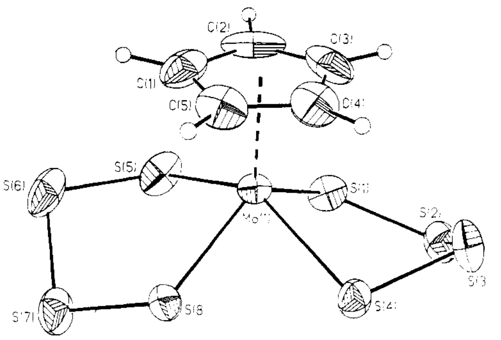


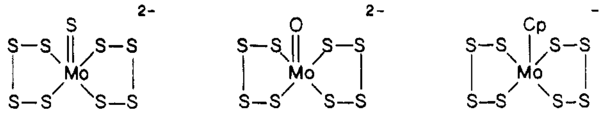
Figure 2. ORTEP view of anionic fragment of II, $[(C_5H_5)Mo(S_4)_2]^-$, with thermal ellipsoids at 35% probability. Important distances (Å): Mo(1)-S(1) = 2.305 (2), Mo(1)-S(4) = 2.446 (2), Mo(1)-S(5) = 2.430 (1), Mo(1)-S(8) = 2.336 (2), S(1)-S(2) = 2.141 (2), S(2)-S(3) = 2.031 (2), S(3)-S(4) = 2.061 (2), S(5)-S(6) = 2.073 (3), S(6)-S(7) = 2.022 (3), S(7)-S(8) = 2.124 (2), Mo(1)-C(1) = 2.310 (7), Mo(1)-C(2) = 2.286 (8), Mo(1)-C(3) = 2.334 (6), Mo(1)-C(4) = 2.368 (5), Mo(1)-C(5) = 2.349 (6). Some important angles: S(1)-Mo(1)-S(4) = 86.2 (1)°, S(1)-Mo(1)-S(5) = 76.4 (1)°, S(4)-Mo(1)-S(8) = 74.5 (1)°, S(5)-Mo(1)-S(8) = 87.1 (1)°, Mo(1)-S(1)-S(2) = 114.7 (1)°, Mo(1)-S(4)-S(3) = 101.8 (1)°, Mo(1)-S(5)-S(6) = 104.0 (1)°, Mo(1)-S(8)-S(7) = 113.7 (1)°, S(1)-S(2)-S(3) = 100.4 (1)°, S(2)-S(3)-S(4) = 101.0 (1)°, S(5)-S(6)-S(7) = 100.3 (1)°, S(6)-S(7)-S(8) = 99.3 (1)°.

for side-bonded disulfide ligands. The compound is isostructural with the previously reported $[(C_5H_5)Mo(CO)_2(Se_2)]^-$ anion,[12] and the neutral $(C_5H_5)Re(CO)_2(S_2)$,[13] and is otherwise unremarkable.

Reaction of I with S_8, either in situ or after isolation and redissolving in acetonitrile, results in formation of $[(C_5H_5)Mo(S_4)_2]^-$ (II) as a dark red-purple compound. It can be isolated as well-formed dark purple crystals in the presence of $(C_6H_5)_4PBr$.[14] Compound II has been characterized both analytically[10] and crystallographically.[15] It contains a well-separated $(C_6H_5)_4P^+$ cation and II in the unit cell. Compound II has a Mo(IV) central atom in a pseudo square-based pyramid, with the two S_4^{2-} chelates occupying the basal positions and the cyclopentadienyl ligand occupying the axial site (see Figure 2). Alternatively, the geometry could be defined as a piano-stool configuration[16] with the sulfide ligands as four legs of the stool.

The Mo–S distances in compound II show considerable variation, ranging from 2.305 (2) to 2.446 (2) Å. The S–S distances show a real but not very pronounced bond alternation around the rings, varying from 2.022 (3) to 2.141 (2) Å. This variation has been fully discussed previously.[17] The five-membered rings are in an envelope configuration and do not appear to be perturbed by the presence of the cyclopentadienyl ring. Similarly, the molybdenum–ring carbon distances average 2.33 Å, which is typical for these types of complexes. Thus the cyclopentadienyl group does not appear to exert any steric strain upon the complex.

The bis(tetrasulfido) complex II is of considerable interest as it extends the homologous series $[S{=}Mo(S_4)_2]^{2-}$ and $[O{=}Mo(S_4)_2]^{2-}$ [17] to $[(Cp)Mo(S_4)_2]^-$.



In addition to providing a comparison between the reactivity of oxo, sulfido, and cyclopentadienyl groups, it is one of the very few organic derivatives of a molybdenum sulfide anion. It should be noted that two very interesting high-valent complexes of rhenium and vanadium have been reported, which contain cyclopentadienyl, oxo, and tetrasulfido ligands.[18] The chemistry of the molybdenum sulfide anions is extensive, as is that of the neutral organometallic sulfides. However, to our knowledge no cyclopentadienyl anion has been previously isolated and characterized. Compound II can be conveniently prepared and may provide an entry into some unusual and useful metal sulfide chemistry.

Acknowledgment. Support by the National Science Foundation (CHE-8802217) is gratefully acknowledged.

Registry No. I·$(C_6H_5)_4P^+$, 122116-26-1; II·$(C_1H_5)_4P^+$, 122116-28-3; $[(C_5H_5)_2Mo_2(CO)_6]$, 12091-64-4; K_2S_3, 37488-75-8.

Supplementary Material Available: Complete crystal data, tables of positional parameters, complete tables of distances and angles, and tables of anisotropic thermal parameters for both compounds (14 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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[14] The production of $[(C_5H_5)Mo(CO)_2(S_2)]^-$ was carried out as described above, but before filtration, 0.15 g (4.7 mmol) of elemental sulfur was added to the reaction mixture. The mixture was stirred for 1 h at 25 °C, and the resultant purple solution was filtered and layered with 3 mL of diethyl ether. The solution was stored at 4 °C overnight, producing 0.147 g of lustrous black crystals in good (70%) yield.

[15] The crystallographic determination of II was performed similarly to that described above: space group monoclinic, $P2_1/n$, $Z = 4$, $a = 12.462$ (2) Å, $b = 16.879$ (3) Å, $c = 15.823$ (2) Å, $\beta = 106.88$ (1)°, $V = 3185$ Å^3, $R = 0.0434$, $R_w = 0.0561$.

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Proton Transfer from (Methoxymethylcarbene)pentacarbonylchromium(0) in Aqueous Solution

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Summary: Evidence is presented that the reaction of (methoxymethylcarbene)pentacarbonylchromium(0) with OH^- and piperidine leads to reversible deprotonation of the methyl group and has a $pK_a = 12.3$. The rate constants are found to be remarkably low, even for a proton transfer from carbon that leads to the formation of a resonance-stabilized carbanion.

We wish to report a kinetic study of the proton transfer from (methoxymethylcarbene)pentacarbonylchromium(0) (1).[2] 1 is a prototype Fischer transition-metal carbene complex.[3,4] It has been known for ca. 20 years that the

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[1] Permanent address: Department of Chemistry, California State University, Fresno, CA 93740.

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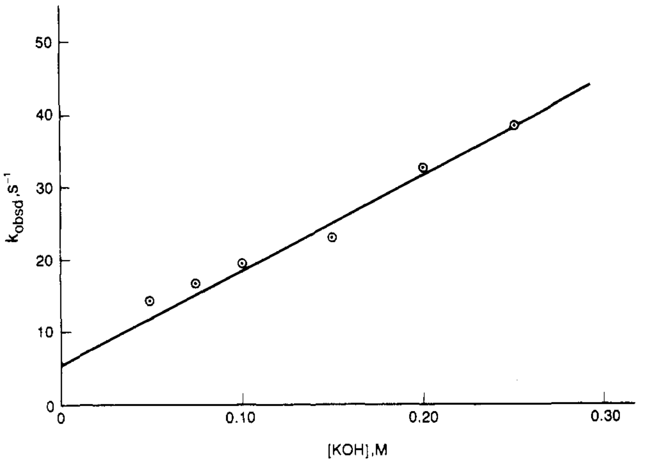


Figure 1. Plot of k_{obsd} against potassium hydroxide concentration for the fast reaction in water at 20 °C and I = 0.50 M (KCl).

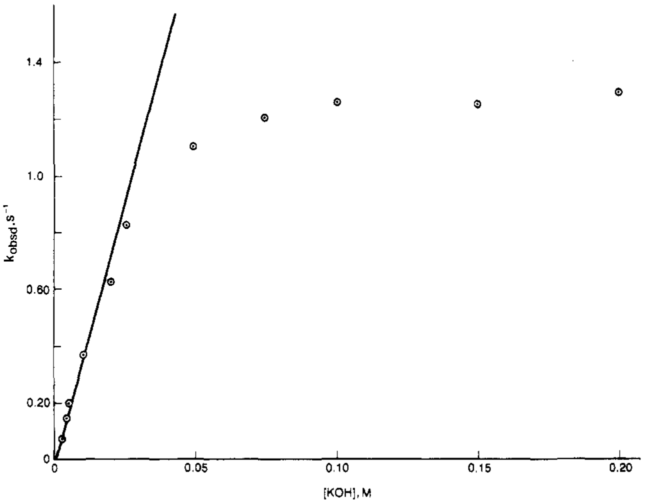


Figure 2. Plot of k_{obsd} against potassium hydroxide concentration for the slow reaction in water at 20 °C and I = 0.50 M (KCl).

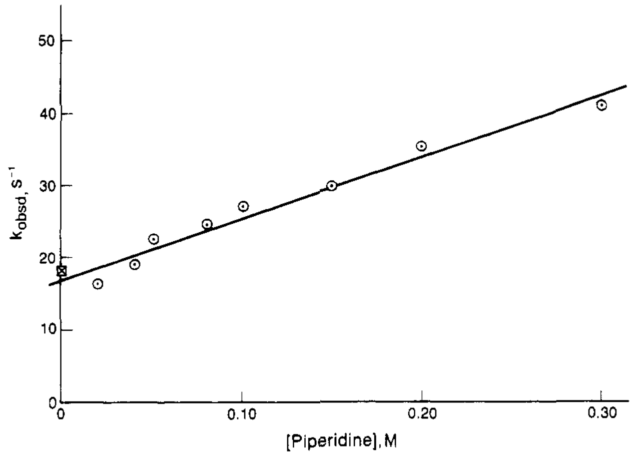
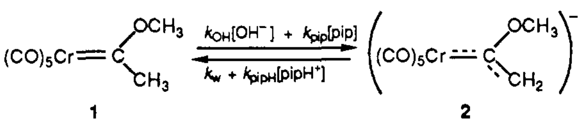


Figure 3. Plot of k_{obsd} against piperidine concentration for the fast reaction at pH 12.74 in water at 20 °C and I = 0.50 M (KCl).

hydrogens α to the carbene carbon in such complexes show remarkable acidity,[5,6] but, except for one study,[7] no kinetic measurements have been reported.

We have determined rates of proton transfer with hydroxide ion and piperidine as base catalysts. Two kinetic processes were observed after mixing aqueous solutions of **1** with an excess of KOH in a stopped-flow spectrophotometer. The faster of the two shows a decrease in absorbance at 367 nm (λ_{max} of **1**) and is linear in KOH concentration with a nonzero intercept (Figure 1), whereas the slower process (decrease in absorbance at 233 nm, short wavelength λ_{max} of **1**) shows a curvilinear dependence on hydroxide ion concentration (Figure 2). The data for the fast process are consistent with a reversible proton transfer from the methyl side chain of **1**[5,6,8] that follows the rate law, $k_{obsd} = k_{OH}[OH^-] + k_w$, in which k_{OH} and k_W are as defined in eq 1.

The following observations support this conclusion. (1) The reaction is catalyzed by piperidine at constant pH, with an intercept equal to that observed in the absence of piperidine (Figure 3). This result is consistent with the rate law of eq 2 for the base-catalyzed proton transfer reaction of eq 1.



$$(CO)_5Cr{=}C(OCH_3)CH_3 \underset{k_w + k_{pipH}[pipH^+]}{\overset{k_{OH}[OH^-] + k_{pip}[pip]}{\rightleftharpoons}} \left((CO)_5Cr{\cdots}C(OCH_3)CH_2\right)^- \qquad (1)$$

1 **2**

$$k_{obsd} = k_{OH}[OH^-] + k_{pip}[pip] + k_w + k_{pipH}[pipH^+] \qquad (2)$$

(2) The amplitude (change in absorption) of this process is independent of piperidine concentration in the range from 0.02 to 0.30 M (over this same concentration range, k_{obsd} increased ca. 2.5-fold). This result is consistent with a proton transfer reaction in which the equilibrium depends on the pH and not the concentration of the buffer. On the other hand, the amplitude increases with increasing [KOH] at low concentrations and levels off at high concentrations, as expected for an increasing shift of the equilibrium toward **2** (eq 1).

(3) The rate constant ratio k_{OH}/k_{pip} = 135/69 = 1.96 is in the range typical for the deprotonation of carbon acids (e.g. 3.71 for acetylacetone,[9] 1.60 for 1,3-indandione,[10] 6.79 for phenylnitromethane,[11] 3.00 for 9-cyanofluorene[12]) but inconsistent with nucleophilic attack (e.g. 1.79 × 10^{-3} for benzylidenemalononitrile,[13] 9.30 × 10^{-4} for benzylidene Meldrum's acid,[14] 3.02 × 10^{-3} for 1-chloro-2,4-dinitrobenzene[15]).

Acidity Constant. From the slope and intercept of Figure 1 an equilibrium constant of 22 M^{-1} is calculated

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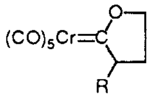
for proton transfer between **1** and the hydroxide ion. This value agrees satisfactorily with a value of 27 M^{-1} calculated from the kinetic data for the slower process[16] assuming that the curvilinear dependence on hydroxide ion concentration is a manifestation of coupling to the proton transfer equilibrium. From the equilibrium constant of 22 M^{-1} and pK_w (13.72 at 20 °C, $I = 0.5$ M) a pK_a of 12.3 is calculated for **1**. This is 4.3 pK_a units higher than the pK_a of *p*-cyanophenol in water, while in THF the acidities of **1** and *p*-cyanophenol are about the same.[6b] From this comparison one may deduce that water provides much less solvational stabilization to **2** than to the *p*-cyanophenolate ion, indicating that the charge in **2** is highly dispersed.

Rate Constants. Our k_{OH} value of 135 $M^{-1}\ s^{-1}$ is much higher than k_{OD} reported for the deprotonation of **3a** (3.07 $M^{-1}\ s^{-1}$) and **3b** (1.97 $M^{-1}\ s^{-1}$) by OD^- in acetone-d_6/D_2O (3.6:1 by volume) at 38 °C.[7] However, a reevaluation of the kinetic data on these latter reactions suggests k_{OD} values in the order of $10^3\ M^{-1}\ s^{-1}$.[17] Since the acidities of **3a** and **3b** are comparable to that of **1**,[7] this new estimate for k_{OD} is consistent with our result when the difference in solvent and temperature is taken into account.



3a: R = H
b: R = CH_3

Intrinsic Rate Constant. On the basis of $k_{pip} = 69\ M^{-1}\ s^{-1}$ and $pK_a^{pip} = 11.52$ an *intrinsic* rate constant[18] for deprotonation of **1** by secondary amines can be estimated as $\log k_0 = \log (k_{pip}/q) - \beta(\Delta pK + \log (p/q))$.[18,19] Assuming $\beta = 0.5$ affords $\log k_0 = 2.08$. Since $\Delta pK + \log (p/q) = -0.48$ is quite small, any error in the assumed Brønsted β value is of little consequence. Our $\log k_0$ is quite low, lower than for any carbon acid studied to date[18,21] except for nitroalkanes.[11] There is accumulating evidence of an inverse relationship between resonance stabilization of carbanions and the intrinsic rate constant for their formation,[18] which is the result of the resonance stabilization lagging behind bond changes in the transition state.[18] Our low $\log k_0$ value therefore suggests that **2** must derive much of its stabilization from a resonance rather than a polar effect, which is consistent with the solvent effect on the pK_a discussed above. Similar conclusions have been reached regarding the rather low intrinsic rate constants in the deprotonation of hydride transition-metal complexes.[22]

Acknowledgment. This research has been supported by Grant CHE-8617370 from the National Science Foundation.

Registry No. 1, 20540-69-6.

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Insertion of Ethylene into Zr-Si and Hf-Si Bonds

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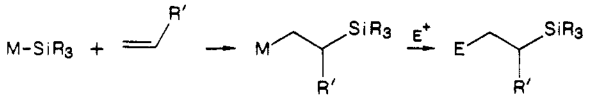
Summary: The zirconium and hafnium silyl derivatives $Cp^*Cl_2MSi(SiMe_3)_3$ and $CpCp^*Zr[Si(SiMe_3)_3]Cl$ (M = Zr, Hf; Cp* = η^5-C_5Me_5; Cp = η^5-C_5H_5) undergo clean insertion reactions with ethylene to give the β-silylalkyl complexes $[Cp^*Cl_2ZrCH_2CH_2Si(SiMe_3)_3]_2$ (**1a**), $Cp^*Cl_2HfCH_2CH_2Si(SiMe_3)_3$ (**1b**), and $CpCp^*Zr[CH_2CH_2Si(SiMe_3)_3]Cl$ (**2**), respectively. These reactions are photochemically and thermally induced. Complex **1a** is dimeric in both the solution and solid states, whereas **1b** is monomeric in solution. Crystals of **1a** are triclinic, $P\bar{1}$, with *a* = 9.247 (4) Å, *b* = 12.643 (6) Å, *c* = 14.519 (6) Å, α = 79.64 (3)°, β = 81.25 (3)°, γ = 75.33 (4)°, *V* = 1605 (1) $Å^3$, *Z* = 1, R_F = 4.46%, and R_{wF} = 5.31%. The quantum yield for formation of **2** (λ = 380–470 nm, benzene-d_6) in the presence of excess ethylene is 2.5, implying a radical chain mechanism initiated by homolytic cleavage of a M–Si bond.

We have discovered transition-metal–silicon bonds that are reactive toward insertion of unsaturated substrates such as CO, CNR, and organic carbonyls.[1] These reactions involving d^0 metal silyl complexes represent new routes to Si–C bonds and therefore have potentially important synthetic applications. Insertion of alkenes into M–Si bonds are also of interest, since the resulting β-silylalkyls could provide β-functional organosilicon compounds via reaction chemistry analogous to that based on hydrozirconation[2] (eq 1). Also, it appears that such insertions may occur in some transition-metal-catalyzed hydrosilations.[3,4] Relevant investigations by Wrighton and co-workers have recently produced the first observation of insertion of an unactivated, monoalkene (C_2H_4) into the metal–silicon bond of photochemically activated $Cp^*(CO)_2FeSiMe_3$ (Cp* = η^5-C_5Me_5).[4] With the goal of developing chemistry based on "silylzirconation" (eq 1), we initially examined the behavior of d^0 silyls $Cp_2Zr(SiMe_3)Cl$ and $Cp_2Zr[Si(SiMe_3)_3]Cl$ toward ethylene.[5] However,



(1)

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