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Experimental Evidence for β-Methyl Migration in the Course of Fe^+-Mediated Alkane Formation from Silazanes in the Gas Phase[†]

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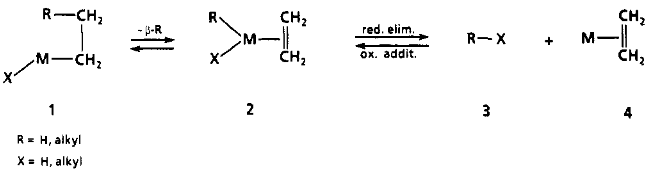
Summary: The Fe^+-induced elimination of CH_3CD_3 from $CD_3N(Si(CH_3)_3)_2$ is best explained in terms of a β-methyl migration to the metal ion, followed by reductive elimination of ethane. The study of the reactions of bare Fe^+ with the analogous silazanes and silanes $X(Si(CH_3)_3)_2$ (X = NH, ND, CH_2, CD_2) uncovers further remarkable gas-phase processes; these include a degenerate methyl migration preceding alkane loss.

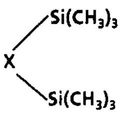
A problem of topical interest concerns the operation of β-methyl shifts to transition-metal centers M, which is thought to be the key step in Ziegler–Natta olefin polymerization reactions and related oligomerizations as well as β-methyl eliminations.[1] While, for example, ethylene insertion into highly electrophilic lanthanide–, actinide–, and early-transition-metal–alkyl bonds has been described, such migrating insertion reactions (Scheme I: 2 → 1; R = alkyl) have rarely been observed for stable organometallic complexes. In particular, the elegant experimental work of Brookhart and Lincoln[2] clearly establishes that for the reverse reaction 1 → 2 the rate of β-hydrogen transfer (R = H) is on the order of 10^{10} faster than β-methyl migration (R = CH_3).

In the gas-phase studies of transition-metal-*ion* complexes, the situation of β-hydrogen versus β-methyl migration has also been clouded for quite some time, as no consensus seems to exist whether an authentic β-methyl shift to a transition-metal ion is operative or not.[3] The dilemma is due to the fact that the intermediates, from which eventually reductive elimination of alkanes occurs, can be generated by two pathways, oxidative addition of a CC bond followed by a β-hydrogen transfer, or vice versa.[3] Strictly speaking, none of the previously reported systems permit an unequivocal distinction.

Scheme I



The findings of recent experimental and ab initio MO studies that several silyl-substituted complexes of transition metals contain unusual intramolecular agostic Si–C^γ bonds *to the metal centers*[4] *prompted us to investigate the* gas-phase ion chemistry of bare Fe^+ with the silane derivatives **5a,b**–**7a,b**, as these substrates possess the structural prerequisites necessary for the unambiguous identification of a β-methyl migration to a metal center.



	X
5a	NCH_3
5b	NCD_3
6a	NH
6b	ND
7a	CH_2
7b	CD_2

The metastable ion (MI) mass spectrum[5] of **5a**–Fe^+ is

[†] Dedicated to Professor Helmut Vorbrüggen on the occasion of his 60th birthday.

(1) See, for example: (a) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (c) Pardy, R. B. A. *J. Organomet. Chem.* **1981**, *216*, C29. (d) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594. (e) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (f) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (g) Lehmkuhl, H. *Pure Appl. Chem.* **1986**, *58*, 495. (h) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A. V.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (i) Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1647.

(2) Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719.

(3) For publications advocating one or the other view, see: (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1322. (b) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (d) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (e) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (f) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117. (g) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346. (h) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92. (i) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 5986. (j) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 4228. (k) Prüse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2856. (l) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439. (m) Hässelbarth, A.; Prüsse, T.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 213. (n) Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 9018. (o) Karrass, S.; Eller, K.; Schwarz, H. *Chem. Ber.* **1989**, *124*, 939. (p) Karrass, S.; Schwarz, H. *Organometallics* **1990**, *9*, 2034. (q) Eller, K.; Schwarz, H. *Inorg. Chem.*, in press. (r) For an interesting example of the sequence "insertion/β-methyl shift/olefin loss in the reaction $Cp_2ZrCD_3^+ + CH_2{=}C(CH_3)_2 \rightleftarrows Cp_2ZrCH_3^+ + CH_2{=}C(CH_3)CD_3$, see: Christ, C. S., Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596.

(4) (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725. (b) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (d) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (e) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108. (f) van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. The common structural feature in all these studies is often of the type $M{-}X^\alpha{-}Si^\beta(C^\gamma H_3)_2CH_3$.

(5) The experimental setup has been described repeatedly in earlier papers.[3i–k,m,o–q] Briefly, Fe^+ is generated by 100-eV electron impact ionization of $Fe(CO)_5$ in the presence of the organic substrates (1:10). The resulting complexes are accelerated to 8-keV kinetic energy, mass-selected at a resolution of 3000–5000 (10% valley definition) by using B(1)E(1) of our modified ZAB-HF machine, which is of BEBE configuration. The unimolecular reactions occurring in the field-free region between E(1) and B(2) were recorded by scanning B(2). Signal-averaging techniques were used to improve the S/N ratio. A total of 10–20 scans were accumulated by on-line processing of the data with the VG 11/250 or the AMD-Intectra data system. All samples were synthesized by known literature procedures ((a) Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540. (b) Bestmann, H. J.; Wölfel, G. *Chem. Ber.* **1984**, *117*, 1250), purified and characterized by standard laboratory techniques. We note that in the MI mass spectra of the Fe^+-*free* silanes **5a,b**–**7a,b** the only reaction observed is due to loss of a methyl radical from the $Si(CH)_3$ group. Thus, the *reactions described in the present note are indeed induced by the metal* ion Fe^+. For a discussion of the 70-eV spectra of these compounds, see: Tomás, J.; Miklős, P. *Org. Mass Spectrom.* **1975**, *10*, 859.

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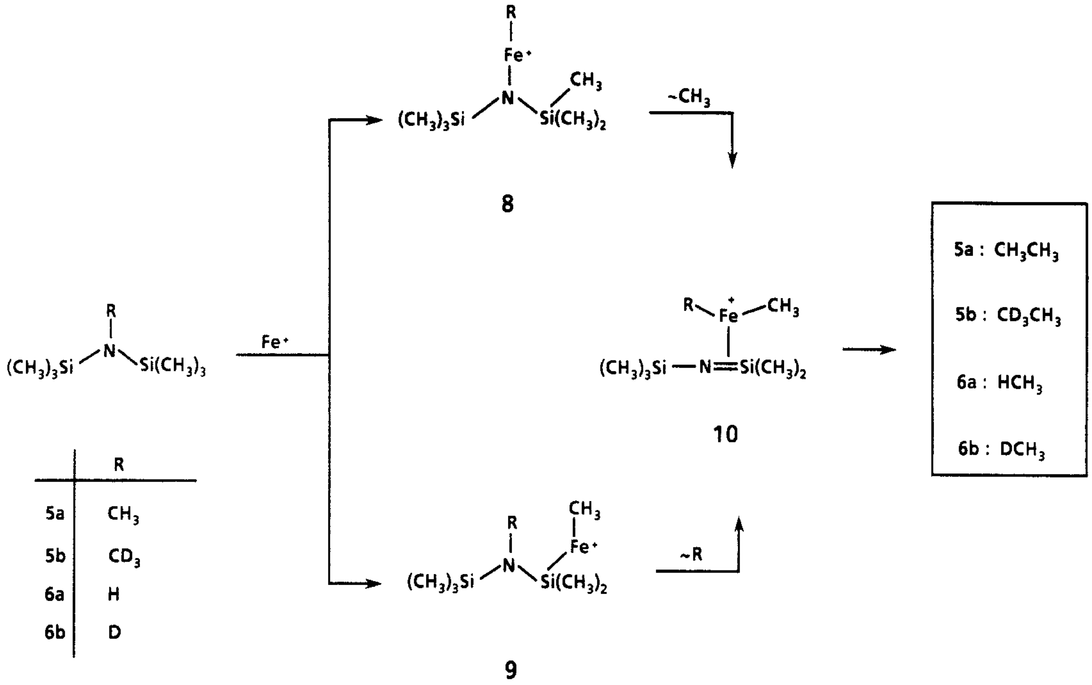
Scheme II



dominated by the loss of C_2H_6 (77% total fragment ion current; minor processes that are not discussed in this context are due to the eliminations of H_2 (16%) and $(CH_3)_3SiH$ (5%)). In the MI spectrum of the NCD_3-labeled isotopomer **5b**–Fe^+, the signal due to ethane loss is split into two components; one corresponds to $C_2H_3D_3$ and the other to C_2H_6, which are formed in a 1.3:1 ratio. Other $C_2H_{6-x}D_x$ ($x = 1, 2$) isotopomers are *not* formed in the dissociation of **5b**–Fe^+. This result has two important implications.

(1) In spite of the fact that there exist two possibilities (**8** → **10** and **9** → **10**) for the generation of intermediate **10**, loss of CH_3CD_3 requires the operation of a β-methyl transfer in one stage. From **10**, reductive elimination of CH_3CD_3 takes place (Scheme II).

(2) Elimination of C_2H_6 from **5b**–Fe^+ points to either a reversible step operative in the formation of **10** (for example **8** ⇄ **10** or **9** ⇄ **10**) or, alternatively, a second mechanism (Scheme III) in which the Fe^+ directly couples two methyl groups of the silyl substituents (**11**). A distinction between these fundamentally different mechanisms is easily provided by the determination of the kinetic energy release, T,[6] associated with losses of $C_2H_3D_3$ and C_2H_6 from **5b**–Fe^+. If C_2H_6 is formed via a route different from that for the formation of $C_2H_3D_3$, the T values should be different. This is *not* the case, as evidenced by Figure 1. In contrast, the $T_{0.5}$ values are practically identical, 33 ± 1 meV (for loss of $C_2H_3D_3$) and 34 ± 1 meV (for loss of C_2H_6). In addition, the "n" value, introduced by Holmes and Terlouw[7] as a quantitative measure to estimate the deviation of the signal from a pure Gaussian-shaped signal (for which $n = 2$), is for both reaction channels very similar with $n = 2.0 \pm 0.1$ (C_2H_6 loss) and $n = 1.9 \pm 0.1$ ($C_2H_3D_3$ loss). Thus, we conclude that Fe^+-mediated generation of CH_3CH_3 from **5b** is *not* the result of a distinct reaction path. Rather, this product is due to a partially degenerate isomerization of **5b**–Fe^+, which may proceed via reversible steps in the formation of intermediate **10** (Scheme II).[8] We note, however, that the observed ratio for the losses of CH_3CD_3/CH_3CH_3 (1.3:1) is not identical with that calculated for a complete equilibration of one CD_3 and three CH_3 groups (1:1) or with that for an equilibration of six CH_3 groups with one CD_3 group; for the latter a ratio of 1:2.5 would result. There are several explanations conceivable to account for the deviation. However, as no distinction is yet possible, we refrain from discussing them.

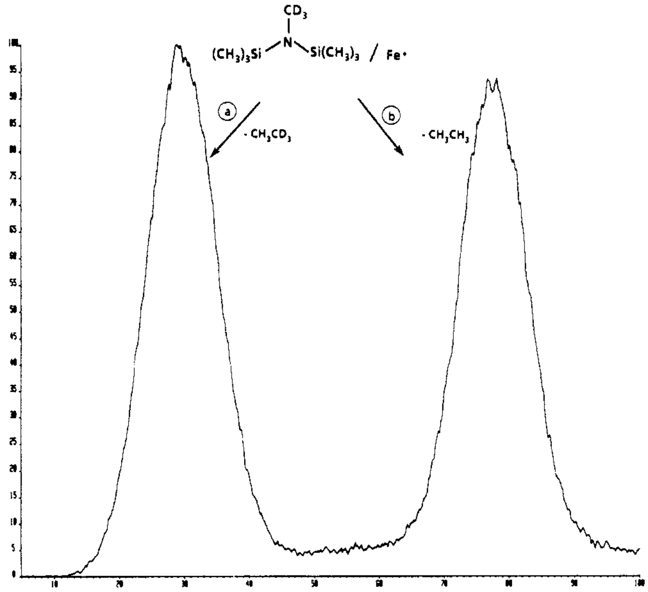


Figure 1. Kinetic energy release, T, for losses of (a) $C_2H_3D_3$ and (b) C_2H_6 from **5b**–Fe^+.

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[6] (a) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1983. (b) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

[7] Holmes, J. L.; Terlouw, J. K. *Org. Mass. Spectrom.* **1980**, *15*, 383.

[8] For further examples demonstrating the suitability of T measurements as a probe to distinguish and characterize organometallic processes, see: (a) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P.; Bowers, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 1. (b) Schulze, C.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *88*, 291. (c) van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991. (d) van Koppen, P. A. M.; Bowers, M. T.; Beauchamp, J. L. *Organometallics* **1990**, *9*, 625.

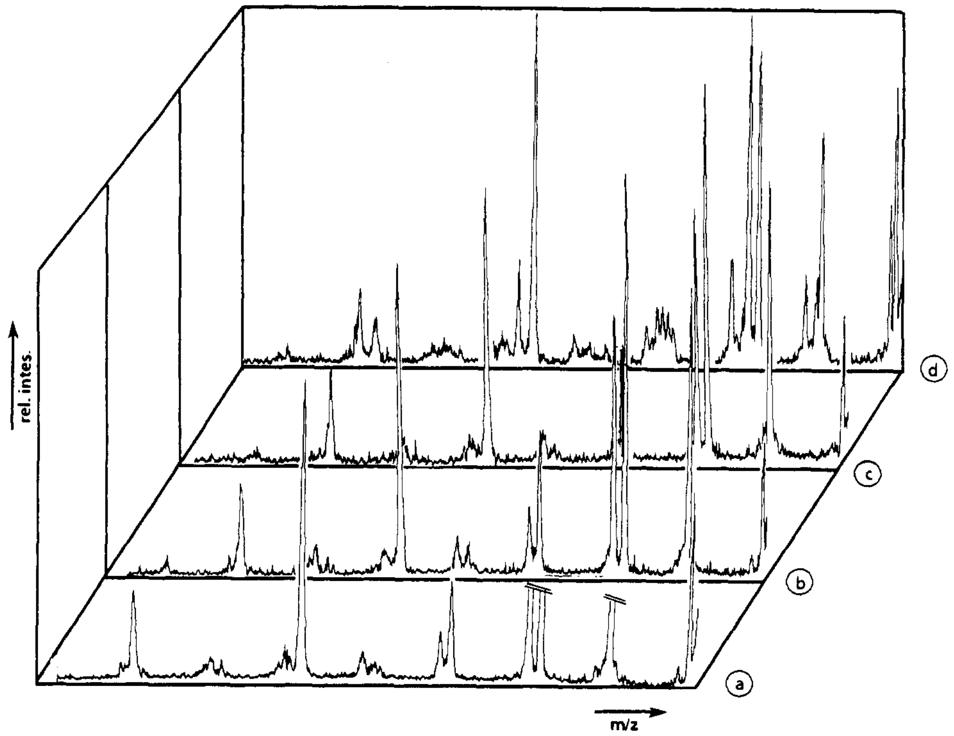
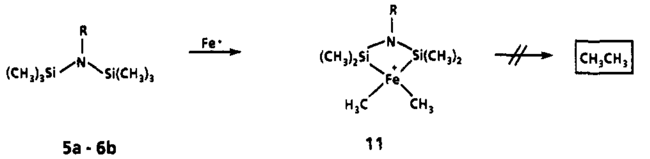


Figure 2. Collisional activation mass spectra (collision gas helium; $p \approx 10^{-6}$ Torr) of ions formed by unimolecular losses of alkanes RCH_3: (a) CH_4 loss from **6a**–Fe^+; (b) C_2H_6 loss from **5a**–Fe^+; (c) $C_2H_3D_3$ loss from **5b**–Fe^+; (d) C_2H_6 loss from **5b**–Fe^+.

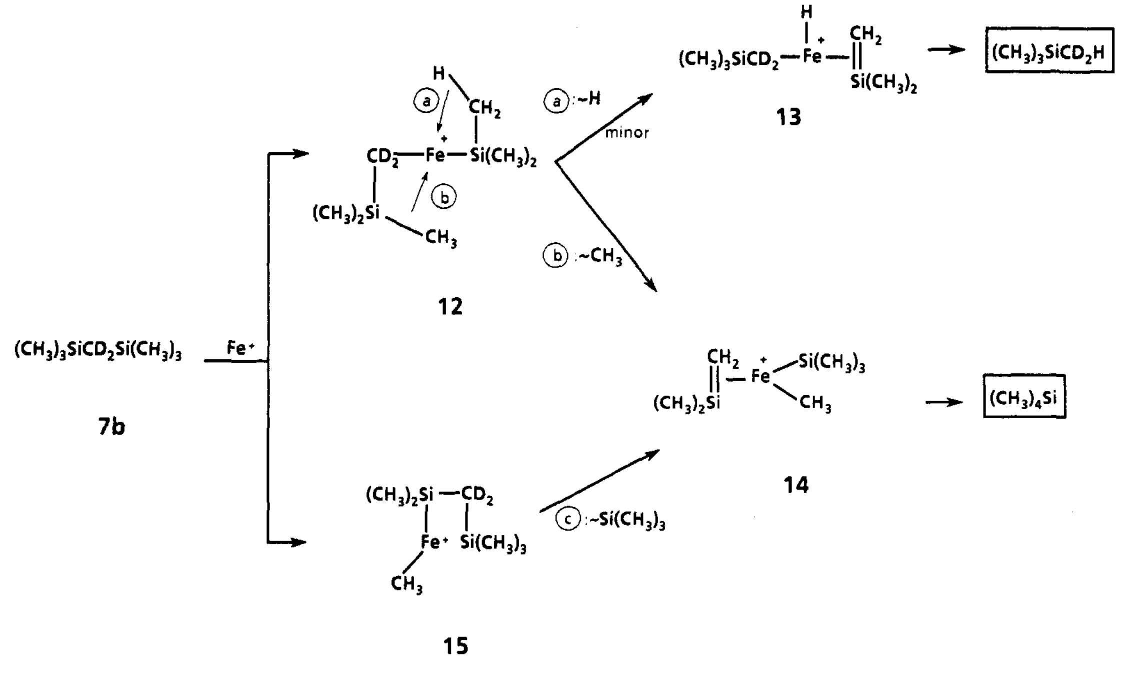
Scheme III



Not surprisingly, the MI spectrum of **6a**–Fe^+ is dominated by the loss of CH_4 (61% total fragment ion current), while the elimination of C_2H_6 is much less prominent (3%). The study of the ND-labeled complex **6b**–Fe^+ results in quantitative mass shifts, supporting the mechanism suggested in Scheme II (e.g. we observe losses of only CH_3D and C_2H_6).

Further support that the species generated by loss of CH_4 from **6a** is identical with that generated by ethane loss from the *N*-methyl analogues **5a**,**b** is provided by a collisional activation (CA) experiment (Figure 2). If the products of unimolecular losses of RCH_3 (R = H, CH_3, CD_3) from the Fe^+ complexes of **5a**,**b** and **6a** are mass-selected and subjected to high-energy collisions with helium targets, one obtains the CA spectra shown in Figure 2. We do note the perfect agreement in spectra a–c, which clearly supports our conjecture that identical ions are formed. In addition, the identical spectra also rule out the

Scheme IV



existence of Scheme III as an additional route for C_2H_6 loss from **5a**,**b**. We also note from the partial $\Delta m = 3$ shifts in Figure 2d that the CD_3 group has become indistinguishable from the remaining CH_3 group. However, H/D scrambling is not operative.

Finally, in the MI mass spectrum of **7a**–Fe^+ elimination of $(CH_3)_4Si$ is the by far most favored reaction (90% total fragment ion current).[9] For the CD_2-labeled complex **7b**–Fe^+ losses of $(CH_3)_4Si$ and of $(CH_3)_3SiCD_2H$ are observed in a ratio of >50:1. While this isotope distribution strongly indicates that sequence a of Scheme IV is, at best, of quite minor importance, a clear-cut distinction between paths b and c is not yet possible. We note the absence of C_2H_6 loss from either **7a**–Fe^+ or **7b**–Fe^+.[10,11]

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(9) For the reductive elimination of $(CH_3)_4Si$ from isolable $(CO)_4Fe(CH_3)Si(CH_3)_3$ complexes in solution, see: Blakeney, A. J.; Gladysz, J. A. *Inorg. Chim. Acta* **1980**, *53*, L 25.

(10) A reviewer has suggested that the failure of **7a** and **7b** to undergo Fe^+-induced loss of ethane may point to the operation of yet another mechanism for loss of ethane from the Fe^+ complexes of **5** and **6** "in which the Fe^+ ion first complexes with the lone pair on the nitrogen. Following this, the metal does not insert, but the energy of complexation is sufficient to induce the elimination within the intact, complexed molecule". We leave it to the reader to decide whether this proposal is superior to the one outlined in Scheme II.

(11) A β-methyl migration has been recently uncovered to be operative in the dissociative rearrangement of $(CH_3)_3COFe^+OC(CD_3)_2$ to give rise to $(CH_3)_2CO$ and $CH_3FeO^+C(CD_3)_2$ and *not* $FeOC(CD_3)_2CH_3^+$: Schröder, D.; Schwarz, H. *Angew. Chem.*, in press.

Additions and Corrections

R. Allen Williams, Timothy P. Hanusa,* and John C. Huffman: Structures of Ionic Decamethylmetallocenes: Crystallographic Characterization of $(Me_5C_5)_2Ca$ and $(Me_5C_5)_2Ba$ and a Comparison with Related Organolanthanide Species. **1990**, *9*, 1128–1134.

The calculated value for the unit cell of $Cp^*{}_2Ca$ in Table I is incorrect. The proper value is 3684.27 Å^3. In Table II, the isotropic thermal parameter listed for carbon C(16) of $Cp^*{}_2Ca$ should be 18. All other values in Tables I and II are correct.