with products and ratios determined by ^{1}H NMR. The ratio of 7 to 14 and 15 was 97:3 with the ratio of 15:14 5:1.

Reaction of 3 with Pd(PPh$_3$)$_2$(C$_2$H$_4$) and Benzyl Bromide. The bridgehead olefin 3 (0.004 g, 0.031 mmol), Pd(PPh$_3$)$_2$(C$_2$H$_4$),[35] and benzyl bromide (0.028 g, 0.17 mmol) were mixed in 0.5 mL of CDCl$_3$ at room temperature. ^{1}H NMR analysis after 20 min revealed 7 and two bridgehead benzylated products 18 and 19
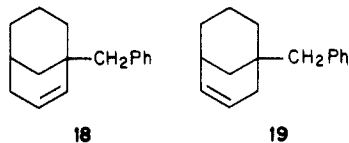
18   **19**

in a 7:18:19 ratio of 15:1:3. 18 and 19 were isolated by preparative GLC and characterized by ^{1}H NMR and MS as a 1:5 mixture, respectively. 18: ^{1}H NMR δ 7.24 (t, J = 6.3 Hz, 2 H), 7.17 (d, J = 6.3 Hz, 2 H), 7.12 (t, J = 6.3 Hz, 1 H), 5.80 (d, t, J_d = 9.7 Hz, J_t = 3.9 Hz, 1 H), 5.48 (d, J = 9.7 Hz, 1 H), 2.64 (d, J = 13.1 Hz, 1 H), 2.53 (d, J = 13.1 Hz, 1 H), 2.21 (b s, 1 H), 2.06 (d, J = 15.0 Hz, 1 H), 1.76 (d, J = 15.0 Hz, 1 H), 1.64 (m, 2 H), 1.39 (m, 4 H), 1.25 (m, 1 H), 1.20 (m, 1 H); MS m/e M$^+$ 212.1. 19: ^{1}H NMR (CDCl$_3$) δ 7.23 (t, J = 6.3 Hz, 2 H), 7.10 (t, J = 6.3 Hz,

1 H), 7.08 (d, J = 6.3 Hz, 2 H), 5.79 (d, t, J_d = 9.6, J_t = 3.4 Hz, 1 H), 5.60 (b t, J = 8.7 Hz, 1 H), 2.49 (d, J = 12.9 Hz, 1 H), 2.44 (d, J = 12.9 Hz, 1 H), 2.43 (b s, 1 H), 2.15 (d, J = 15.3 Hz, 1 H), 1.72 (d, J = 15.3 Hz, 1 H), 1.58 (m, 3 H), 1.37 (m, 4 H), 1.20 (m, 1 H).

Electrochemistry of Transition-Metal π-Complexes. 8.[1]
Oxidation of Chromium, Molybdenum, and Tungsten Sulfur Ylide Complexes

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Electrochemical oxidation of λ^6-thiabenzene 1-oxide complexes 1–3[2] and λ^4-thiabenzene complexes 4–6[2] at a Pt electrode in methylene chloride is found to proceed in a chemically reversible manner if Cr is the central metal and partly or completely irreversibly for Mo and W as the central metals. Cyclic voltammetry and chronopotentiometry confirm a single electron oxidation in all cases. Chemical oxidation of the Cr derivative 1d using N(p-BrC$_6$H$_4$)$_3$PF$_6$ as the oxidant precipitates the salt [1d]PF$_6$, which was characterized by analysis, spectroscopy, and magnetic moment. The redox potentials observed are discussed with reference to those found for the related complexes M(arene)(CO)$_3$ and MCp(CO)$_3^-$.

According to the molecular structure determined by single-crystal X-ray diffraction[3] the M(CO)$_3$ unit in λ^6-thiabenzene 1-oxide and in λ^4-thiabenzene complexes is bound solely to the dienyl part of the ylidic (η^5-C$_5$R$_5$)S-(O)R′ or the (η^5-C$_5$R$_5$)SR′ ligand, formally charged negatively. Thus with respect to their chemical and redox properties one may expect these complexes to occupy a position intermediate between the neutral arene tricarbonyl complexes 7 and the cyclopentadienyl tricarbonyl anions 8 of the group 6 metals. A basic metal center is evidenced by, e.g., the facile nitrosylation of 1–3 leading to the corresponding [ML(CO)$_2$NO]$^+$ cations.[4,5] Protonation occurs at the 2-position of the ylidic ring ligand and yields cations [M(diene)(CO)$_3$(solv)]$^+$.[6] Reductive dealkylation with LiBEt$_3$H transforms 1–3 into the anions [M(C$_5$R$_5$SO)(CO)$_3$]$^-$,[7,8] which react analogous to the cyclopentadienyl tricarbonyl anions with NO to give nitrosyl

complexes M(C$_5$H$_3$R$_2$SO)(CO)$_2$NO[9] or with halogens to produce halo complexes M(C$_5$H$_3$R$_2$SO)(CO)$_3$X, X = Cl, Br, and I.[8]

Apart from these reactions where the redox step is coupled to changes in the ligand sphere, electrochemically effected electron transfer in an inert solvent and in the absence of potential ligands was thought to provide data for the comparison of the novel sulfur ylide complexes with the more common analogues 7 and 8. We present results on the electrochemical oxidation of sulfur ylide/complexes

(1) Part 7: Koelle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J.; Boehm, M., *J. Am. Chem. Soc.* **1984**, *106*, 4152.
(2) Weber, L. *Angew. Chem.* **1983**, *95*, 539.
(3) Weber, L.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1978**, *111*, 1709.
(4) Weber, L. *Chem. Ber.* **1981**, *114*, 1.
(5) Weber, L.; Boese, R. *Chem. Ber.* **1983**, *116*, 197.
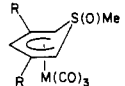(6) Weber, L., unpublished results
(7) Weber, L. *Chem. Ber.* **1979**, *112*, 99.
(8) Weber, L.; Wewers, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 68.
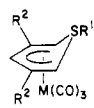(9) Weber, L.; Vehreschild-Yzermann, D.; Krüger, C.; Wollmershäuser, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 198.

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Table I

a. Electrochemical Parameters for the Oxidation and the Reduction of λ⁶-Thiabenzene 1-Oxide Complexes 1-3 in Methylene Chloride


no.	M	R	conf^a	$\overline{E}_1$,^{b} V	$E_p{}^a$, V	$E_p{}^c$, V	ΔE_p, mV	$i_p{}^c/i_p{}^{a,c}$ V	$E_p{}^a(2)$,^{d} V	$E_p{}^c(2)$,^{e} V	EC – pr,^{f} V
1a	Cr	Ph	anti	0.543	0.575	0.510	65	0.95 (0.02)	1.1	-1.8	
1b	Cr	Ph	syn	0.580	0.610	0.550	60	0.97 (0.02)	1.23	-1.95	
1c	Cr	Me	anti	0.460	0.493	0.430	65	1.02 (0.02)	1.1		
1d	Cr	Me	syn	0.520	0.555	0.488	67	1.04 (0.05)	1.2		
1e	Cr	t-Bu	anti	0.516	0.545	0.486	60	0.96 (0.05)	1.25		
2a	Mo	Ph	syn	0.77	0.84 0.735	0.70	140	0.5 (10.0) (0.10)		-1.8	0.01
2b	Mo	Me	syn		0.715			(0.10)		-2.13	0.18
2c	Mo	t-Bu	syn	0.700	0.740	0.660	80	0.91 (1.00) 0.06 (0.02)			0.18
3a	W	Ph	syn		0.785			(0.02)		-1.65	0.17
3b	W	Me	syn		0.715			(0.10)		-1.17	0.07
3c	W	t-Bu	syn	0.652	0.685	0.620	65	0.66 (0.02)		-2.2	

b. Electrochemical Parameters for the Oxidation and the Reduction of λ⁴-Thiabenzene Complexes 4-6 in Methylene Chloride

no.	M	R¹	R²	$\overline{E}_1$, V	$E_p{}^a$, V	$E_p{}^c$, V	ΔE_p, mV	$i_p{}^c/i_p{}^a$, V	$E_p{}^a(2)$, V	$E_p{}^c(2)$, V
4a	Cr	Et	Ph	0.396	0.430	0.360	70	1.0 (0.02)	0.99	-2.04
4b	Cr	Me	Ph	0.385	0.420	0.356	64	0.95 (0.05)	1.10	-2.04
4c	Cr	Me	Me	0.309	0.340	0.280	60	1.0 (0.02)	0.93	
4d	Cr	Me	t-Bu	0.317	0.346	0.286	60	0.97 (0.05)	1.10	
5	Mo	Et	Ph	0.58 irreversible at all scan rates						
6	W	Et	Ph	1.08 irreversible at all scan rates						

^{a} Conformation of the S(O)Me group. ^{b} Mean of anodic and cathodic peak potential. ^{c} Peak current ratio at scan rate v (V/s). ^{d} Peak potential of second, irreversible oxidation. ^{e} Peak potential of the irreversible reduction. ^{f} Peak potential of an EC product formed at the first oxidation. All potentials in V relative to [CoCp₂]$^{+/0}$ vs. SCE, see text.

1-6 and on the chemical oxidation of 1d to give an isolable radical cation salt.
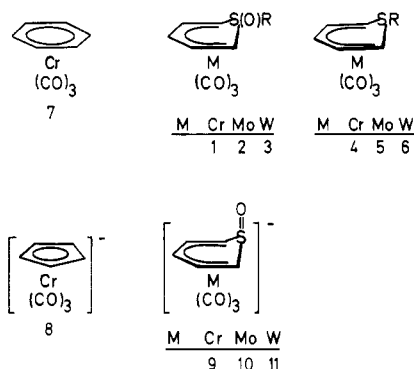
Experimental Section

The electrochemical equipment as described previously[10,11] had been supplemented by a signal recorder (EG & G 4102) for the registration of rapid scans. The solutions were 0.1 M in tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ca. 5×10^{-4} M in the electroactive complex. The reference electrode was a SCE contacted to the solution through an asbestos frit. Calibration of the potential zero was done by registering the [CoCp₂]$^{+/0}$ transition from added [CoCp₂]Cl subsequent to the measurement of the sulfur ylide complex. All potential values given for the latter refer to a [CoCp₂]$^{+/0}$ potential of -0.920 V vs. SCE. For all of the complexes studied cyclic voltammograms were run in methylne chloride and, in addition,

for a number of them, in THF and acetonitrile. In cases where the first oxidation at 0.3-0.8 V was found chemically irreversible or partly reversible (2, 3, 5, and 6) the number of electrons transferred per molecule, n, was evaluated from anodic current chronopotentiograms. A constant current was chosen so as to lead to transition times τ between 15 and 25 s. Under the assumption of a first-order followup reaction of the electron number n can be evaluated from the straight line plots of log $(\tau^{1/2} - t^{1/2})$ vs. $E(t)$.[12]

syn-Tricarbonyl(1,3,5-trimethylthiabenzene 1-oxide)-chromium(I) Hexafluorophosphate. To 0.964 g (2.00 mmol) of N(p-BrC₆H₄)₃ in 25 mL of methylene chloride was added 0.506 g (2.00 mmol) of AgPF₆; the mixture was stirred for 10 min at 0 °C. The blue solution was filtered and a solution of 0.584 g (2.00 mmol) of *syn*-tricarbonyl(1,3,5-trimethylthiabenzene 1-oxide)-chromium(0), 1d, in 20 mL of methylene chloride was added dropwise. The yellow precipitate was filtered, washed with 5 mL of methylene chloride, and dried under vacuum to yield 0.541 g (62%) of yellow microcrystals: IR (KBr) ν_{CO} 1955 (s), 1908 (sh), 1866 (s), 1840 cm⁻¹, $\nu_{S=O}$ 1205 (m) cm⁻¹; magnetic moment[13] μ = 1.88 μ_B (300-80 K) with θ = -25 K. Anal. Calcd for C₁₁H₁₂CrF₆O₄PS: C, 30.31; H, 2.77; Cr, 11.89. Found: C, 30.29; H, 2.88; Cr, 12.08.

Results

Cyclic voltammetric parameters for complexes 1-6 are given in Table I, and chronopotentiometric parameters are collected in Table II. A typical cyclic voltammetric curve

(10) Koelle, U. *J. Organomet. Chem.* **1978**, *152*, 225.
(11) Koelle, U. *J. Organomet. Chem.* **1978**, *157*, 327.

(12) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; p 440.

(13) χ vs. T was measured from 300 to 80 K at a Faraday balance. Exact Curie-Weiss behavior is observed in this temperature interval. We are indebted to Dr. Lueken, Institute of Inorganic Chemistry, Technical University of Aachen, and his colleagues for the measurements.

Table II. Chronopotentiometric Parameters for
Mo and W Complexes

no.	$\tau,^a$ s	$i, \mu A$	$E_{\tau/4},$ V	n^b
2a	17.4	25	0.733	1.10
2b	13.4	50	0.96	1.11
2c	22.5	55	0.77	1.13
3a	21.4	20	0.67	1.01
3b	17.0	25	0.690	1.01
5	14.5	30	0.525	0.98

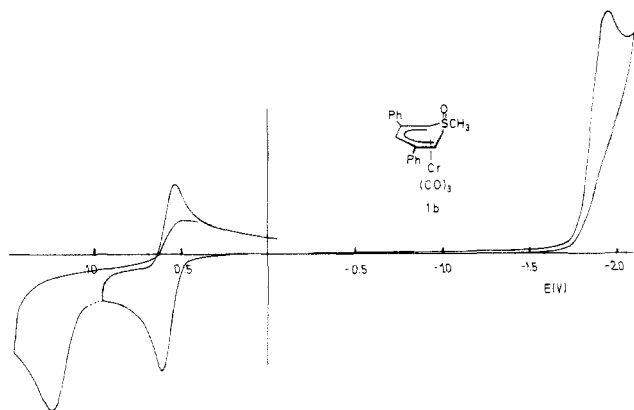^{a} Transition time. ^{b} Number of electrons transferred.

Figure 1. Cyclic voltammogram of **1b** in methylene chloride (scan rate = 100 mV/s; potential in V vs. SCE).

is depicted in Figure 1. All of the Cr complexes exhibit, in methylene chloride as solvent, a reversible oxidation (E_1 in Table I) at about 0.5 V for the λ^6-thiabenzene oxide and at 0.3–0.4 V for the λ^4-thiabenzene complexes. The peak separation in the cyclic voltammograms is indicative of a one-electron oxidation. No follow-up peaks are detected. The same oxidation was found reversible in THF for compounds **1b**, **1d**, and **4a–c** at any sweep rate; oxidation of **1c** in THF at a sweep rate of <20 mV/s is irreversible. Likewise all chromium complex oxidations in acetonitrile were irreversible. Beyond the first oxidation at E_1 there occurs a second, irreversible oxidation at more positive potentials ($\sim$1.2 V) and an irreversible reduction around –2 V, both of which are apparent one-electron transitions as inferred from the respective peak heights.

Oxidation of the Mo and W complexes **2**, **3**, **5**, and **6** is found more positive than that of their Cr analogues. Dependent on scan rate and substitution pattern, it occurs partly reversibly or irreversibly with a follow-up peak at $\sim$0.2 V. The variation of the peak current ratio with the scan rate in general is as expected for an EC process (cf. **2c** in Table I as an example). Therefore, the appearance of some of the electron transitions is considered to be irreversible due to follow-up reactions, fast on the electrochemical time scale. (Only in the case of **3c** is a peak current ratio decreasing and a peak separation increasing with faster scans, 65 mV at 20 mV/s and 125 mV at 500 mV/s, indicative of a follow-up reaction coupled to slow electron transfer.)

Since also the reduction of the Mo and W complexes is shifted anodically with respect to the analogous Cr compounds, it appears further separated from the supporting electrolyte decomposition ($\sim$–2 V in CH_2Cl_2) and has a peak height approximately equal to that of the first oxidation, thus indicating an equal number of electrons transferred in both processes.

The number of electrons transferred with the first oxidation of **2**, **3**, and **4** was determined by chronopotentiometry and found near one in all cases (Table II).

Bulk electrolysis experiments on the plateau of the first oxidation undertaken with the Cr complexes **1**, as well as

in situ oxidation of the electrochemical solutions with $N(p\text{-}BrC_6H_4)_3PF_6$ did not lead to isolable organometallic cations. In constrast, chemical oxidation of **1d** with this oxidant precipitates a yellowish salt, insoluble in methylene chloride. Carbonyl absorptions shifted to higher wavenumbers, the paramagnetism corresponding to one unpaired electron, and the analytical data show this salt to be [**1d**]PF_6. The salt is insoluble in less polar solvents and undergoes spontaneous decomposition in polar solvents. Its successful isolation thus is due merely to its rapid precipitation from the methylene chloride solution.

Discussion

Influence of the Ligand on the Redox Potentials.
Determination of redox potentials vs. an internal standard couple yields a set of internally consistent potential values independent of uncertainties and variations of the potential of the reference electrode due to nonaqueous–aqueous interface effects. On such an internal potential scale small differences (to about ±5 mV) must be considered chemically significant.

The influence of the substituents at the sulfur ylide ligand is seen in the oxidation potentials E_1 for compounds **1** and **4**. Substituting two phenyl groups by alkyl groups shifts this potential 60–80 mV more negative. A similar trend is observed in the peak and mean potentials of the Mo and W complexes **2** and **3**. Considering the two syn/anti pairs **1b**/**1a** and **1d**/**1c**, it is seen that oxidation of the anti isomer is easier (more negative) by 40–60 mV, which implies a stronger donor character of the anti-thiabenzene oxide ligand, a result not evidenced by the ν_{CO} frequencies.[3]

A markedly stronger electron-donating character of the λ^4-thiabenzene as compared to the λ^6-thiabenzene oxide ligands is revealed by comparing the oxidation potentials E_1 of the analogously substituted pairs **1a**/**4a**, **1c**/**4c**, and **1e**/**4d**, where the Cr complexes of the former are oxidized more easily by 150–200 mV. This influence cannot be due to a direct interaction between sulfur and the central metal but is transmitted through the cyclohexadienyl part of the ligand.

Cyclic voltammograms of (λ^4-thiabenzene) molybdenum and tungsten complexes **5** and **6** are not very conclusive and do not allow the evaluation of meaningful potential values.

Comparison with Arene Tricarbonyl Complexes 7 and Cyclopentadienyl Tricarbonyl Anions 8.
The oxidation of arene tricarbonyl complexes has been studied by Lloyd et al.[14] A one electron oxidation to a monocation was detected in methylene chloride at potentials around 0.7 V vs. SCE [$Cr(C_6H_6)(CO)_3$ (**7a**), 0.71 V; $Cr(C_6H_4Me_2)(CO)_3$ (**7b**) 0.64 V], 150 mV more positive than **1** (cf. **7a** with **1a**/**1b** and **7b** with **1c**/**1d**). The effect of a substituent on the ring ligand on the oxidation potentials is of the same order for both classes (30–40 mV/Me). In contrast to the thiabenzene and thiabenzene oxide complexes, where the oxidation occurs without decomposition on the cyclovoltammetric time scale, oxidation of (arene)chromium tricarbonyl complexes in all cases gives rise to follow-up reactions.

Madach and Vahrenkamp[15] have shown that the $CrCp(CO)_3$ dimer in diluted benzonitrile solution is in rapid equilibrium with $\sim$1% of its monomer. Consequently the electrochemical oxidation of the anion complex

(14) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768.

(15) Madach, T.; Vahrenkamp, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *34B*, 573.
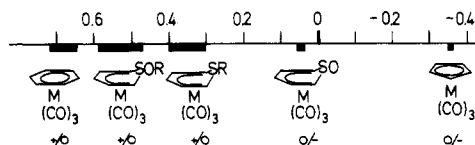
Figure 2. Comparison of redox potentials of group 6 metal tricarbonyl complexes in methylene chloride. The redox couple in each case represents an 18/17 valence electron change.

8 corresponds to the reversible change between the anion and the neutral radical. We found the same electrochemical characteristics for **8** in methylene chloride where the oxidation of the anion occurs with $E_{1/2}$ = –0.36 V vs. SCE, which is 0.92 V negative of **1** and 0.76 V negative of **4** (comparison is made with respect to the phenyl derivatives in view of the fact that phenyl and hydrogen as ligand substituents lead to nearly identical redox potentials).

We have further studied the oxidation of anions **9–11** in methylene chloride. It was found irreversible for **10** and **11** (peak potentials around 0.25 V) and partly reversible for **9** at scan rates >5 V/s, where $E_{1/2}$ is about –0.05 V, both values being more positive than the oxidation of the anion **8**. The cyclovoltammograms for the oxidation of these anionic complexes are not consistent with a simple dimerization of the neutral radical but indicative of the formation of several electroactive follow-up products.

As depicted in Figure 2 λ^6-thiabenzene oxide and λ^4-thiabenzene complexes, with respect to their redox properties, lie between the neutral arene tricarbonyl and the anionic cyclopentadienyltricarbonyl complexes though

closer to the former. The cathodic shift exhibited by the redox potentials of **1** and **4** with respect to **7** may in part be due to the lack of cyclic conjugation in the ylide complexes, which in general facilitates the oxidation.[16] The difference in redox potentials between **1** and **4**, on the one hand, and within the syn/anti pairs **1a**/**1b** and **1d**/**1c**, on the other hand, demonstrates the importance of configuration and substitution at the sulfur center for the redox properties of the complex. Similar conclusions as drawn for the Cr complexes are valid for Mo and W homologues.

Due to the fact that second- and third-row transition-metal complexes are less prone to tolerate deviations from the 18-electron configuration, their redox transitions tend to be more irreversible and meaningful potential values are not easily obtained.

(16) Cf. $Cr(C_6H_6)(CO)_3{}^{+/0}$ = 0.71 V/$Cr(C_7H_8)(CO)_3{}^{+/0}$ = 0.67 V;[14] $FeCp_2{}^{+/0}$ = 0.49 V/$Fe(\eta^5\text{-}C_7H_9)_2{}^{+/0}$ = 0.21 V; $CoCp(\eta^4\text{-}C_4H_4)^{+/0}$ = ~0.95 V/$CoCp(\eta^4\text{-}C_6H_8)^{+/0}$ = 0.32 V. Koelle, U., unpublished results; potentials in methylene chloride vs. SCE.

Synthesis and Investigation of Isomerization Reactions of Terminal Iron–Alkenyl Complexes

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The reaction of a variety of anionic nucleophiles (Nuc) with $[CpFeCO[P(OPh)_3](\eta^2\text{-}CH_2{=}C{=}CH_2)]BF_4$ leads to a new family of terminal alkenyl complexes, $CpFeCO[P(OPh)](\eta^1\text{-}C(CH_2Nuc){=}CH_2)$ (Nuc = H, Me, Ph, CH=CH$_2$, C≡CMe, SPh). Dissolving these complexes in CHCl$_3$ or other solvents in the presence of alumina (or upon alumina chromatography) causes a 1,3-hydrogen shift isomerization reaction that leads for the last four nucleophiles to $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Nuc]$ derivatives. For Nuc = Me, an equilibrium mixture of the terminal alkenyl complex (21%), $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Me]$ (72%), and $CpFeCO[P(OPh)_3](\eta^1\text{-}(Z)\text{-}C(Me){=}C(Me)H)$ (7%) is established. The (E)-2-butenyl isomer can also be prepared directly by the reaction of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]BF_4$ with Li[HB-(sec-Bu)$_3$]. Reaction of this same η^2-butyne complex with Li[HBEt$_3$] leads to a mixture of Z (57%) and E (43%) isomers. A similar reaction using Li[DBEt$_3$] shows that the Z isomer forms by direct trans addition to the alkyne whereas the E isomer forms from addition to the Cp ring followed by internal cis transfer from the ring to the alkyne. Both the pure E isomer and the mixture isomerize in CHCl$_3$ or upon chromatography to the same equilibrium mixture as the terminal butenyl isomer. A variety of deuterium labeling and protonation studies are reported that indicate that the intermediates in these isomerization reactions are the cationic carbene complexes formed by simple protonation of the alkenyl complexes.

Introduction

It has been recently shown that a wide variety of iron–alkenyl complexes can be prepared from the addition of anionic nucleophiles to cationic η^2-alkyne[1] or vinylidene

complexes[2] (eq 1 and 2). Both reactions are generally regio- and/or stereoselective, and for reaction 1, trans addition of the nucleophile has been proven (the case where Nuc = H is an exception,[3] vide infra). Thus by

(1) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134 and references therein.

(2) Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876.

(3) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710.