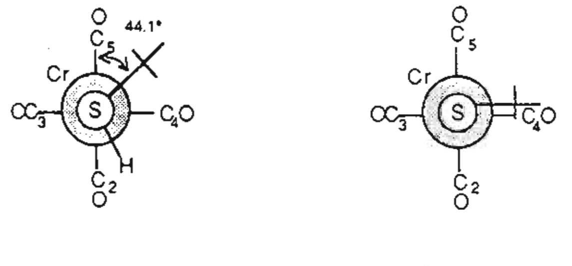


Figure 1. Thermal ellipsoid plot at 50% probability of $(Bu^tSH)Cr(CO)_5$ with numbering scheme.



$(Bu^tSH)Cr(CO)_5$

$Bu^tSCr(CO)_5^-$

Figure 2. Projection of the S–C(Bu^t) vector onto the $Cr(CO)_4$ equatorial plane of $(Bu^tSH)Cr(CO)_5$ (this work) and $Bu^tSCr(CO)_5^-$.[2] For the former, carbonyls 4 and 5 are displaced below the plane by ca. 6°. In the latter, carbonyl 4 is displaced by 13°.

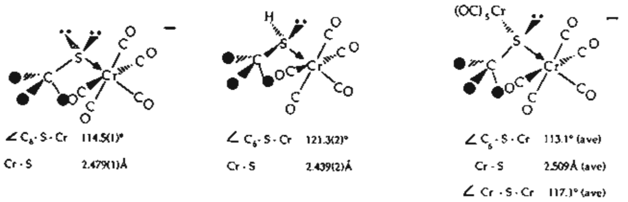
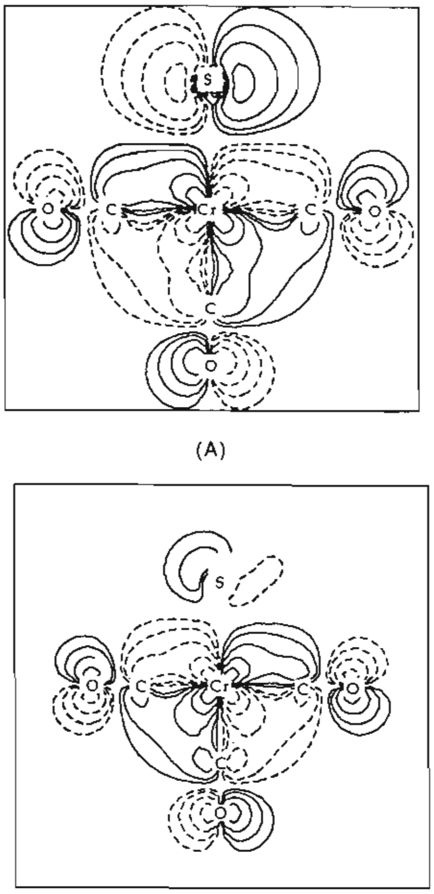


Figure 3. Comparison of the structures of $(Bu^tSH)Cr(CO)_5$, $Bu^tSCr(CO)_5^-$, and $Bu^tS[Cr(CO)_5]_2^-$.

S–C(6) vector bisects these two carbonyls with a C(6)–S–Cr–C(4) dihedral angle of 44.1° (Figure 2). For comparison, Figure 2 also shows that the Bu^t group of the anion, $Bu^tSCr(CO)_5^-$,[2] lies directly above one equatorial CO (C(6)–S–Cr–C(4) dihedral angle of 0°), displacing it 13° below the equatorial plane. Despite the ∠Cr–S–C angle of 121.3 (2)°, suggesting a possible sp^2 hybridization of S, the pyramidal character of S is ensured by the ∠Cr–S–H angle of 106°.

Figure 3 focuses on the (minor) structural variations among $(Bu^tSH)Cr(CO)_5$, $Bu^tSCr(CO)_5^-$, and $(\mu\text{-}Bu^tS)[Cr(CO)_5]_2^-$.[2] The smaller Cr–S–C angle and longer Cr–S bond distance of the anion as compared to the protonated neutral derivative may be accounted for by a relief of S-lone-pair repulsion in the latter, permitting a less sterically interactive positioning of the Bu^t group with respect to the equatorial plane. The abatement of steric crowding permits better Cr–S overlap and hence a shorter Cr–S bond distance in the thiol complex as compared to the thiolate. Alternatively, the makeup of the HOMO in d^6 thiolates[18] would suggest the shorter Cr–S bond distance of the thiol complex is a consequence of diminished S–Cr antibonding character upon protonation. The Fenske–Hall-derived[19] atomic orbital composition of the HOMO of $HSCr(CO)_5^-$ is 41% Cr d_{yz} and 30% S $3p_y$, and as noted in Figure 4, the orbital is largely Cr–S π^*. In contrast, the constituents of the HOMO of $(H_2S)Cr(CO)_5$ is <1% S $3p_y$ and 58% Cr d_{xz}, d_{yz} orbitals. The binuclear anion $(\mu\text{-}Bu^tS)[Cr(CO)_5]_2^-$ may be viewed as analogous to the thiol in that one electron pair of S is taken up by one $Cr(CO)_5$ fragment. The larger Cr–S distance here is due to both steric repulsions as well as the bridge bonding. Interestingly, although both anions in Figure 3 have longer Cr–S bonds than the neutral thiol derivative, the latter is less stable toward sulfur ligand loss.



(A)

(B)

Figure 4. Contour plot in the *yz* plane of the 32nd molecular orbitals (HOMO) of $HSCr(CO)_5^-$ (A) and $(H_2S)Cr(CO)_5$ (B) derived from Fenske–Hall calculations. The highest contour lines correspond to 0.25 $(e\cdot Å^{-3})^{1/2}$, and each successive contour line value is related by a factor of 2.

Comments. The selection of the Bu^{t}SH derivative of $Cr(CO)_5$ for crystallographic analysis was based on the availability of analogous structures for comparison,[2] as well as for sterically optimizing the possibility of η^2-RSH interaction. Such three-center bonding was inferred from spectroscopic studies of the TBP d^8 Fe(0) complex $(\eta^2\text{-MeSH})Fe(CO)_3(PEt_3)$.[1] In fact, there is no crystallographic evidence for metal interaction with both S and H despite the observed "chromium effect"[20] on the thiol proton, i.e., an upfield chemical shift.

There was no indication of S–H oxidative addition to Cr, either for the Bu^{t}SH complex of $Cr(CO)_5$ or in the more electron-rich

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(18) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191.

(19) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. Bond distances and angles were taken from the crystal structures of $[PPN][Bu^tSCr(CO)_5]^2$ (∠Cr–S–H = 114° and *d*(Cr–H) = 1.34 Å) and $(Bu^tSH)Cr(CO)_5$ (∠Cr–S–H = 109.5° and *d*(Cr–H) = 1.34 Å).

(20) For example, the hydride complexes of chromium carbonyls such as $HCr(CO)_5^-$ (−7.0) and $(\mu\text{-H})[Cr(CO)_5]_2^-$ (−19.5) experience a larger upfield chemical shift (ppm) than the tungsten analogues $HW(CO)_5^-$ (−4.0) and $(\mu\text{-H})[W(CO)_5]_2^-$ (−12.5).

$Cr(CO)_4(PEt_3)$. Even the more optimal conditions of providing $Cr(CO)_5$ access to a weaker S–H bond, i.e., that of PhSH, under photolytic conditions did not promote oxidative addition. Under the same conditions, however, oxidative chemistry is observed for the more readily oxidizable heavier metal cogener, $(PhSH)W(CO)_5$. The latter results are consistent with earlier reports of the photolysis reaction of $W(CO)_6$ and PhSH or PhSSPh leading to $(\mu\text{-PhS})_2[W(CO)_4]_2$ and $W(CO)_2[(\mu\text{-PhS})_2[W(CO)_4]_2]_2$.[11] Our results lend credence to a $(PhSH)W(CO)_5$ complex as intermediate in such reactions—and to the necessity of CO loss.

Oxidative addition of S–H is patently favored for d^8 Fe(0) complexes and the intermediate thiolate hydrides are stabilized by the presence of electron-donating ligands. For d^6 Cr(0) complexes, the RSH ligand loss path has a lower E_{act}, and electron-donating ligands further lower this barrier for the $Cr(CO)_4L$ moiety—presumably due to an enhanced antibonding character of the S_{3p}–$Cr_{3d_{xz},d_{yz}}$ HOMO. Clearly, for d^6 metals made extremely electron rich and possessing very labile ligands, such as $Mo(diphos)_2(N_2)_2$, oxidative addition is expected and does readily occur.[21] A complete understanding of the contributing factors to E_{act}, such as open-site accessibility, metal oxidation potential, or possible structural rearrangements, awaits more detailed studies and theoretical analyses.

Finally we comment on the fact that solid-state Cr–S bond distances do not correlate with Cr–S bond lability in solution. The lower solution stability toward sulfur ligand loss of the RSH complexes as compared to the RS^- derivatives is most reasonably due to the ability of the former to engage in hydrogen bonding, thus facilitating ligand loss via an interchange mechanism.

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Supplementary Material Available: Tables of crystallographic data, all bond lengths and bond angles, and anisotropic thermal parameters (3 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(21) Shortman, C.; Richards, R. L. *J. Organomet. Chem.* **1985**, *286*, C3.

Contribution from the Departments of Chemistry, University of Tennessee,
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Electrochemical Oxidative Addition Involving Dirhodium(I) Complexes Containing Transoid Bridging Bis(diphenylphosphino)methane Ligands. Crystal Structure of a Dirhodium(II) Complex with an Unusual Folding of the Diphosphine Ligand

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Received April 11, 1989

The two-electron electrochemical oxidation of complexes such as $[Rh_2(\mu\text{-dppm})_2(t\text{-BuNC})_2(\mu\text{-A})]PF_6$ (dppm = bis(diphenylphosphino)methane; A = pyrazolate derivative) is facilitated by the presence of neutral Lewis bases such as pyridine derivatives or anionic ligands such as Cl^-, Br^-, I^-, SCN^-, NO_3^-, and CH_3COO^-. Several of the oxidative-addition products have been isolated and characterized. The NO_3^- and CH_3CO^- derivatives were also obtained by the reaction of the pyrazolato-bridged dirhodium(I) complexes with HNO_3 and CH_3COOH, respectively. The paramagnetic Rh_2^{3+} species generated by a one-electron oxidation of the parent dirhodium(I) complexes undergo disproportionation in the presence of the anionic ligands (except NO_3^-). The addition of NO_3^- to the Rh_2^{3+} species results in oxidation to form a dinitrato Rh_2^{4+} complex. The mechanism of the disproportionation reaction of the Rh_2^{3+} species in the presence of halide ions is discussed. One mechanism is believed to involve electron exchange between two Rh_2^{3+} species with simultaneous addition of two anions to the resulting Rh_2^{4+} species. The operative mechanism depends on the nature of the Rh_2^{3+} species and the nature of the anion. If the potential at which the anion ion is oxidized is more negative that the potential at which the Rh_2^{3+} species is reduced, the mechanism involves the oxidation of the anion followed by an oxidative-addition reaction. This second mechanism was found to be operative for the reaction of some of the dicarbonyl Rh_2^{3+} species with Br^- and I^-. The occurrence of different mechanisms for the disproportionation reactions is supported by the $^{31}P\{^1H\}$ NMR data. When the electrochemical oxidation of the dirhodium(I) or the disproportionation of the dirhodium(I,II) complexes that contain the pyrazolate anion (pz) is conducted in CH_2Cl_2 containing CH_3COO^- ions, the complex abstracts a Cl from the solvent to form $[Rh_2(\mu\text{-dppm})_2(t\text{-BuNC})_2(\mu\text{-pz})Cl_2]PF_6$, which was completely characterized by a single-crystal X-ray analysis. Crystals of the complex are monoclinic, space group $P2_1/c$, with $a = 12.355$ (2) Å, $b = 20.759$ (9) Å, $c = 24.689$ (5) Å, $\beta = 96.82$ (2)°, $V = 6287$ (5) Å^3, and $Z = 4$. The methylene moieties of the transoid bridging dppm ligands are folded away from the bridging pyrazolate ligand, and thus they have an orientation which contrasts with that previously found and believed to be favored for dppm-bridged A-frame complexes.

Transition-metal complexes containing diphosphine ligands have been the subjects of numerous investigations in recent years, in part because of their potential applications in homogeneous catalysis.[1] During catalytic processes, the metal centers invariably undergo oxidative-addition and reductive-elimination processes. Thus, factors affecting the propensities of metal centers to undergo these reactions are of considerable importance in designing more efficient catalytic agents. In this light, we have been investigating the effects of ligand modifications on the chemical and electrochemical oxidative processes involving diphosphine-bridged dirhodium complexes.

We recently reported some results of our investigations of pyrazolato-bridged dirhodium complexes that contain the Rh_2^{2+} core and two transoid bridging bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm), or bis(diphenylarsino)methane (dpam) ligands.[2] These complexes were shown to have structure I. It was found that for the dicarbonyl complexes where there is no substituent (Y) in the 4-position of the pyrazolate ring, reactions with Cl_2 and Br_2 not only result in oxidative addition at the metal centers to produce complexes with the Rh_2^{4+} core but also result in substitution at the 4-position of the heterocyclic ring. In contrast, the reaction with I_2 results only in oxidative addition at the metal centers.

Previous electrochemical studies of similar dirhodium complexes[3] indicate that coordinating species in solution drastically

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[†] University of Tennessee.
[‡] Duke University.

(1) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; Chapter 5. Sanger, A. R. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; Chapter 6. Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

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