The Enthalpy of Insertion of Sulfur into the Metal−Hydrogen Bond. Synthetic, Structural, and Calorimetric Study of the Complexes $HS-M(CO)_3C_5R_5$ [M = Cr, Mo, W; R = H, Me]

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Synthetic and calorimetric studies of the sulfhydryl complexes $HS-M(CO)_3C_5R_5$ (M = Cr, R = Me; M = Mo, W, R = H, Me) are reported. The Mo and W complexes can be obtained in high yield by reaction of the hydrido complexes $H-M(CO)_3C_5R_5$ with $Ph_3Sb{=}S$, which readily undergoes single S atom transfer to the metal−hydrogen bond yielding the metal−sulfhydryl complex. Direct reaction between the metal hydrides and a limited amount of sulfur also yields the sulfhydryl complexes as the dominant organometallic product. At sulfur atom/metal hydride ratios higher than 1/1, additional products formulated as $HS_n-M(CO)_3C_5R_5$ are detected. The enthalpies of insertion of sulfur from $Ph_3Sb{=}S$ and S_8 into the metal−hydrogen bond have been determined by solution calorimetry. The $HS-M(CO)_3C_5R_5$ complexes (M = Mo, W) are readily desulfurized by PCy_3 for R = H, but not for R = Me. The M−SH bond strength estimates for the complexes $HS-M(CO)_3C_5Me_5$ increases in the order Cr (46) < Mo (55) < W (63) (kcal/mol). The $HS-Mo(CO)_3C_5Me_5$ group has a pK_a value at least 4 pK_a units less acidic than that of $H-Mo(CO)_3C_5Me_5$. The crystal structure of $HS-W(CO)_3C_5Me_5$ is reported.

Introduction

The chemistry of metal/sulfur/hydrogen systems is both complex and important. Coordinated thiols and sulfhydryls no doubt play an important role in catalytic processes such as hydrodesulfurization[1] and also in biochemical systems such as nitrogen fixation.[2] Despite that, there is very little physical data on the nature of the M−SH bond.[3] We have recently reported thermochemical studies which led to M−SR bond strength estimates for chromium,[4] molybdenum,[5] and tungsten[6] thiolate complexes. These studies were based on reactions of disulfides as shown in eqs 1−3.

$$H-Mo(CO)_3C_5R_5 + RSSR \rightarrow RS-Mo(CO)_3C_5R_5 + RSH \quad (1)$$

$$^{\bullet}Cr(CO)_3C_5Me_5 + {}^1/_2RSSR \rightarrow RS-Cr(CO)_3C_5Me_5 \quad (2)$$

$$W(CO)_3(PCy_3)_2 + {}^1/_2RSSR \rightarrow RS-W(CO)_3(PCy_3)_2 \quad (3)$$

To the authors' knowledge, there is no information about the enthalpy of formation of sulfhydryl complexes L_nM-SH. This is of interest not only to compare the M−SH bond to the corresponding M−SR bond but also to allow either measurement or calculation of reactions such as the formal desulfurization shown in eq 4 and H atom transfer in eq 5. Determining the

$$L_nM-SH \rightarrow L_nM-H + \text{“S”} \quad (4)$$

$$L_nM-SH \rightarrow L_nM{=}S + \text{“H”} \quad (5)$$

thermochemical driving force for reactions in eqs 4 and 5 depends on knowing the relative (or absolute) M−SH as well as M−H and M=S bond strengths.

The greater kinetic reactivity of metal sulfhydryl versus metal thiolate is well-known.[3] A practical consequence is that while a wide range of complexes $L_nM-(SR)_x$ have been prepared, there are fewer corresponding compounds of the formula $L_nM-(SH)_x$. Insertion of sulfur into the Pt−H bond has recently been reported[7] by Jones and co-workers. Of relevance to this paper is the report that the complex $HS-W(CO)_3C_5H_5$ can be prepared[8a] from the corresponding tungsten hydride and ethylene sulfide according to eq 6. The sulfhydryl complex has been

$$H-W(CO)_3C_5H_5 + C_2H_4S \rightarrow HS-W(CO)_3C_5H_5 + C_2H_4 \quad (6)$$

reported[8b,c] to react with organic *N*-polysulfido phthalimide derivatives as shown in eq 7. The organometallic polysulfido complexes were reported to decompose to thiolate complexes by desulfurization, although the fate of the extruded sulfur is not described.

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(1) Transition Metal−Sulfur Chemistry. *ACS Symp. Ser.* **1996**, *653*.

(2) *Molybdenum Enzymes, Cofactors, and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, D.C., 1993.

(3) To our knowledge there are no reports of the M−SH bond strength. For report of M−SR bond strengths in a related system, see: Dias, A. R.; Simoes, J. A. M. *Polyhedron* **1988**, *7*, 1531.

(4) (a) Ju, T. D.; Capps, K. B.; Lang, R. F.; Roper, G. C.; Hoff, C. D. *Inorg. Chem.* **1997**, *36*, 614. (b) Ju, T. D.; Lang, R. F.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 5328.

(5) Mukerjee, S. L.; Gonzalez, A. A.; Nolan, S. P.; Ju, T. D.; Lang, R. L.; Hoff, C. D. *Inorg. Chim. Acta* **1995**, *240*, 175.

(6) Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Byran, C. J.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 7917.

(7) Morton, M. S.; Lachicotte, R. J.; Vicic, D. A.; Jones, W. D. *Organometallics* **1999**, *18*, 227.

(8) (a) Beck, W.; Danzer, W.; Thiel, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 582. (b) Shaver, A.; Hartgerink, J.; Lai, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938. (c) Shaver, A.; McCall, J. M.; Bird, P. H.; Ansari, N. *Organometallics* **1983**, *2*, 1894. (d) Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1997**, *65*, 1190.

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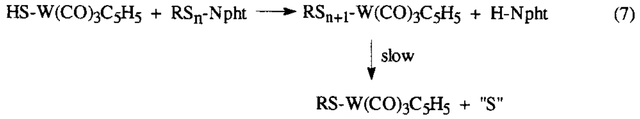

$$\begin{array}{c} HS\text{-}W(CO)_3C_5H_5 + RS_n\text{-}Npht \longrightarrow RS_{n+1}\text{-}W(CO)_3C_5H_5 + H\text{-}Npht \\ \Big\downarrow \text{slow} \\ RS\text{-}W(CO)_3C_5H_5 + \text{"S"} \end{array} \qquad (7)$$

The capability of compounds to store and release sulfur by sulfur atom transfer (SAT) reactions is controlled by both thermodynamic and kinetic factors that are not fully understood. Not long ago, Jason[9] showed the ability of $Ph_3As{=}S$ and $Ph_3Sb{=}S$ to efficiently serve as S atom transfer reagents. We have recently reported the enthalpies of sulfurization of a series of tertiary phosphines, arsines, and stibines forming the corresponding sulfides[10] (eq 8). This provided a range of sulfur atom

$$R_3E + {}^1/_8S_8 \rightarrow R_3E{=}S \qquad (E = P, As, Sb) \qquad (8)$$

transfer enthalpies which we are currently extending to other main group and transition metal systems capable of formal sulfur atom insertion. In that regard, the metal−hydride functional group represents a good target, and we discuss here our studies of sulfurization and desulfurization to metal hydrides $H{-}M(CO)_3C_5R_5$.

Experimental Section

General Procedure. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or in a Vacuum Atmospheres glovebox. Solvents were purified by distillation from sodium/benzophenone under argon into flame-dried glassware. H_2S (99.5%) from Matheson Gas was used as obtained. $Ph_3Sb{=}S$ and PCy_3 were commercially available and used without further purification. Orthorhombic sulfur (99.9995%), obtained from Johnson Mathey, was further recrystallized from carbon disulfide. The complexes $H{-}M(CO)_3C_5R_5$ (M = Cr, R = Me; M = Mo, W, R = H, Me),[11] $Na^+[Mo(CO)_3C_5Me_5]^{-11}$, $PhS{-}M(CO)_3C_5Me_5$ (M = Cr,[4] Mo[5]), and $MeS{-}Cr(CO)_3C_5Me_5$[4] were prepared and purified by standard literature procedures. Kinetic studies and infrared measurements were made on a Perkin-Elmer 2000 FT-IR equipped with an i-series microscope. NMR data was recorded on a Varian VXR 400 spectrometer. Calorimetric measurements were made using techniques described in detail elsewhere.[4,6] The crystal structure of $HS{-}W(CO)_3C_5Me_5$ was determined on a Siemens SMART diffractometer.

Preparation of the Complexes $HS{-}M(CO)_3C_5R_5$ (M = Cr, R = H; M = Mo, W, R = H, Me). From $H{-}M(CO)_3C_5R_5$ and $Ph_3Sb{=}S$. In the glovebox a solution of 0.4 mmol $H{-}M(CO)_3C_5R_5$ in 10 mL of tetrahydrofuran was transferred onto 0.4 mmol of solid $Ph_3Sb{=}S$ with stirring. After 1 h, the reaction was complete as determined by FT-IR spectroscopy. Spectroscopic data, IR and NMR, for the complexes are summarized in Table 2. Concentration of the solution to about 2−3 mL followed by addition of heptane and cooling to −20 °C afforded the crystalline complexes in 70−90% yield, except for $HS{-}Cr(CO)_3C_5Me_5$ and $HS{-}Mo(CO)_3C_5H_5$, which are unstable at ambient temperature.

From $H{-}M(CO)_3C_5R_5$ and S_8. To a solution of 0.4 mmol of $H{-}M(CO)_3C_5R_5$ in 10 mL of tetrahydrofuran was added a solution of 0.05 mmol of S_8 in 1 mL of tetrahydrofuran with stirring. After 1 h, the reaction was complete as determined by FT-IR. Removal of the solvent in vacuo gave the crude complexes $HS{-}M(CO)_3C_5R_5$ in yields greater than 80% except for the unstable $HS{-}Cr(CO)_3C_5Me_5$ and $HS{-}Mo(CO)_3C_5H_5$.

Kinetics. $H{-}Mo(CO)_3C_5Me_5$ and $Ph_3Sb{=}S$. Under an atmosphere of CO, 25 mL of a 0.01059 M toluene solution of $H{-}Mo(CO)_3C_5Me_5$ was allowed to equilibrate to a temperature of 15 °C. One milliliter of this solution was removed to obtain a spectrum of the stock solution prior to beginning the reaction. To this solution was added 4.5 mL of a 0.05588 M $Ph_3Sb{=}S$ solution, yielding a solution with $[H{-}Mo(CO)_3C_5Me_5]$ and $[Ph_3Sb{=}S]$ = 0.00880 M. This procedure was repeated in tetrahydrofuran. The reaction obeyed second-order kinetics: rate = $k_{obs}[H{-}Mo(CO)_3C_5Me_5][Ph_3Sb{=}S]$ in both toluene and THF with values for k_{obs} at 15 °C of 0.15 $M^{-1}\ s^{-1}$ in THF and 0.0079 $M^{-1}\ s^{-1}$ in toluene.

Table 1. Crystal Data and Structure Refinement for $HS{-}W(CO)_3C_5Me_5$

empirical formula	$C_{13}H_{16}O_3SW$
fw	436.17
temp	173(2) °C
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2(1)/c$
unit cell dimens	$a = 7.3394(1)$ Å $b = 8.5719(2)$ Å $c = 23.0617(5)$ Å $\alpha = 90°$ $\beta = 96.466(1)°$ $\gamma = 90°$
vol	1441.64(5) Å^3
Z	4
density (calcd)	2.010 g/cm^3
abs coeff	81.54 cm^{-1}
F(000)	832
cryst size	0.36 × 0.18 × 0.16 mm^3
θ range for data collection	1.78−27.50°
index ranges	$-8 \le h \le 9, -11 \le k \le 8, -25 \le l \le 29$
reflns collected	10 279
indept reflns	3310 [R(int) = 0.0242]
completeness to θ = 27.50°	99.8%
abs corr	integration by crystal faces
min and max abs	0.109, 0.343
refinement meth	full-matrix least squares on F^2
data/restraints/params	3310/4/185
goodness of fit on F^2	1.233
final R indices [$I > 2\sigma(I)$]	R1 = 0.0261, wR2 = 0.0522 [2987]
R indices (all data)	R1 = 0.0323, wR2 = 0.0534
extinction coeff	0.0085(3)
largest diff peak and hole	1.386 and −0.603 e Å^{-3}

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR2 = [\sum[w(F_o2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[s^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Spectroscopic Data for the Complexes $HS{-}M(CO)_3C_5R_5$

	^{1}H NMR (ppm) (C_6D_6; 25 °C)	IR (cm^{-1}) (25 °C)
$HS{-}Cr(CO)_3C_5Me_5$	1.37 (C_5H_5), −3.23 (SH)	2008, 1949 (toluene)
$HS{-}Mo(CO)_3C_5H_5$	4.53 (C_5H_5), −2.93 (SH)	2034, 1954 (toluene) 2033, 1950 (THF)
$HS{-}Mo(CO)_3C_5Me_5$	1.48 (C_5Me_5), −2.21 (SH)	2021, 1941 (toluene) 2021, 1938 (THF)
$HS{-}W(CO)_3C_5H_5$	4.52 (C_5H_5), −2.48 (SH)	2029, 1940 (toluene) 2028, 1936 (THF)
$HS{-}W(CO)_3C_5Me_5$	1.54 (C_5Me_5), −1.95 (SH)	2017, 1928 (toluene) 2016, 1925 (THF)

Reactions. Reaction of $H{-}W(CO)_3C_5H_5$ with Excess S_8. A solution of S_8 (58.3 mg, 0.23 mmol) in 10 mL of toluene was syringed on top of $H{-}W(CO)_3C_5H_5$ (54.0 mg, 0.16 mmol). FT-IR peaks at 2031 and 1940 cm^{-1} were consistent with the formulation $HS_n{-}W(CO)_3C_5H_5$. Further, ^{1}H NMR showed peaks at 4.96, 4.90, and 4.84 ppm (C_5H_5) in C_6D_6 also consistent with the formulation $HS_n{-}W(CO)_3C_5H_5$, as well as peaks at 4.52 ppm (C_5H_5) and −2.48 ppm (SH) due to $HS{-}W(CO)_3C_5H_5$.

Reaction of $HS_n{-}W(CO)_3C_5H_5$ with *n* Equiv of PCy_3. Four milliliters of the $HS_n{-}W(CO)_3C_5H_5$ solution (2031 and 1940 cm^{-1}) from above was syringed on top of solid PCy_3 (207.8 mg, 0.74 mmol) with a rapid conversion (seconds) to $HS{-}W(CO)_3C_5H_5$ (2029 and 1940 cm^{-1}) and a much slower conversion (hours) to $H{-}W(CO)_3C_5H_5$ (2020 and 1926 cm^{-1}) as seen by FT-IR.

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(9) Jason, M. E. *Inorg. Chem.* **1997**, *36*, 2641.

(10) Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861.

(11) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Vol. 3, pp 1191−1195.

Reaction of $HS_n-W(CO)_3C_5H_5$ with *n* Equiv of $H-W(CO)_3C_5H_5$. A solution of $H-W(CO)_3C_5H_5$ (114.2 mg, 0.34 mmol) in 15 mL of THF was syringed on top of solid S_8 (20.7 mg, 0.08 mmol). A rapid reaction occurred as confirmed by the presence of FT-IR peaks at 2029 and 1937 cm^{-1} consistent with the formulation $HS_n-W(CO)_3C_5H_5$. This solution was then syringed on top of solid $H-W(CO)_3C_5H_5$ (100.0 mg, 0.30 mmol) with a slow conversion to $HS-W(CO)_3C_5H_5$ (2028 and 1936 cm^{-1}) as seen by FT-IR.

Reaction of $R'-Mo(CO)_3C_5R_5$ [R = H, R′ = Bz; R = Me, R′ = Me] with $Ph_3Sb{=}S$. A solution of $R'-Mo(CO)_3C_5R_5$ (0.16 mmol) in 10 mL of tetrahydrofuran was transferred onto solid $Ph_3Sb{=}S$ (0.16 mmol) and stirred for about 9 h. FT-IR confirmed no reaction.

Reaction of $MeS-Cr(CO)_3C_5Me_5$ and $PhS-Mo(CO)_3C_5Me_5$ with H_2S. Typically, a solution of $RS-M(CO)_3C_5Me_5$ (0.1 mmol) in 12 mL of tetrahydrofuran was treated with H_2S gas (25 mL, 1.1 mmol). The reaction was complete after 3 h. The formation of $HS-M(CO)_3C_5Me_5$ (M = Cr, 2007 and 1946 cm^{-1}; M = Mo, 2010 and 1921 cm^{-1}) was confirmed by its FT-IR spectrum with decrease in bands due to $RS-M(CO)_3C_5Me_5$ (M = Cr, R = Me, 1997, 1938, and 1915 cm^{-1}; M = Mo, R = Ph, 2020, 1943, and 1927 cm^{-1}).

Reaction of $HS-W(CO)_3C_5H_5$ with PCy_3. To $HS-W(CO)_3C_5H_5$ (104 mg, 0.3 mmol) dissolved in 10 mL of tetrahydrofuran was added a solution of PCy_3 (84 mg, 0.3 mmol) in 5 mL of tetrahydrofuran with stirring. The reaction was complete after 3 h, and the product $H-W(CO)_3C_5H_5$ (2018 and 1924 cm^{-1}) was identified by its FT-IR spectrum. Formation of $S{=}PCy_3$ was confirmed by ^1H NMR by comparison with an authentic sample.

Reaction of $HS-Mo(CO)_3C_5Me_5$ with 10 Equiv of $Na^+[Mo(CO)_3C_5Me_5]^-$. A mixture of solid $HS-Mo(CO)_3C_5Me_5$ (7 mg, 0.02 mmol) and $Na^+[Mo(CO)_3C_5Me_5]^-$ (68 mg, 0.2 mmol) was dissolved in 15 mL of tetrahydrofuran. No formation of $H-Mo(CO)_3C_5Me_5$ was observed by FT-IR.

Reaction of $HS-Mo(CO)_3C_5H_5$ with $Na^+[Mo(CO)_3C_5Me_5]^-$. $HS-Mo(CO)_3C_5H_5$ was prepared in situ from $H-Mo(CO)_3C_5H_5$ (74 mg, 0.3 mmol) and S_8 (10 mg, 0.038 mmol) in 10 mL of tetrahydrofuran. The conversion to the sulfhydryl complex was confirmed by FT-IR (2033 and 1950 cm^{-1}). With stirring, 10 mL of a tetrahydrofuran solution of $Na^+[Mo(CO)_3C_5Me_5]^-$ (101 mg, 0.3 mmol) was added with FT-IR peaks at 1887, 1785, and 1731 cm^{-1}. The exchange reaction was complete within minutes, as seen by FT-IR, to yield $Na^+[Mo(CO)_3C_5H_5]^-$ (1900, 1798, and 1732 cm^{-1}) and $HS-Mo(CO)_3C_5Me_5$ (2021 and 1938 cm^{-1}).

Crystal Structure of $HS-W(CO)_3C_5Me_5$. Crystal growth was achieved by slow cooling of a toluene solution of the complex to − 20 °C. An orange, blocklike single crystal, 0.36 × 0.18 × 0.16 mm, of $HS-W(CO)_3C_5Me_5$ was selected. Data were collected on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation. Cell parameters were refined using up to 7761 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). The structure was solved by the direct methods in SHELXTL5 and refined using full-matrix least squares. Non-H atoms were treated anisotropically, whereas the methyl hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The geometry around the W atom can be described as a four-legged piano stool with the three CO and the HS ligands occupying the square base. The HS and one CO group diagonally located from it are disordered and were refined in two parts. Their site occupation factors were dependently refined to 0.69(1) for the major part, and consequently 0.31(1) for the minor part. The major and minor parts of the CO and HS groups were constrained to be respectively equivalent. Only the proton on the S atom of the major part was located from a difference Fourier map and refined freely but with an isotropic thermal parameter of 1.5 times that of the S atom. Refinement was done using F^2. Crystal and experimental data are summarized in Table 1, and an ORTEP representation is depicted in Figure 1.

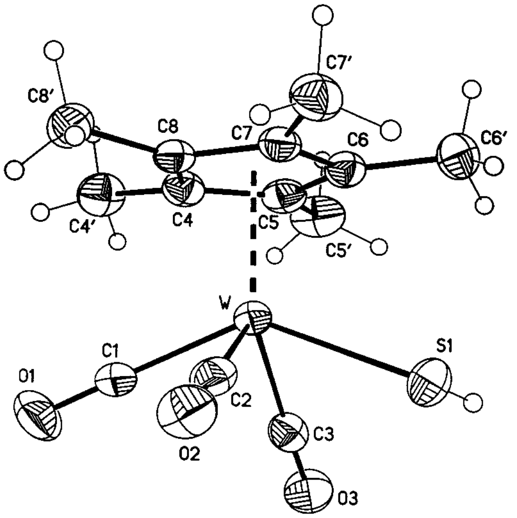


Figure 1. Molecular structure of $HS-W(CO)_3C_5Me_5$ [ORTEP, 50% probability ellipsoids: the minor part of the disorder (S1′, C1′, and O1′) was omitted for clarity]. Selected bond distances (Å) and angles (deg): W−S1 2.522(2), S1−H1 1.04(7), W−S1−H1 108(4).

Results

Reaction of $H-M(CO)_3C_5R_5$ with $Ph_3Sb{=}S$. Reaction of triphenylantimony sulfide and metal hydrides was rapid and quantitative as shown in eq 9. Stable crystalline products could

$$H-M(CO)_3C_5R_5(soln) + Ph_3Sb{=}S(solid) \rightarrow HS-M(CO)_3C_5R_5(soln) + Ph_3Sb(soln) \quad (9)$$

be isolated for M = Mo, R = Me, and for M = W, R = H, Me. The complexes $HS-Mo(CO)_3C_5H_5$ and $HS-Cr(CO)_3C_5Me_5$ could be detected spectroscopically, but decomposed in solution or during attempted workup. Reaction of solid $Ph_3Sb{=}S$ is recommended, since a solution of $Ph_3Sb{=}S$ slowly decomposes to Ph_3Sb and elemental sulfur.[9] Spectroscopic data for the complexes prepared according to eq 9 are summarized in Table 2. Kinetic studies of reaction involving $H-Mo(CO)_3C_5Me_5$ and $Ph_3Sb{=}S$ showed that the reaction obeyed second-order kinetics: rate = $k_{obs}[H-Mo(CO)_3C_5Me_5][Ph_3Sb{=}S]$ in both toluene and THF. The values of k_{obs} at 15 °C were $k_{obs} = 0.15\ M^{-1}\ s^{-1}$ (THF) and $k_{obs} = 0.0079\ M^{-1}\ s^{-1}$ (toluene).

Reaction of $H-M(CO)_3C_5R_5$ with S_8. Reaction of the metal hydrides and purified S_8 in tetrahydrofuran solution yielded the metal sulfhydryl complexes as well as varying amounts of polysulfido hydride complexes as summarized in eq 10 for tungsten. The nature of the products formed in eq 10 depended

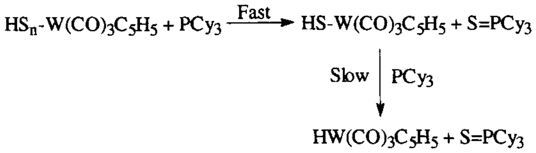
$$H-W(CO)_3C_5H_5 + S_8 \rightarrow HS-W(CO)_3C_5H_5 + HS_n-W(CO)_3C_5H_5 \quad (10)$$

on the metal/sulfur ratio, the specific metal complex, and the solvent and temperature. If a deficiency of sulfur was used such that the molar M/S ratio ≫ 1, conversion to the metal sulfhydryl complex based on sulfur as the limiting reagent was quantitative as determined by both IR and NMR spectroscopy. A similar pattern of stability for the sulfhydryl complexes prepared in this way with those obtained from $Ph_3Sb{=}S$ was observed. The complexes $HS-Mo(CO)_3C_5H_5$ and $HS-Cr(CO)_3C_5Me_5$ could again be characterized spectroscopically, but decomposed in solution. In the case of $HS-Cr(CO)_3C_5Me_5$, the principal products of decomposition could be identified as the known complexes $[C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5]$, $[C_5Me_5(CO)_2Cr(\mu\text{-}S_2)Cr(CO)_3C_5Me_5]$, and $[C_5Me_5(CO)_2Cr-(\mu\text{-}S_2)Cr(CO)_2C_5$-

Me_5].[12] In the case of $HS{-}Mo(CO)_3C_5H_5$, insoluble precipitates were formed and not characterized.

Reaction of sulfur with the metal hydrides at metal hydride/sulfur ratios higher than 1/1 provided evidence for formation of polysulfide complexes $HS_nM(CO)_3C_5R_5$ analogous to the alkyl polysulfides reported earlier[8] as shown in eq 7. For the polysulfide hydrides the carbonyl IR bands were shifted to higher wavenumbers (2−3 cm^{-1}) and the NMR signals of the C_5H_5 ring were shifted downfield. Chemical evidence for this formulation was generated by the fact that addition of excess hydride to the already formed polysulfide complexes resulted in smooth reaction to produce the metal sulfhydryl complex (eq 11). Furthermore, addition of excess PCy_3 to $HS_n{-}W(CO)_3C_5H_5$ resulted in rapid conversion (seconds) to $HS{-}W(CO)_3C_5H_5$ and $S{=}PCy_3$ followed by a much slower conversion (hours) to $H{-}W(CO)_3C_5H_5$ and $S{=}PCy_3$ as shown in eq 12. Attempts to separate the mixture of polysulfide complexes formed in eq 10 failed. In the presence of excess sulfur, insoluble material, presumably consisting of dimeric and polymeric higher oxidation state sulfides, was formed.[13]

$$\mathrm{HS}_n\mathrm{-W(CO)_3C_5H_5} + n\mathrm{H-W(CO)_3C_5H_5} \rightarrow (n{+}1)\ \mathrm{HS-W(CO)_3C_5H_5} \quad (11)$$



(12)

Reaction of R′−Mo(CO)₃C₅R₅ with Ph₃Sb=S. Reaction of alkyl molybdenum complexes and triphenylantimony sulfide was attempted to see if S atom insertion into the metal alkyl bond forming thiolate complexes would occur. As shown in eq 13 in tetrahydrofuran over a period of 8 h, no reaction was observed for R = H, R′ = Bz, and R = Me, R′ = Me.

$$\mathrm{R'{-}Mo(CO)_3C_5R_5 + Ph_3Sb{=}S} \not\rightarrow \mathrm{R'S{-}Mo(CO)_3C_5R_5 + Ph_3Sb} \quad (13)$$

Reaction of MeS−Cr(CO)₃C₅Me₅ and PhS−Mo(CO)₃C₅Me₅ with H₂S. A third route to the sulfhydryl complexes investigated was thiol/hydrogen sulfide exchange as shown in eqs 14 and 15. In the presence of excess hydrogen sulfide the reactions proceeded quantitatively as shown. The chromium sulfhydryl complex obtained by this method had spectroscopic properties identical to those of the complex, obtained in reactions of the chromium hydride with triphenylantimony sulfide or elemental sulfur as discussed above. Solutions of $HS{-}Cr(CO)_3C_5Me_5$ prepared according to eq 14 were stable for several hours in solution under H_2S and CO, but upon evacuation during workup decomposed and could not be isolated as solids.

$$\mathrm{MeS{-}Cr(CO)_3C_5Me_5 + H_2S \rightarrow MeSH + HS{-}Cr(CO)_3C_5Me_5} \quad (14)$$

$$\mathrm{PhS{-}Mo(CO)_3C_5Me_5 + H_2S \rightarrow PhSH + HS{-}Mo(CO)_3C_5Me_5} \quad (15)$$

Table 3. Calorimetric Data[a] for "S" Insertion into the H−M Bond of $H{-}M(CO)_3C_5R_5$

	−ΔH, sulfur soln		−ΔH, solid S=SbPh₃
	THF	toluene	toluene
$C_5Me_5(CO)_3Mo{-}SH$	12.8 ± 0.4	12.4 ± 0.4	11.3 ± 0.2
$C_5H_5(CO)_3W{-}SH$	11.2 ± 0.3		11.7 ± 0.5
$C_5Me_5(CO)_3W{-}SH$	12.8 ± 0.2	12.2 ± 0.6	12.6 ± 0.8
$C_5Me_5(CO)_3Cr{-}SH$		5.0 ± 0.2[b]	

[a] ΔH in kcal/mol for all species in solution at 30 °C. [b] Calculated on the basis of enthalpy of reaction of $PhS{-}Cr(CO)_3C_5Me_5$ and H_2S as discussed in text.

Solution Calorimetric Studies. Enthalpies of reaction of the metal hydrides with triphenylantimony sulfide were measured as shown in eq 9. We have previously determined that the enthalpy of reaction 16 is + 5.2 ± 0.5 kcal/mol.[10] Subtraction of reaction 16 from reaction 9 yields directly the reaction in eq 17. Calculated enthalpies of reaction (eq 17) based on experimental determination of the enthalpies of reaction (eq 9) are collected in Table 3. In addition, direct measurement of the enthalpy of reaction 17 was also made with limiting sulfur as a reagent. Reactions in THF were faster; however, there is reasonable agreement between data for reaction in toluene and THF indicating little solvent effect on the reaction energetics.

$$\mathrm{Ph_3Sb{=}S(solid) \rightarrow Ph_3Sb(soln) + {}^1/_8S_8(soln)} \quad (16)$$

$$\mathrm{H{-}M(CO)_3C_5R_5(soln) + {}^1/_8S_8(soln) \rightarrow HS{-}M(CO)_3C_5R_5(soln)} \quad (17)$$

Desulfurization of HS−W(CO)₃C₅H₅ by PCy₃. The enthalpy of reaction in eq 18 was measured by solution calorimetry in THF solution.

$$\mathrm{HS{-}W(CO)_3C_5H_5 + PCy_3 \rightarrow H{-}W(CO)_3C_5H_5 + S{=}PCy_3} \quad (18)$$

$$\Delta H = -17.9 \pm 3.0\ \mathrm{kcal/mol}$$

Previously we had reported[10] the enthalpy of reaction in eq 19.

$$\mathrm{PCy_3 + {}^1/_8S_8 \rightarrow S{=}PCy_3} \quad (19)$$

$$\Delta H = -\ 30.9 \pm 1.9\ \mathrm{kcal/mol}$$

Subtraction of reaction 18 from reaction 19 yields a calculated ΔH = − 13.0 ± 2.2 kcal/mol for sulfurization of $H{-}W(CO)_3C_5H_5$. This is in reasonable agreement with other experimental values in Table 3 and gives confidence to the measurements. The enthalpy of reaction 14 was determined to be −0.5 ± 0.3 kcal/mol in toluene solution. As discussed later, this value can be used to estimate the Cr−SH bond strength as well as the enthalpy of sulfurization of the chromium hydride.

Qualitative Studies of p*K*ₐ of HS−M(CO)₃C₅R₅ Complexes. Several attempts were made to bracket the pK_a of the sulfhydryl complex. The first was attempted deprotonation by a metal carbonyl anion according to eq 20. Even in the presence of a 10-fold molar excess of $Na^+[Mo(CO)_3C_5Me_5]^-$, no

$$\mathrm{Na^+[Mo(CO)_3C_5Me_5]^- + HSMo(CO)_3C_5Me_5 \rightleftharpoons HMo(CO)_3C_5Me_5 + Na^+[SMo(CO)_3C_5Me_5]^-} \quad (20)$$

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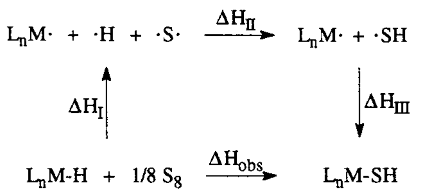
(12) (a) Goh, L. Y.; Hambley, T. W.; Robertson, G. B. *Organometallics* **1987**, *6*, 1051. (b) Hermann, W. A.; Rohrmann, J.; Schafer, A. *J. Organomet. Chem.* **1984**, *265*, C1.

(13) (a) DuBois, M. R.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (b) DuBois, M. R.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. (c) DuBois, M. R.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

Scheme 1



detectable amount of $H-Mo(CO)_3C_5Me_5$ was formed. The limit of detection is estimated to be about 3%, which implies that the equilibrium constant for the reaction in eq 20 is smaller than 10^{-4}. A significant kinetic barrier to this proton transfer reaction[14] is not expected, and this implies that the sulfhydryl complex has a pK_a in tetrahydrofuran solution that is at least 4 pK_a units less acidic for $HS-Mo(CO)_3C_5Me_5$ than $H-Mo(CO)_3C_5Me_5$.

The more electron donating character of the C_5Me_5 ligand, when compared to C_5H_5, is well-known, and $H-Mo(CO)_3C_5Me_5$ is a weaker acid by 3 pK_a units when compared to $HMo(CO)_3C_5H_5$. The equilibrium in eq 21 is rapidly established.[14]

$$Na^+[Mo(CO)_3C_5Me_5]^- + H-Mo(CO)_3C_5H_5 \rightarrow H-Mo(CO)_3C_5Me_5 + Na^+[Mo(CO)_3C_5H_5]^- \quad (21)$$

In that regard, reaction 22 was attempted.

$$[Mo(CO)_3C_5Me_5]^- + HS-Mo(CO)_3C_5H_5 \overset{?}{\rightleftharpoons} H-Mo(CO)_3C_5Me_5 + [S\text{-}Mo(CO)_3C_5H_5]^- \quad (22)$$

Mixing the reactants in eq 22 showed no sign of proton transfer; instead nucleophilic attack of the metal carbonyl anion resulting in SH group transfer occurred as shown in eq 23.

$$Na^+[Mo(CO)_3C_5Me_5]^- + HS-Mo(CO)_3C_5H_5 \rightarrow HS-Mo(CO)_3C_5Me_5 + Na^+[Mo(CO)_3C_5H_5]^- \quad (23)$$

Discussion

This work was begun to see if the utility of triphenylantimony sulfide as a clean single S atom transfer reagent could be extended to transition metal complexes. In fact, reaction of the group VI metal hydrides proceeded cleanly with this reagent and provided a route to determining the enthalpies of formation of those $HS-M(CO)_3C_5R_5$ complexes which were stable in solution. The enthalpies of sulfurization of the metal−hydrogen bond determined here can be used to generate information regarding the M−SH bond strength provided the M−H bond strength is known using the general thermochemical cycle in Scheme 1. The observed enthalpy of sulfurization is shown in Scheme 1 in three steps: $\Delta H_I = BDE(L_nM-H) + \Delta H_{atom}(S)$; $\Delta H_{II} = -BDE(^\bullet SH)$; $\Delta H_{III} = -BDE(L_nM-SH)$. Combining these terms and using literature data[15] leads directly to eq 24.

$$BDE(L_nM-SH) = BDE(L_nM-H) - \Delta H_{obs} - 21.0\ \text{kcal/mol} \quad (24)$$

Using the data in Table 3 for reaction of $Ph_3Sb{=}S$ in toluene and bond dissociation energies for $H-M(CO)_3C_5Me_5$ of 65 kcal/mol for Mo and 70 kcal/mol for W[16] leads to estimates of the M−SH bond strengths of 55 and 63 kcal/mol for the $HS-M(CO)_3C_5Me_5$ bonds for Mo and W, respectively. The enthalpies of sulfurization of the M−H bond calculated on the basis of reaction with $Ph_3Sb{=}S$ are in reasonable agreement with direct measurements with $^1/_8S_8$.

The bond strength of $HS-Mo(CO)_3C_5Me_5$ (55 kcal/mol) is significantly higher than an estimate made earlier for that of $PhS-Mo(CO)_3C_5Me_5$ (41 kcal/mol)[5] based on measurements of the enthalpy of reaction in eq 1. The bond strength estimates for the two different complexes were made using different methods and auxiliary data. Nevertheless, they allow estimation of the enthalpy of reaction in eq 25. Since the S−H bond

$$HS-Mo(CO)_3C_5Me_5 + PhSH \rightarrow PhS-Mo(CO)_3C_5Me_5 + H_2S \quad (25)$$

strength in H_2S (91.2 kcal/mol)[17] is approximately 8 kcal/mol stronger than the S−H bond in PhSH (83.2 kcal/mol),[18] this reaction (eq 25) is expected to proceed as written, unless the Mo−SH bond is more than 8 kcal/mol stronger than the Mo−SPh bond for the complexes. It was surprising to us that the Mo−SH bond strength estimate was 14 kcal/mol higher than that made earlier for the Mo−SPh bond strength. As a check, qualitative investigation of the equilibrium shown in eq 25 was made. It was found to proceed in the reverse direction which provides support for the stronger Mo−SH bond assigned here.

The instability of the complex $HS-Cr(CO)_3C_5Me_5$ formed under oxidative conditions led us to investigate its formation by hydrogen sulfide/thiol exchange. The enthalpy of reaction (eq 14) was found to be −0.5 kcal/mol. Using the Cr−SPh bond strength of 35 kcal/mol[4] and a difference of 10 kcal/mol in the H_2S[17] and PhSH[18] bond strengths leads to a value of 46 kcal/mol for the $HS-Cr(CO)_3C_5Me_5$ bond dissociation energy. The increase in BDEs [Cr (46 kcal/mol) < Mo (55 kcal/mol) < W (63 kcal/mol)] is in keeping with expected periodic trends.[19] Further, using the value for the Cr−H bond strength of 62 kcal/mol and eq 24 leads to a calculated value for ΔH_{obs} of −5 kcal/mol for the sulfur insertion into the Cr−H bond. This is less exothermic than reaction of the corresponding Mo and W complexes by roughly 7 kcal/mol.

The measurements of enthalpies of sulfurization of these metal hydrides can be compared to other values for sulfur atom transfer reactions reported by us earlier and in the literature. It is important to recall that these SAT energies are based on reaction with $^1/_8S_8$ and not a single S atom. The gas phase enthalpy of atomization of $^1/_8S_8$ to a single S atom is 63.6 kcal/mol.[20] Thus while enthalpies of desulfurization of the M−SH complexes to the M−H complexes and $^1/_8S_8$ are only endothermic by 5−13 kcal/mol, reductive elimination of a free S atom would be endothermic by an additional 63.6 kcal/mol. The data for enthalpies of sulfurization by $^1/_8S_8$ for the metal hydrides are in the range −5 to −13 kcal/mol, and this is considerably less than the enthalpies of sulfuriziation by phosphines,[10] which

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(14) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; p 309.

(15) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(16) Data for the Mo−H and W−H bonds are selected from ref 14, Table 9.4 on p 331. Due to experimental errors as well as minor differences in reported values, an error of at least 3 kcal/mol is assigned to the absolute values for the M−H bond strengths.

(17) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed., CRC Press: Boca Raton, FL, 1994.

(18) Bordwell, F. G.; Zhang, X. M.; Satish, A. V.; Cheng, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6605.

(19) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503.

(20) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

are between −20 and −31 kcal/mol. The enthalpy of reaction of $^1/_8S_8$ and H_2 forming H_2S is −5 kcal/mol,[15] but the enthalpy of sulfurization of ethylene forming ethylene sulfide is near zero and the enthalpies of formation of thiols from alkanes and sulfur are typically endothermic by about 10 kcal/mol.[21] These data and other work in progress allow prediction of which sulfur transfer reactions are thermodynamically “allowed”. While kinetic barriers determine whether these reactions can in fact occur, the calorimetric data is of real value in predicting equilibrium position. The calculation that phosphines should be capable of desulfurizing the metal sulfhydryl complexes led us to attempt these reactions. Surprisingly, PCy_3 and other trialkylphosphines were only capable of desulfurizing the metal sulfhydryl complexes $HS-M(CO)_3C_5R_5$ in the case of R = H, but not for R = Me. Less reactive phosphines, like PPh_3, do not react at all or at least react prohibitively slowly. Since all of these reactions, including those of PPh_3, are thermodynamically favorable, there is a clear substituent (steric) influence on the reaction mechanisms. Calorimetric measurements of desulfurization of $HS-M(CO)_3C_5R_5$ by PCy_3 were in reasonable agreement with direct measurements of sulfurization and provided an additional check on the experimental calorimetry data.

While there are over 500 structures with a W−SR bond, there is only one structure of a tungsten complex with a sulfhydryl group W−SH.[22] Thus there is not sufficient data for W−SH bond lengths to make a valid comparison. A search of the April Release of the Cambridge Database[23] revealed the presence of 16 M−SH complexes where M is a transition metal. The geometry of $HS-W(CO)_3C_5Me_5$ resembles a four-legged piano stool. The S1−H1 bond reported here [1.04(7) Å] is shorter than the average of 1.199 Å, while the W−S1−H1 angle [108(4)°] is within 1 esd of the average of 105°. Molecules of $HS-W(CO)_3C_5Me_5$ pack as dimers around a center of inversion due to weak H bonding between S1−H1 and C3−O3 of the symmetry equivalent molecule. The H1···O3 ($1 - x, -y, 1 - z$) distance of 2.69(8) Å is equal to the sum of the H and O van der Waals radii (2.60 Å); angle S1−H1···O3 ($1 - x, -y, 1 - z$) is 152(5)°. All other bond distances and angles are within the expected range.

Reaction of $H-Mo(CO)_3C_5Me_5$ with $Ph_3Sb{=}S$ was shown to occur by a second-order reaction and to be some 20 times faster in tetrahydrofuran compared to toluene. This provides evidence for a polar transition state. A reasonable mechanism for this reaction is shown in eq 26. This would involve initial

$$\begin{aligned} &H-Mo(CO)_3C_5Me_5 + Ph_3Sb{=}S \rightarrow \\ &\qquad [Ph_3SbSH]^+[Mo(CO)_3C_5Me_5]^- \rightarrow \\ &\qquad\qquad Ph_3Sb + HS-Mo(CO)_3C_5Me_5 \end{aligned} \tag{26}$$

protonation of $Ph_3Sb{=}S$, followed by nucleophilic attack of the $[Mo(CO)_3C_5Me_5]^-$ anion with net HS^+ transfer. No intermediates were detected in the reaction, which was monitored by FT-IR spectroscopy. The solvent influence and first-order dependence on each reactant support a polar mechanism. A more detailed study of these sulfur atom transfer reactions is in progress and will be reported later.

Reaction of the metal hydrides with elemental sulfur in solution provides an alternative route to those metal sulfhydryl complexes which are stable. In tetrahydrofuran solution, these reactions are relatively rapid and lead cleanly to the metal sulfhydryl products provided a deficiency of sulfur is used. There is evidence that the first step of sulfurization of the hydrides occurs with formation of polysulfides, $HS_n-M(CO)_3C_5R_5$, which are further degraded by remaining metal hydride.

A disadvantage of reaction of S_8 with metal hydrides is that the initial adduct is certainly a polysulfide which must be further reduced by additional metal hydride in solution. Such polysulfides also have the possibility of undergoing intramolecular oxidative addition and subsequent reactions. It is clear that degradation of a single molecule of S_8 must be a complex multistep process. In the case of the chromium hydride $H-Cr(CO)_3C_5Me_5$, the known complexes[12] $[C_5Me_5(CO)_2Cr{=}S{=}Cr(CO)_2C_5Me_5]$, $[C_5Me_5(CO)_2Cr(\mu\text{-}S_2)Cr(CO)_3C_5Me_5]$, and $[C_5Me_5(CO)_2Cr-(\mu\text{-}S_2)Cr(CO)_2C_5Me_5]$ were identified as the major decomposition products. It is of interest to note that $HS-Cr(CO)_3C_5Me_5$ prepared by hydrogen sulfide/thiol exchange as shown in eq 14 appeared to have increased stability when compared to similar preparations under more oxidizing conditions utilizing either S_8 or $Ph_3Sb{=}S$. This suggests that small amounts of higher valent complexes may serve as catalysts for decomposition of $HS-Cr(CO)_3C_5Me_5$. Additional studies on the mechanisms of these sulfurization reactions are in progress.

To date very little is known about acidities of metal sulfhydryl complexes.[24] Therefore it was of interest to determine at least a qualitative pK_a value for one of the $HS-M(CO)_3C_5R_5$ complexes described in this paper. It is well-known that the first pK_a of H_2S is near 7,[17] while the estimated value for $H-Mo(CO)_3C_5Me_5$ in aqueous media is 9.2.[14] In tetrahydrofuran solution, $HS-Mo(CO)_3C_5Me_5$ is at least 4 pK_a units less acidic than the corresponding hydrido complex, and this implies an estimated aqueous pK_a value of greater than 13 for the sulfhydryl complex. Coordination to the metal for this complex reduces the pK_a by at least 6 pK_a units relative to H_2S.

Conclusion

This work describes our continued interest in the thermochemistry of sulfur atom transfer (SAT) and related reactions. Earlier work[4−6,10] has focused on metal−thiolate bond strengths. This work reports on metal−sulfhydryl bond strengths. There is no dramatic difference in the M−SH and M−SR bond strength if R is an alkyl group. Thus the $C_5Me_5(CO)_3Cr-SR$ bond strength estimates are Ph (36) < Me (43) = H (43) (kcal/mol). The values for Mo[5] display a similar pattern but with the expected stronger overall bond between metal and sulfur. For these complexes at least, which are saturated and do not involve η^2-SH bonding, there is nothing special about SH versus SR (R = alky) in terms of the bond strength to the metal. The M−SR (R = aryl) is approximately 10 kcal/mol weaker than for the alkyl and hydride groups, but that trend is also reflected in the organic thermochemistry.[21]

A number of sulfur compounds are marginally stable with respect to elimination of S_8; for example, most thiols are thermodynamically unstable with respect to desulfurization, and the enthalpy of formation of hydrogen sulfide is only −5 kcal/mol.[15] The enthalpies of reaction of stronger sulfur acceptors such as phosphines are in the range −20 to −31 kcal/mol.[10] The enthalpies of sulfurization of the metal hydrides reported here (−5 to −13 kcal/mol) place them in an intermediate range—in principle capable of abstracting sulfur from weaker acceptors but also capable of having sulfur removed by stronger acceptors.

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(21) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley: New York, 1969.

(22) Kuwata, S.; Mizobe, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1057.

(23) Allen, F. H.; Kinnard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

(24) DuBois, M. R. *Chem. Rev.* **1989**, *89*, 1.

Additional work in progress is aimed at continued mapping of the thermochemistry of metal sulfur complexes as well as study of the detailed mechanisms of these and related reactions.

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Supporting Information Available: Tables 1−5 containing details of data collection and refinement, atomic coordinates, bond lengths, bond angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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