

Evidence for the Activation of Unstrained Carbon-Carbon Bonds by Bare Transition-Metal Ions M^+ ($M = \text{Fe}, \text{Co}$) without Prior C-H Bond Activation

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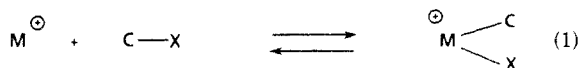
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The metastable ion (MI) decompositions of RNH_2/M^+ complexes ($R = (\text{C}_2\text{H}_5)_2\text{CHCH}_2$, $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$; $M = \text{Fe}, \text{Co}$) in the gas phase have been studied by tandem mass spectrometry with a four-sector instrument of BEBE configuration. The analyses of the MI spectra of isotopically labeled complexes uncover processes which inter alia demonstrate that the loss of C_4H_8 corresponds to a reaction in which site-specific oxidative addition of an unstrained C-C bond to the "anchored" transition-metal ion M^+ takes place without prior C-H bond activation. The intramolecular methyl migration preceding the elimination of C_4H_8 is subject to a secondary kinetic isotope effect of $k_{\text{H}}/k_{\text{D}} = 1.33$ for $M^+ = \text{Fe}^+$ and $k_{\text{H}}/k_{\text{D}} = 1.15$ for $M^+ = \text{Co}^+$ per D atom. Additional processes observed correspond to the generation of molecular hydrogen, methane, ethylene and ethane. All reactions are highly specific, and mechanisms are suggested that are in keeping with the labeling data. For example, both H_2 and C_2H_4 are formed via "remote functionalization" involving the $\omega/(\omega - 1)$ positions of the ethyl side chain of the amines. Ethane contains an intact ethyl group, and one hydrogen is provided via specific β -hydrogen transfer which does not involve the chemically activated CH_2NH_2 group. This methylene group is also "inert" with regard to the reductive elimination of methane from $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CHNH}_2/\text{Co}^+$. According to the labeling experiments, the intermediate from which CH_4 is liberated contains an intact CH_3 group that originates from the quaternary carbon center; the missing hydrogen atom is provided to roughly the same amount by both the second CH_3 group of C(2) and the CH_2 unit of the ethyl group. Again, the $-\text{CH}_2\text{NH}_2$ part does not serve as a hydrogen source for CH_4 .

I. Introduction

Direct insertion of atomic transition-metal ions into C-H bonds is very well documented indeed, and the last two decades have witnessed growing interest in these seemingly specialized gas-phase studies, which actually encompass aspects from areas as diverse as catalysis, bioorganic chemistry, organometallic chemistry, physical organic chemistry, and mass spectrometry.¹ However, in spite of the tremendous progress made in the understanding of the elementary steps of oxidative addition/reductive elimination of C-X bonds to bare transition-metal ions M^+ (eq 1), Armentrout and Beauchamp in the summary and



outlook of their recent review article^{1a} have expressed some frustration. In particular, they note that "it would be of interest to ascertain whether or not atomic ions insert

directly into unstrained C-C bonds, since this process has no significant parallels in condensed phase chemistry. Although implicated by circumstantial evidence and attractive in its simplicity, this process has not been unequivocally substantiated."²

A related, controversially discussed problem of topical interest concerns the operation of β -methyl shifts to transition-metal centers, which is thought to be the key step in Ziegler-Natta olefin polymerization reactions and related oligomerizations.³ While, for example, ethylene insertion into highly electrophilic lanthanide-, actinide-, and early-transition-metal-alkyl bonds has been described, such migrating insertion reactions (eq 2) have rarely been



observed for stable organometallic complexes. In particular, the elegant experimental work of Brookhart and Lincoln⁴ clearly establishes that the rate of β -hydrogen transfer ($R = \text{H}$) is on the order of 10^{10} faster than β -methyl migration ($R = \text{CH}_3$).

The situation in the gas phase has also been clouded for quite some time, as no consensus seems to exist as to

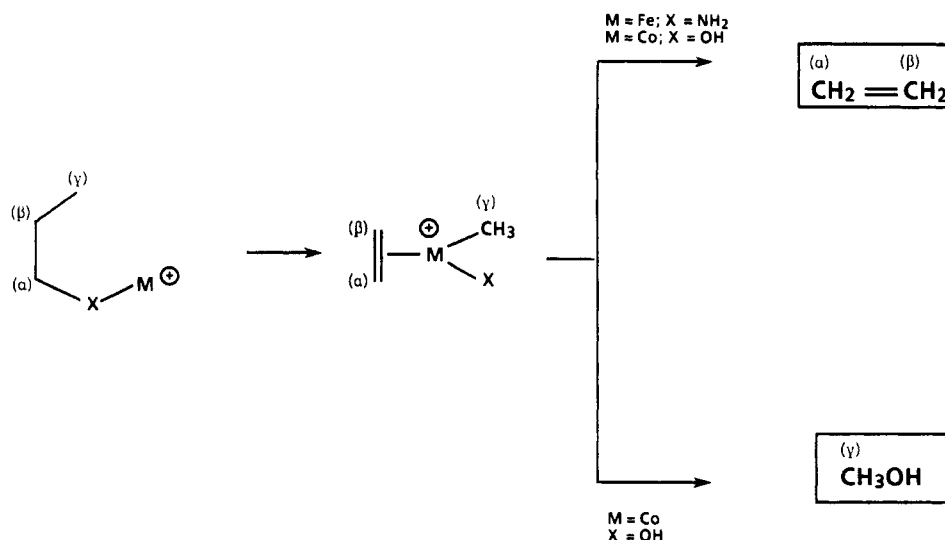
(1) Selected references: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Müller, J. *The Organic Chemistry of Iron*; Academic Press: New York, 1978. (c) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (d) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (e) Freiser, B. S. *Talanta* **1985**, *32*, 697. (f) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (g) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, The Netherlands, 1987; No. 193, p 97. (h) Ridge, D. P. *Ibid.*, p 165. (i) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623. (j) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum: New York, 1989. (k) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Structures*; Werner, H., Erker, G., Eds.; Springer-Verlag: Heidelberg, FRG, 1989; p 203. (l) More than 100 references on the reactions of bare transition-metal ions with organic substrates, together with a detailed discussion of the reactions of gaseous octyne isomers with Fe^+ , may be found in: Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (m) Beauchamp, J. L. In *High Energy Processes in Organometallic Chemistry*; Suslick, K. E., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987. (n) Buckner, S. W.; Freiser, B. S. *Polyhedron* **1988**, *7*, 1583. (o) Allison, J.; Mavridis, A.; Harrison, J. F. *Polyhedron* **1988**, *7*, 1559. (p) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (q) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1989**, *22*, 315. (r) Eller, K.; Schwarz, H. *Chimia* **1989**, *43*, 371. (s) Russell, D. H., Ed. *Gas Phase Inorganic Chemistry*; Plenum: New York, 1989.

(2) Examples as well as leading references for "circumstantial evidence" of direct insertion of M^+ into C-C bonds may be found in: (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (b) Freas, R. B.; Ridge, D. P. *Ibid.* **1980**, *102*, 7129. (c) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1980**, *102*, 1736. (d) Tsaropoulos, A.; Allison, J. *Ibid.* **1985**, *107*, 5085. (e) Prüsse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2856. (f) Häslebarth, A.; Prüsse, T.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 213.

(3) 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) Penckert, 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.; 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.

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

Scheme I



Scheme II

	Δm	neutral molecule	% abundance	
			M = Fe	M = Co
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CCH}_2\text{NH}_2/\text{M}^+$ 1a-M^+ $\text{M} = \text{Fe/Co}$	2	H ₂	71	76
	16	CH ₄		9
	28	C ₂ H ₄		3
	30	C ₂ H ₆		8
	56	C ₄ H ₈	29	4

whether an authentic β -methyl shift to a transition-metal ion is operative or not.⁵ For example, quite recently we were able to demonstrate⁶ that a β -alkyl migration to a metal ion center does not exist for $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}/\text{M}^+$ ($\text{X} = \text{NH}_2, \text{OH}; \text{M}^+ = \text{Fe}^+, \text{Co}^+$). Rather, both *n*-propanol and *n*-propylamine undergo, inter alia, M^+ -mediated ($\text{M} = \text{Fe}, \text{Co}$) reactions, in the course of which C_2H_4 and CH_3OH are generated in a highly specific fashion via an intermediate that is due to the oxidative addition of the $\text{C}(\beta)\text{--C}(\gamma)$ bond to the "anchored" metal ion M^+ (Scheme I).

In this contribution⁷ evidence will be presented that bare metal ions M^+ ($\text{M} = \text{Fe}, \text{Co}$) anchored to the NH_2 group

of primary amines are capable of intramolecularly activating *unstrained* C-C bonds in a highly site-specific mode without prior C-H bond activation. In addition, mechanistic details for the reductive eliminations of molecular hydrogen, methane, ethylene, and ethane are uncovered.

II. Experimental Section

The experimental setup has been described in earlier papers.^{11,2b,c,5g,h,j,6,7} Briefly, metal ions are generated either by 100-eV electron impact ionization of $\text{Fe}(\text{CO})_5$ or $\text{Co}(\text{acac})_2$ or by bombardment of CoCl_2 with 8-keV xenon atoms, with use of a procedure originally developed by Freas and Campana.⁸ The sputtered metal ions (or organometallic species of unknown composition) were then reacted in the ion source of a modified VG Instruments ZAB-HF four-section mass spectrometer⁹ with the organic substrates. The resulting RNH_2/M^+ complexes¹⁰ are accelerated to 8-keV kinetic energy, mass-selected at a resolution of 3000–5000 (10% valley definition) by using $\text{B}(1)\text{E}(1)$. The unimolecular reactions occurring in the field-free region between

(5) For examples advocating one or the other view, see: (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1981, 103, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* 1982, 1, 963. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Ibid.* 1983, 2, 1818. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1983, 105, 5197. (e) Tolbert, M. A.; Beauchamp, J. L. *Ibid.* 1984, 106, 8117. (f) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* 1988, 92, 92. (g) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* 1988, 110, 5986. (h) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *Ibid.* 1989, 111, 4228. (i) References 2b,c. (j) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* 1989, 8, 2439.

(6) (a) Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 607. (b) Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.* 1989, 111, 9018.

(7) For preliminary communications, see: (a) Karrass, S.; Schwarz, H. *Helv. Chim. Acta* 1989, 72, 633. (b) Karrass, S.; Eller, K.; Schwarz, H. *Chem. Ber.* 1989, 123, 939.

(8) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* 1985, 107, 6202.

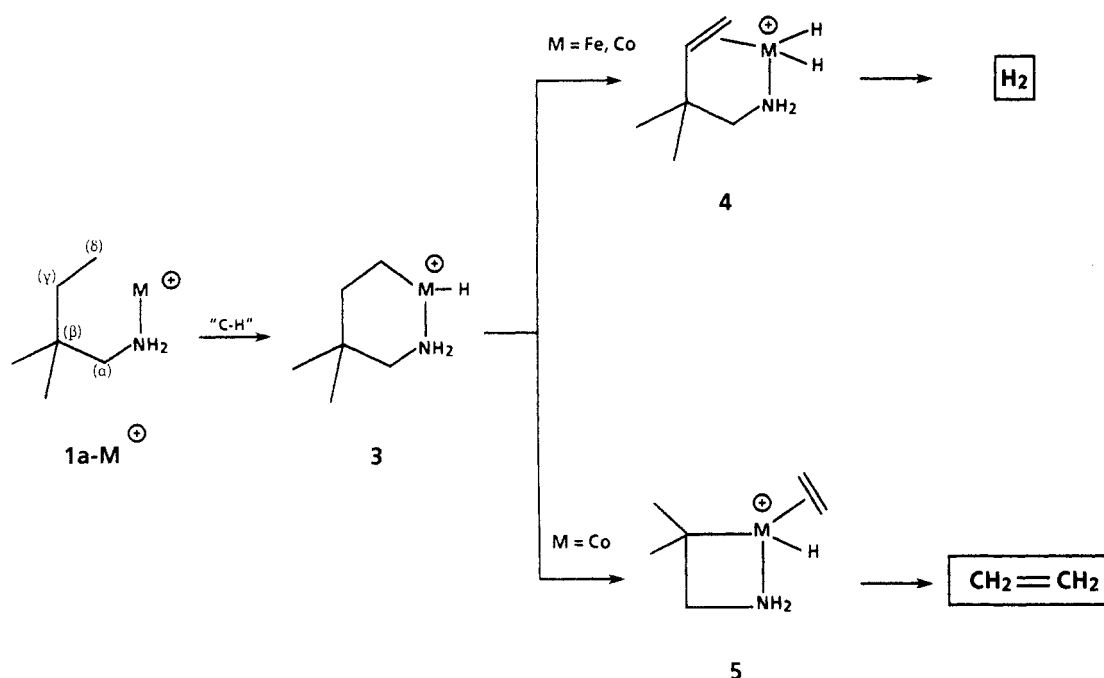
(9) This instrument is of BEBE configuration (B stands for magnetic sector and E for electric sector). For a description of the basic three-sector machine and its operation, see: Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* 1986, 21, 665.

(10) It should be mentioned that the detailed mechanism by which the RNH_2/M^+ complexes are formed is open to speculation. The pressure in the ion source is, however, high enough to collisionally stabilize the complexes by multiple collisions.

Chart I

$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ 1a	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CD}_2\text{NH}_2$ 1b	$\text{CH}_3\text{CD}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ 1c	$\text{CD}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ 1d
$(\text{CH}_3\text{CH}_2)_2\text{CHCH}_2\text{NH}_2$ 2a	$(\text{CH}_3\text{CH}_2)_2\text{CHCD}_2\text{NH}_2$ 2b	$(\text{CH}_3\text{CH}_2)_2\text{CDCH}_2\text{NH}_2$ 2c	$\text{CH}_3\text{CD}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{NH}_2$ 2d
$\text{CD}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{NH}_2$ 2e	$\text{CD}_3\text{CD}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{NH}_2$ 2f	$(\text{CD}_3\text{CH}_2)_2\text{CHCH}_2\text{NH}_2$ 2g	$\text{CD}_3\text{CD}_2\text{CH}(\text{CD}_3\text{CH}_2)\text{CH}_2\text{NH}_2$ 2h

Scheme III

Table I. Neutral Products Formed from Fe^+ and Co^+ Complexes of (2,2-Dimethylbutyl)amine Isotopomers^a

	1b-Fe ⁺	1b-Co ⁺	1c-Fe ⁺	1c-Co ⁺	1d-Fe ⁺	1d-Co ⁺
H_2	100	100				
HD			100	100	100	100
CH_4		100		65		100
CH_3D				35		
C_2H_4		100				
$\text{C}_2\text{H}_2\text{D}_2$				100		100
C_2H_6		100				
$\text{C}_2\text{H}_4\text{D}_2$				100		
$\text{C}_2\text{H}_3\text{D}_3$						100
C_4H_8	100	100			100	100
$\text{C}_4\text{H}_6\text{D}_2$			100	100		

^aData are given as sums of the percentages of neutral products, for each neutral normalized to 100%.

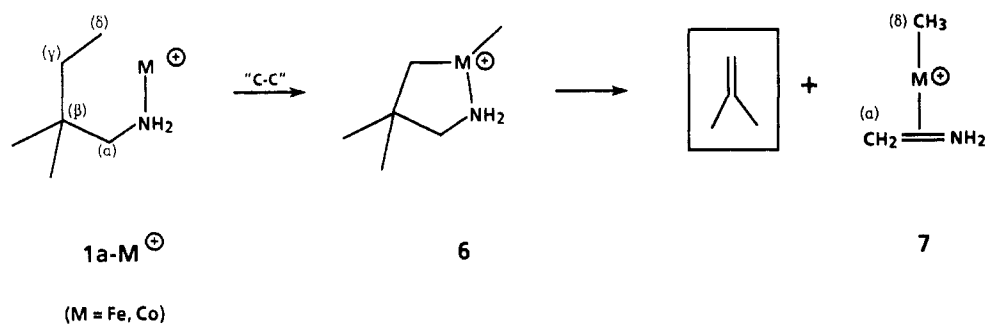
E(1) and B(2) were recorded by scanning B(2). Signal-averaging techniques were used to improve the signal-to-noise ratio (10–100 scans). All spectra were processed on line with the VG 11/250 or the AMD-Intectra data system. The reproducibility of the data given in Tables I–III is better than $\pm 2\%$. * Values of “100%” quoted for a given isotopomer distribution indicate that the other isotopomers are practically absent; i.e., if they are formed at all, their relative abundance is $<1\%$ for the reaction of interest. The compounds shown in Chart I were synthesized and purified by standard laboratory procedures and characterized by established spectroscopic techniques.

III. Results and Discussion

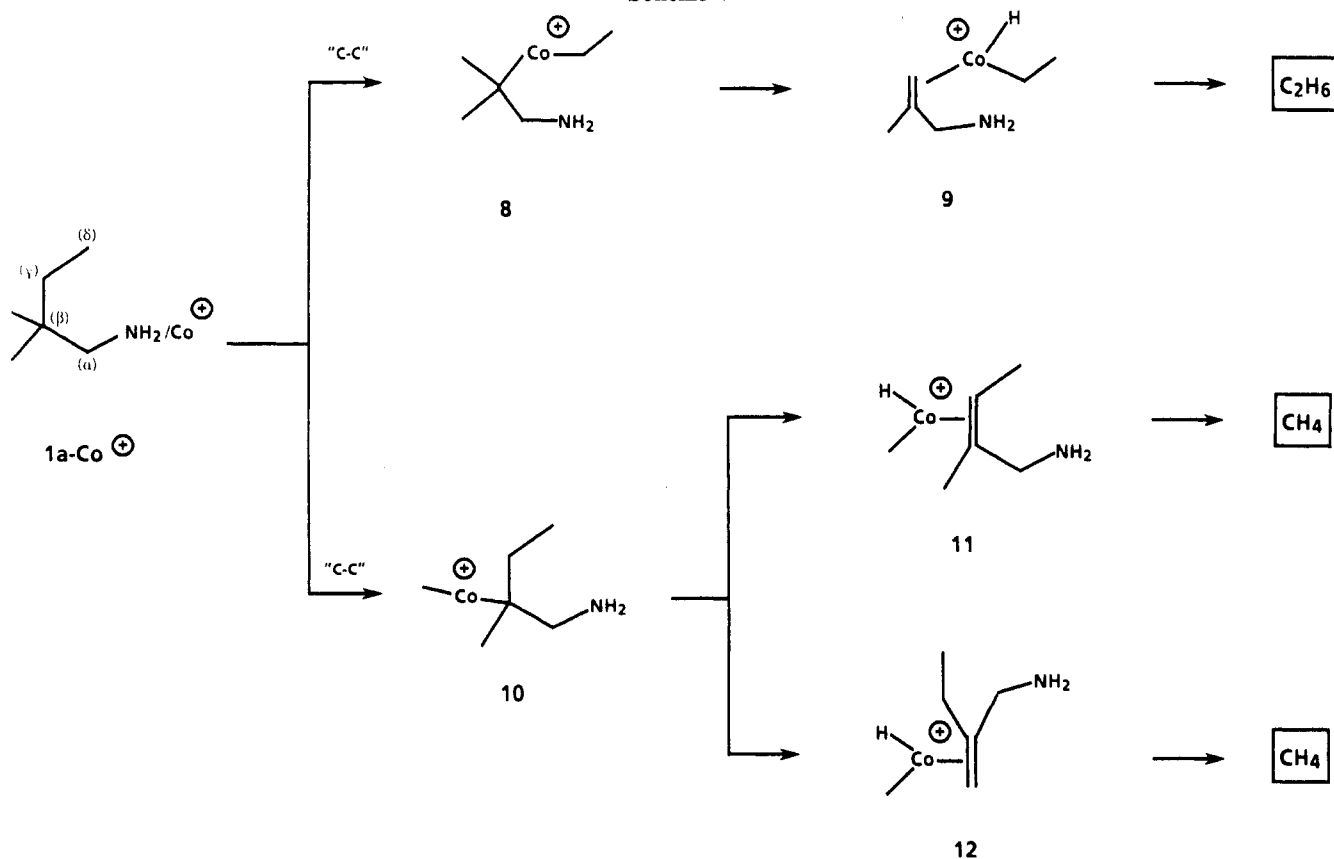
1. $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2/\text{M}^+$ Systems (1-M⁺). The product distributions of metastable ions of the Fe^+ and Co^+ complexes of **1a** are given in Scheme II. Obviously, Co^+ exhibits a much richer chemistry with the amines **1a** and **2a** (see below) than Fe^+ . This was also noted earlier^{2a,b,6} for the reactions of alcohols with Co^+ and Fe^+ . Although the *actual* structures of both the ions and the neutral species¹¹ are unknown, the study of the isotopomers **1b–d** (Table I) provides a detailed insight with

(11) Owing to sensitivity limitations, we were unable to apply the otherwise powerful method of collisionally induced dissociative ionization (CIDI), a variant of neutralization-reionization mass spectrometry (NRMS), for the characterization of the neutral species generated from the organometallic complexes. However, on energetic grounds there cannot exist any doubt that mass differences (Δm) of 2, 16, and 28 amu must correspond to intact H_2 , CH_4 , and C_2H_4 molecules. The generation of, for example, CH_3CH would be too costly energetically. As will be shown, $\Delta m = 30$ amu indicates the loss of authentic C_2H_6 and not, as observed in other areas, sequential losses of $\text{C}_2\text{H}_4/\text{H}_2$. See, for example: (a) Czekay, G.; Eller, K.; Schröder, D.; Schwarz, H. *Angew. Chem. Int. Ed. Engl.* 1989, 28, 1277. (b) Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.*, in press. (c) Reference 5j. For leading references on CIDI and NRMS, see: (d) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* 1987, 87, 485. (e) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 805. (f) Terlouw, J. K. *Adv. Mass Spectrom.* 1989, 11, 984. (g) Holmes, J. L. *Ibid.* 1989, 11, 53. (h) Schwarz, H. *Pure Appl. Chem.* 1989, 61, 685. (i) Holmes, J. L. *Mass Spectrom. Rev.* 1989, 8, 513. (j) McLafferty, F. W. *Science* 1990, 247, 925.

Scheme IV



Scheme V



regard to the genesis of the species formed.

The labeling data prove that molecular hydrogen and ethylene originate from the *ethyl* group exclusively; hydrogen is generated in a clean 1,2-elimination mode, and ethylene is also formed without any hydrogen-exchange processes. The mechanism suggested in Scheme III ("remote functionalization"¹²) is in keeping with the experimental finding:¹³ Insertion of the complexed metal ion into the terminal C-H bond generates the intermediate **3**, which serves as a branching point for both the β -hydrogen transfer ($3 \rightarrow 4$) and cleavage of the β -C-C bond ($3 \rightarrow 5$). While the former reaction dominates the MI spectra of either metal ion complex, the reaction $3 \rightarrow 5$ is only observed for $M^+ = Co^+$.¹⁴

Common to the two metal ions is the generation of C_4H_8 . As evidenced by the labeling results (Table I), this hydrocarbon is formed in a highly specific fashion; the neutral species contains neither the CH_2 group adjacent to the NH_2 function nor the methyl group of the ethyl side chain. These findings rule out **5** (Scheme III) as a conceivable intermediate en route to the production of $(CH_3)_2C=CH_2$ via a cycloreversion process.¹⁵ The fact that exclusively

(12) For a discussion of this concept and leading references, see: (a) References 1k,p,r. (b) Stepnowski, R. M.; Allison, J. *Organometallics* 1988, 7, 2097.

(13) As stated in the text, structural assignments are fictitious. This holds true in particular for species **5** (Scheme III), for which several conceivable alternatives exist, and several other ionic species.

(14) A reviewer has rightly argued that β -hydrogen transfer via intermediate **3** (Scheme III) is unlikely on the grounds that metallacycles, in contrast to acyclic alkyl-substituted transition-metal complexes, are not prone to undergo this reaction (this has, indeed, been known for decades from numerous studies of organometallic systems; see for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987). Rather, he suggests that the (kinetically favored) intermediate **3** via a reversible deinsertion/insertion reaction gives rise to a five-membered metallacycle. The latter may then rearrange to **4**. We agree that both mechanistic variants cannot be distinguished on the basis of the labeling experiments. However, we would expect to observe from the five-membered metallacycle—via β -C-C cleavage—elimination of $CH_3CH=C(CH_3)_2$; this is not observed experimentally.

Scheme VI

	Δm	neutral molecule	% abundance M = Fe	% abundance M = Co
$(C_2H_5)_2CHCH_2NH_2/M^+$ 2a-M⁺ M = Fe/Co	2	H ₂	87	72
	28	C ₂ H ₄		6
	30	C ₂ H ₆		18
	56	C ₄ H ₈	13	4

C₄H₈ is split off from the metal complexes of both **1b** and **1d**, while C₄H₆D₂ is eliminated from **1c-M⁺**, strongly supports the mechanism proposed in Scheme IV. The remarkable feature of this mechanism is the fact that *no* C-H bond activation is involved in the metal ion mediated cleavage of C-C bonds! The reaction commences with an insertion of the anchored metal ion M⁺ (M = Fe, Co) into the C(γ)-C(δ) bond (Scheme IV: **1a-M⁺** $\rightarrow$ **6**). From the metallacycle so formed, via β -C-C bond cleavage, the neutral C₄H₈ species (presumably isobutene) is detached. It remains open to speculation whether the detachment step proceeds in a concerted fashion or via ligated metal ion complexes. Similarly, the actual structure of the product ion **7** is unknown.

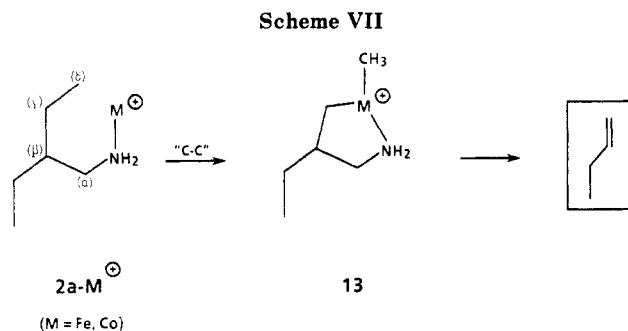
The two remaining reactions to be discussed for **1a-d** are the Co⁺-mediated losses of methane and ethane. Common to both processes is that (i) the alkyl part of the RH neutral species (R = methyl, ethyl) is specifically provided by the metal and ethyl groups attached to the quaternary carbon atom and (ii) the CH₂NH₂ unit does not provide the missing hydrogen atom. With regard to the formation of ethane, the missing hydrogen is provided by the methyl groups attached to C(β). (Scheme V: **8** $\rightarrow$ **9**).¹⁶

For the generation of methane, two different C-H sites serve as hydrogen sources. Losses of CH₄ and of CH₃D from **1c-Co⁺** and of CH₄ only from **1b-Co⁺** and **1d-Co⁺** clearly denote a methyl group attached to C(β) as well as a methylene moiety of the ethyl group as the hydrogen sources (Scheme V: **10** $\rightarrow$ **11** and **10** $\rightarrow$ **12**). This finding is quite unexpected, as previous studies^{2a,5h} had demonstrated that a methylene unit is more prone to undergo β -hydrogen transfer to a metal ion center than a methyl group. In the present case, the data for **1c-Co⁺** indicates that β -hydrogen transfer from a methyl group is favored by a factor of 1.23 (after statistical correction) over that from a methylene unit. However, as this holds true only if this step is not subject to a kinetic isotope effect, the factor of 1.23 represents an upper limit.¹⁷

Table II. Neutral Products Formed from Fe⁺ Complexes of (2-Ethylbutyl)amine Isotopomers^a

	2b-Fe ⁺	2c-Fe ⁺	2d-Fe ⁺	2e-Fe ⁺	2f-Fe ⁺	2g-Fe ⁺
H ₂	100	98	75	67	77	10
HD		2	25	33	11	90
D ₂					12	
C ₄ H ₈	100			30		
C ₄ H ₇ D		100				
C ₄ H ₆ D ₂			100		40	
C ₄ H ₅ D ₃				70		100
C ₄ H ₄ D ₄					60	

^a See footnote a in Table I.



All the labeling data for the generation of CH₄ and C₂H₆ are in line with the mechanism suggested in Scheme V.^{16,17} It is assumed that the two elimination reactions commence with activation of a C-C bond of a *quaternary* carbon atom. This interpretation is in keeping with a trend noted earlier by Radecki and Allison,¹⁸ they noted that the probability of a C-C bond to be oxidatively added to a transition-metal ion is dependent upon its bond strength, which itself follows the degree of substitution of a given carbon atom. The C-C insertion steps are followed by β -hydrogen transfer and terminated by reductive elimination of either CH₄ or C₂H₆. We note, however, that the very same products (including the label distribution) would result if the reverse sequence were operative, i.e., C-H bond activation preceding β -alkyl migration. We stress, however, that this duality does *not* apply to the generation of C₄H₈ (discussed above).

2. (CH₃CH₂)₂CHCH₂NH₂/M⁺ Systems (2-M⁺). The product distributions of metastable ions of the Fe⁺ and Co⁺ complexes of **2a** are given in Scheme VI. We again note that the chemistry of Co⁺ is much richer than that

(15) Examples of the reductive opening of metallacycles as well as bimolecular metathesis reactions of transition-metal ions in the gas phase are discussed in: (a) References 1c,f,n, 5b, and 6. (b) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1985**, *107*, 2605. (d) Kang, H.; Beauchamp, J. L. *Ibid.* **1986**, *108*, 5663. (e) Buckner, S. W.; Gard, J. R.; Freiser, B. S. *Ibid.* **1988**, *110*, 6606.

(16) As suggested by a reviewer, most of the structures shown in Schemes V and VIII should have the nitrogen atom anchored to the metal ion. We agree, but for the sake of simplicity (having *no* real structural information; see also ref 13!) we have refrained from giving too detailed structural drawings in these schemes. We further agree that **8** might also serve as an intermediate to eventually generate ethylene.

(17) We are grateful to a reviewer for having pointed out that for intermediate **10**, which "may consist of a nascent metallacyclobutane", geometrical constraints may favor β -hydrogen transfer from a CH₃ group over that from an RCH₂ group.

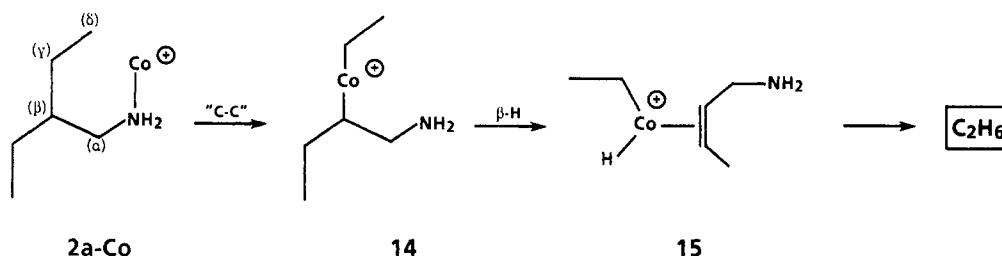
(18) Radecki, B.; Allison, J. *Organometallics* **1986**, *5*, 411.

Table III. Neutral Products Formed from Co⁺ Complexes of (2-Ethylbutyl)amine Isotopomers^a

	2b-Co ⁺	2c-Co ⁺	2d-Co ⁺	2e-Co ⁺	2f-Co ⁺	2g-Co ⁺	2h-Co ⁺
H ₂	100	100	72	69	89		
HD			28	31		100	71
D ₂					11		29
C ₂ H ₄	100	100	69	25	65		
C ₂ H ₂ D ₂			31	35 ^b		100	55
C ₂ D ₄					35		45
C ₂ H ₆	100	100		35 ^b			
C ₂ H ₅ D			41		50		
C ₂ H ₄ D ₂			59				
C ₂ H ₃ D ₃				40		100	45
C ₂ HD ₅					50		55
C ₄ H ₈	100			43			
C ₄ H ₇ D		100					
C ₄ H ₆ D ₂			100		26		
C ₄ H ₅ D ₃				57		100	
C ₄ H ₃ D ₅					74		100

^a See footnote a in Table I. ^b The isobaric nature of C₂H₂D₂ and C₂H₆ does not permit us to sort out the individual abundances.

Scheme VIII



of Fe⁺. In addition, a comparison of the MI spectra of the isomeric complexes of 1a-Co⁺ and 2a-Co⁺ reveals that in the latter no signal due to the generation of CH₄ is present. This may support our proposal that loss of CH₄ is a result of the initial insertion of the anchored metal ion in a C-C bond of a *quaternary* carbon atom (1a-Co⁺ → 10; Scheme V) followed by β -hydrocarbon transfer.¹⁹

A. Elimination of Molecular Hydrogen from 2-M⁺. The labeling data reveal a strikingly different behavior of the two metal ions M = Fe, Co. While for the Co⁺ complexes the reaction is highly specific (exclusive involvement of the $\omega/(\omega - 1)$ positions of the ethyl group in analogy to Scheme III), the selectivity of Fe⁺ complexes is much less. In fact, except for the CH₂ group adjacent to the NH₂ function, hydrogen atoms from *all* CH bonds contribute with varying degrees to the production of molecular hydrogen. In particular, it remains open to speculation whether reversible β -hydrogen atom shifts or different, competing mechanisms for CH bond activation are operative. However, the major part of H₂ generated from 2-Fe⁺ still originates from the $\omega/(\omega - 1)$ positions (remote functionalization).

B. Generation of C₄H₈ from 2-M⁺. This reaction is metal ion highly specific for both metal ions; the label distributions for C₄H_{8-x}D_x (Tables II and III) prove that the neutral molecule is generated without any positional exchange processes preceding the elimination step. The olefin, presumably 1-butene, is built up from C(β), C(γ), and C(δ). In the course of the reaction, the anchored metal ion inserts into the C(γ)-C(δ) bond (Scheme VII: 2a-M⁺ → 13). From the metallacycle so formed, via β -C-C bond cleavage, the neutral C₄H₈ is detached. Quite remarkably,

the labeling data reveal a relatively large secondary isotope effect for the "migration" of CH₃ versus CD₃, favoring the former by factors of 2.33 (M = Fe) and 1.73 (M = Co). This corresponds to isotope effects of $k_H/k_D = 1.33$ and 1.15 per D atom, respectively. These values are in the range expected for the sp³ → sp² hybridization of alkyl groups.²⁰ Can the high specificity for the generation of C₄H₈ also be explained by using a radically different mechanism, as for example the following one?²¹ Homolytic cleavage of the C(α)-C(β) bond of 2a-M⁺ generates an ion/dipole complex consisting of CH₃CH₂CHCH₂CH₃ and CH₂NH₂/M⁺. From the 1-methylpropyl radical so formed, CH₃ might then be transferred—via a β -radical cleavage—to the ionic part, thus eventually generating 1-butene. While such a reaction is also likely to be subject to a secondary kinetic isotope effect,²² we would find it extremely difficult to provide a rationale for the specific cleavage of the C(α)-C(β) bond, as the difference in ionization energies, IE, of M (<8 eV^{1a}) versus that of RNH₂ (IE_v = 9.40 eV^{23a} or IE_a = 8.71 eV^{23b} for R = C₄H₉) exclude substantial charge transfer from the amine to M⁺. Thus, no amine radical cation is likely to be generated; the latter species, however, would be viewed as a prerequisite for a homolytic cleavage of the C(α)-C(β) bond. We conclude

(20) Streitwieser, A.; Jagow, R. H.; Fakey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* 1958, 80, 2326.

(21) The consideration of this alternative was the result of a detailed discussion of our findings with Professor R. Keese, Bern, Switzerland, to whom we are very grateful for having drawn our attention to this aspect.

(22) For many examples on secondary isotope effects of a similar magnitude operative in the losses of methyl and ethyl radicals from radical cations in the gas phase, see: (a) Weiske, T.; Schwarz, H. *Chem. Ber.* 1983, 116, 323. (b) Weiske, T.; Halim, H.; Schwarz, H. *Ibid.* 1985, 118, 495. (c) Weiske, T.; Schwarz, H. *Tetrahedron* 1986, 42, 6245.

(23) (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Inota, S. *Handbook of Hel Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981. (b) Levin, R. D.; Lias, S. G. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1982, NSRDS-NBS71.

(19) This comment has invited an argument from a reviewer, who, rightly, states that CH₄ loss is often seen from linear alkanes. Though this is true, the point, however, is that for *functionalized* alkanes the elimination of CH₄ is a relatively minor reaction except for highly branched substrates; for examples see: references 2c, and 3g,h.

that the reaction suggested in Scheme VII is consistent with all experimental findings, and we note that the process of M^+ -mediated formation of C_4H_8 from **2** can be accounted for in terms of C-C bond activation without C-H activation.²⁴

C. Co^+ -Mediated Formation of C_2H_4 and C_2H_6 from **2.** These two reactions are, again, remarkably specific. Ethylene formation involves the $\omega/(\omega - 1)$ positions of an ethyl chain, as is the case for the production of molecular hydrogen (see above). We suggest that the two reactions which are subject to large primary kinetic isotope effects favoring the elimination of H_2 versus HD and D_2 and of C_2H_4 versus $C_2H_2D_2$ and C_2D_4 , respectively, proceed in the same way as the analogous reactions of the isomeric complex **1**- Co^+ (Scheme III).

(24) Prof. P. Armentrout (private communication to H.S., Nov 1989) has suggested an alternative mechanism that proceeds through an initial C-H bond activation step. While this variant cannot be ruled out with certainty, in contrast to the simplicity of Scheme VII it is extremely complex and introduces several assumptions, none of which have to be made by postulating direct C-C bond activation.

High specificity is also the hallmark for the generation of ethane from **2**- Co^+ , in that the reaction is not preceded by any exchange processes. The neutral species is built up by an intact ethyl group and a hydrogen atom that is provided by the methylene part of the second ethyl group. All other positions are inert. From the ratio of $C_2H_4D_2$ versus C_2H_5D (for **2d**- Co^+) and of C_2HD_5 versus $C_2H_3D_3$ (for **2h**- Co^+) one can estimate the isotope effect $k_H/k_D = 1.3$. The data given in Table III for the formation of ethane from **2**- Co^+ are in line with the mechanism postulated in Scheme VIII.

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Silylative Decarbonylation. 3. Transfer Selectivity and Substituent Rate Effects¹

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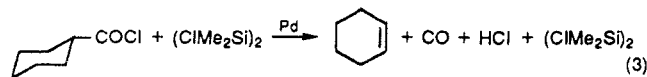
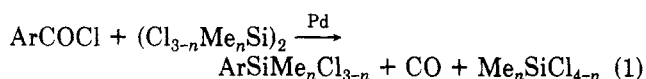
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This report describes investigations into those variables that affect the rate of the silylative decarbonylation reaction of aromatic acid chlorides and chloromethylsilanes. Electron-withdrawing substituents on the aromatic acyl halide enhanced the rate of product formation, and a Hammett analysis of a series of competitive reactions gave a ρ value of +2.4. Sequential replacement of chloride for methyl on the disilane did not result in a similar rate enhancement. The reactions were first order in disilane reagent as shown by continuous carbon monoxide monitoring. The use of unsymmetrical disilanes in reactions with acid chlorides resulted in the preferential transfer of the lesser chlorinated silicon to the aromatic ring and chlorination of the more halogenated silicon. Introduction of as few as one chlorine, e.g., chloropentamethylsilane, led to the exclusive formation of decarbonylated products in stark contrast to hexamethylsilane reactions. Mechanistic implications of these observations are discussed.

Introduction

The palladium-catalyzed reaction of aromatic acid chlorides with methylchlorosilanes yields predominately arylchlorosilane products (eq 1).² This process, which we have termed silylative decarbonylation, provides a convenient and general route to many previously unavailable substituted arylchlorosilanes and siloxanes from which a variety of novel high-temperature silicone polymers and copolymers can be prepared.³ In contrast, the metal-catalyzed reaction of hexamethyldisilane with analogous aromatic acid chlorides gives primarily acyltrimethylsilanes

(eq 2), except in the case of aromatic acid chlorides bearing



very strong electron-withdrawing substituents.^{2a,4} Aliphatic acid chlorides are not silylated by methylchlorosilanes when subjected to analogous reaction conditions but instead undergo decarbonylation and β -hydrogen elimination to yield olefins, HCl, and CO (eq 3).^{2a,5}

(1) (a) Part 2: Rich, J. D. *Organometallics* 1989, 8, 2606. (b) Preliminary results of this work were presented at the VIII International Symposium on Organosilicon Chemistry, June 7-12, 1987, St. Louis, MO.

(2) (a) Rich, J. D. *J. Am. Chem. Soc.* 1989, 111, 5886. (b) Rich, J. D. U.S. Patent 4,709,054, 1987, to General Electric Co. (c) Rich, J. D. U.S. Patent 4,604,477, 1986, to General Electric Co.

(3) (a) Rich, J. D.; Liu, W. L. U.S. Patent 4,563,154, 1985. (b) Rich, J. D. U.S. Patent 4,604,442, 1986; U.S. Patent 4,678,610, 1987. (c) Policastro, P. P.; Rich, J. D. U.S. Patent 4,668,754, 1987. (d) Rich, J. D.; Policastro, P. P.; Hernandez, P. K. U.S. Patent 4,794,153, 1988; 4,780,501 (1989, all to General Electric Co.

(4) (a) Yamamoto, Y.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* 1980, 1653. (b) Eaborn, C.; Griffiths, R.; Pidcock, A. *J. Organomet. Chem.* 1982, 225, 331.

(5) See: Tsuji, J.; Piro, P.; Wender, I. In *Organic Synthesis via Metal Carbonyls*, Wiley-Interscience: New York, 1977; Vol. 2, pp 631-636 and references therein.