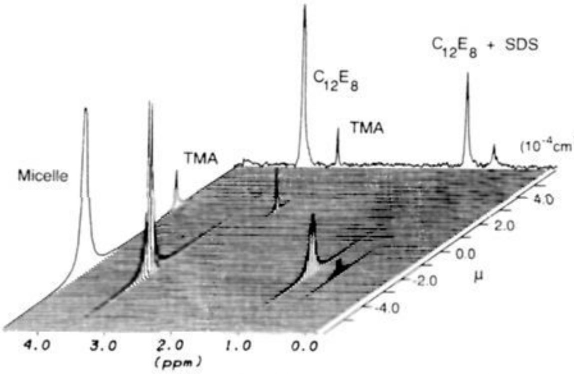

Figure 2. The mobility-ordered 2D-NMR spectrum of a sample containing TMA and mixed micelles.

^{1}H spectra were obtained with a Brüker AC-250 spectrometer with custom-built probe and ENMR electronics as previously described.[1,8,9] The parameters were $K = 770$ cm^{-1}, $\Delta = 0.500$ s, $T_e = 25.0$ ms, $A = 0.0820$ cm^2, and $\kappa = 0.320$ mS·cm^{-1}. The ∇ values in Figure 1b for SDS protons show that the mobility is negative.

Figure 2 displays the complete mobility-ordered spectrum (MOSY) for a sample containing TMA (2.00 mM) with mixed micelles (1.50 mM SDS and 4.00 mM octaethylene glycol dodecyl ether ($C_{12}E_8$)). The data were obtained in an STE-ENMR experiment with $K = 722$ cm^{-1}, $\Delta = 0.400$ s, $T_e = 25.0$ ms, $A = 0.0986$ cm^2, and $\kappa = 0.273$ mS·cm^{-1}. Data collection was limited to currents below 0.75 mA because of heating effects at higher currents. In this current range the HOD signal (not shown) was constant and confirmed the absence of electroosmosis and convection. The severely truncated data sets were successfully transformed by means of the linear prediction (LPZOOM) procedure,[10] but other analysis schemes for limited data sets could have been used. The mobilities obtained from the peak maxima reported by LPZOOM are 2.75×10^{-4} and -1.55×10^{-4} cm^2·V^{-1}·s^{-1} for protons in TMA and micelles, respectively. It should be noted that the peak at 3.51 ppm is entirely associated with $C_{12}E_8$ and its position on the mobility axis indicates that this neutral compound is migrating with the micelle. Also, the mobility of the TMA cation in the mixture is less than the value of 3.60×10^{-4} cm^2·V^{-1}·s^{-1} reported for TMA alone in aqueous solution[11] and suggests a possible interaction between the anionic micelle and $(Me)_4N^+$. This is a topic for future study. Figure 2 clearly shows the range and resolution of mobilities that are now accessible in 2D-ENMR.

We conclude with comments about the line widths. Since the migration time Δ is held constant, there can be no diffusional broadening in the mobility dimension; however, the intensities depend on the diffusion coefficients as indicated in eq 1. Polydispersity, of course, leads to damped oscillations of intensity versus current and thus to line broadening, and in favorable cases the interferograms can be transformed to obtain the mobility distribution function.[2] However, no damping was evident in the data sets used to generate Figure 2, and the line widths resulted from intensity noise and the LPZOOM procedure. The line widths in the chemical shift dimension are consistent with the magnetic field inhomogeneity over the 5-mm nonspinning sample.

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A New Reaction for the Synthesis of Carbene Precursors from Aldehydes and $Cp(CO)_2Fe^-M^+$ (M = Na, K)

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Electrophilic iron carbene complexes are of interest as highly reactive intermediates for metal-catalyzed cyclopropanation reactions, for which there is considerable potential synthetic utility. Due to lability, these carbene complexes are often generated from their corresponding precursors prior to use. Several techniques have already been devised for the generation of electrophilic iron carbenes from their precursors;[1] however, each has inherent limitations. We report here a simple, efficient strategy for synthesis of electrophilic iron carbene precursors from readily available aldehydes of low toxicity.

The precursors **4** for the electrophilic iron carbene complexes were prepared in very good to moderate yield by the reaction of the Fp anion **1** with aldehydes **2**. The resulting alkoxides **3** were trapped with chlorotrimethylsilane[2] (Scheme I). In a typical reaction,[3] 1.2–4 equiv of aldehyde were added to 1 equiv of the Fp anion in dried and degassed tetrahydrofuran at −78 °C. The solution was stirred for 1–3 h at −78 °C, and 1–2 equiv of chlorotrimethylsilane were added dropwise to the solution. The mixture was stirred at −78 °C for an additional hour. The crude product was concentrated under vacuum, and elution from a low-temperature silica gel or alumina column with a 5% THF–pentane mixture provided pure (siloxyalkyl)irons **4a,b** as red-brown oils and **4c** as a cream-colored solid. Precursor **4d** was purified by extraction with pentane at −78 °C and concentrated under vacuum due to its thermal instability. The precursors **4** were characterized by spectroscopic methods.[4,5]

The reaction depicted in Scheme I is apparently the first successful nucleophilic addition of a metal anion to an aldehyde.[6] Gladysz[7] failed to observe any reaction between the manganese

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(1) Previously, the most widely used techniques to synthesize carbene precursors from Fp anion utilized α-chloroalkyl methyl ethers (ClCH(R)-OCH_3). (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. The use of α-chloroalkyl methyl thioethers ($ClCH(R)SCH_3$) to produce considerably more stable precursors was also exhibited. (b) O'Connor, E. J.; Brandt, S.; Helquist, P. *Ibid.* **1987**, *109*, 3739. (c) Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231. An alternative to the α-ether has been devised involving hydride reduction of a Fischer carbene. (d) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (e) Casey, C. P.; Miles, W. H. *J. Organomet. Chem.* **1983**, *254*, 333. Another, less frequently used, technique utilizes iron vinyl complex protonation to synthesize iron carbenes. (f) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (g) Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (h) Kremer, K. A. M.; Kuo, G. H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (i) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

(2) Treatment of the alkoxide intermediate with methyl iodide or trimethyloxonium tetrafluoroborate generated only the methyl complex Cp-$(CO)_2FeCH_3$ and Fp dimer. No $FpCH(OCH_3)R$ was formed, indicating that neither CH_3I nor $(CH_3)_3O^+BF_4^-$ was an effective trapping reagent for the alkoxide **3** intermediate.

(3) Details contained in the supplementary material.

(4) See the supplementary material for complete spectral and analytical data.

(5) Cutler has recently published a paper for the synthesis of Fp–(α-siloxyalkyl) complexes as "stable products" from FpCOR complexes by hydrosilation in the presence of a manganese acetyl catalyst. Hanna, P. K.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1991**, *10*, 31. Similarly, we have found by observation that the siloxy phenyl iron and siloxy *p*-methoxyphenyl iron complexes **4a,c** are stable, allowing acquisition of the CH microanalysis. The siloxy methyl iron complexes **4b,d** are less stable.

(6) Hegedus has reacted $Cr(CO)_5^{2-}$ with tertiary amides in the presence of chlorotrimethylsilane to produce aminocarbene complexes through $(CO)_5Cr^-(NR'_2CRO^-)$. This reaction is restricted to tertiary amides. See: Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.

(7) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766.

Scheme I

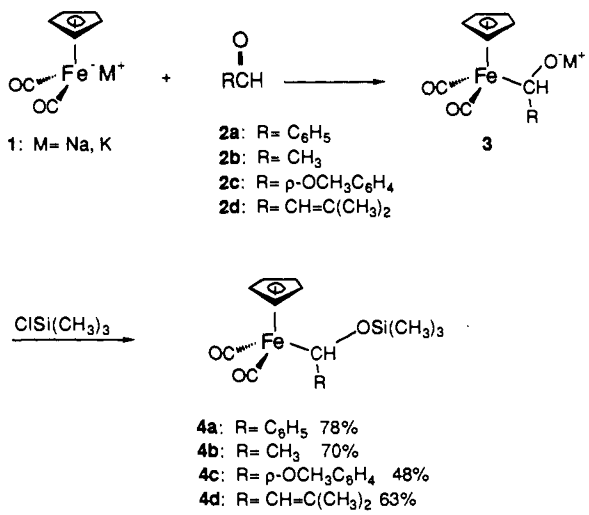


Table I. Cyclopropanes from Precursors **4**

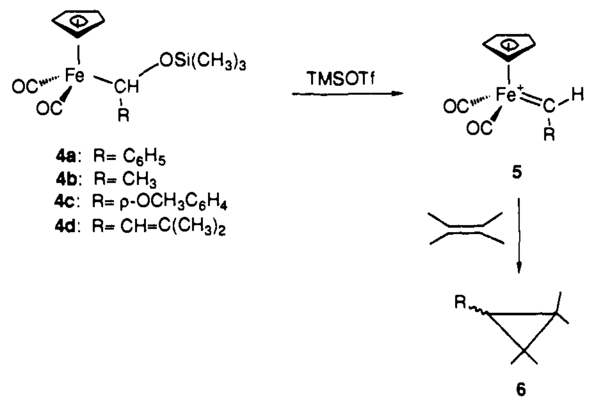
precursor	olefin	yield (%)
4a	styrene	68 (all cis)[a,b]
	cyclopentene	62 (all endo)[a,b]
	2-methyl-2-butene	88 (all cis)[a,b]
4b	styrene	72 (all cis)[b,c]
4c	styrene	38 (4:1)[a,b,d]
4d	styrene	44 (1:2)[a,b,d]

[a] Isolated, unoptimized yield. [b] Ratios were determined by GC and/or ^{1}H NMR spectroscopy.[3] [c] Determined by GC with results calibrated against an internal standard. [d] Cis:trans ratio.

pentacarbonyl anion and benzaldehyde at room temperature. However, he did propose the existence of a related manganese alkoxide anion $(CO)_5Mn(C_6H_5CHO^-Li^+)$ as a fleeting intermediate in the reduction of the manganese pentacarbonyl acyl complex by trialkylborohydrides.[8] Gladysz's findings and the following observations are consistent with the chemistry described in Scheme I, although the mechanism of this reaction has not yet been defined. There is no apparent reaction between chlorotrimethylsilane and the aldehyde nor between silyl complex Cp$(CO)_2FeSi(CH_3)_3$ and the aldehyde under the reaction conditions. Despite some uncertainty as to the exact mechanism, this reaction provides an efficient and convenient synthetic approach to various (siloxyalkyl)iron complexes.

To determine the potential utility of this strategy, the (siloxyalkyl)irons **4** were separately treated with 1.1-1.7 equiv of trimethylsilyl triflate at -78 °C in the presence of 2-4 equiv of olefin (Scheme II). In situ generation of the carbene complex **5**[9] produced the corresponding cyclopropane **6**.[1c,f,g,10] The results are summarized in Table I. It is readily apparent from the unoptimized results for the new precursors **4a,b** that they are efficient. They also exhibit very high cis selectivity[11] when reacted with acyclic alkenes. In addition, precursor **4a** shows very high endo selectivity with cyclopentene. Reaction of styrene with both

Scheme II



4c and **4d** gave different selectivities. Precursor **4d** provided the trans isomer as the major product, which is consistent with a related precursor reported previously.[1f,10e] Precursor **4c** preferred the cis isomer, exhibiting higher selectivity than a related precursor with propene.[10f]

The synthesis of (siloxyalkyl)iron complexes **4** from inexpensive and readily available aldehydes demonstrates rather clearly a new, simple synthetic technique for the preparation of electrophilic iron carbene complexes. More importantly, a new reaction for the Fp anion has been developed which has potential synthetic utility. Work is underway to determine the versatility of this method by utilizing a greater variety of aldehydes and extending the study to ketones. In addition, mechanistic studies of the reaction are being pursued.

Supplementary Material Available: Experimental procedures and spectral data for the syntheses of **4a–d** and their reactions with alkenes (8 pages). Ordering information is given on any current masthead page.

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[8] Selover, J. C.; Marsi, M.; Parker, D. W.; Gladysz, J. A. *J. Organomet. Chem.* **1981**, *206*, 317.

[9] The color changed from yellow to purple upon addition of triflate. No NMR studies were carried out to characterize the intermediate as a carbene; however, numerous studies[1a-e] of related precursors have identified the intermediate as a carbene.

[10] (a) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1981**, *103*, 979. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258. (d) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *Ibid.* **1981**, *103*, 1862. (e) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808. (f) Broom, M. B. H. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1982.

[11] The stereoselectivity of our results differs from that obtained by Brookhart[10b,c] for cyclopropanation of the Fp-(α-methoxymethyl) precursor with styrene versus our **4b** with styrene. However, our results are consistent with those of Helquist et al.[1c,10d]

Selective Coloration of Spiro Pyridopyrans for Guanosine Derivatives

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The artificial receptors that recognize and bind to specific nucleoside bases are of current interest.[1] Especially, recent discoveries of the role of GTP-binding regulatory proteins (G-proteins)[2] and of the cap-binding protein (CBP)[3] have stimulated the investigation on the chemical recognition of guanine.[4] We recently introduced a new type of spiro benzopyran possessing a monoaza-crown ring as a recognition site, isomerization of which to the colored merocyanines was induced by recognition of al-

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