Table V. Cr$^+$–O and Cr–O Bond Dissociation Energies[a]

bond energy	this study	lit
$D°(\text{Cr}^+\text{–O})$	85.3 ± 1.3	76 ± 7[b]
		80 ± 3[c]
		86 ± 5[d]
$D°(\text{Cr–O})$	110 ± 2	101 ± 7[b]

[a] In kcal mol^{-1}. [b] $D°(\text{M}^+\text{–O}) = D°(\text{M–O}) + \text{IP(M)} - \text{IP(MO)}$. $D°(\text{Cr–O})$ from the following: Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1961**, *34*, 664. [c] Table 1. [d] Recent measurement by the following: Armentrout, P. B., et al., to be published.

abstraction, C–C bond cleavage, and formation of oxygen-containing products including aldehydes. An examination of reactions of Cr$^+$ with C$_3$H$_6$O isomers provides useful information concerning reaction pathways involved in alkene oxidation by CrO$^+$. The major pathways include allylic oxidation, which proceeds via abstraction of allylic hydrogen by CrO$^+$, and formation of chemically activated metallacycle intermediates by cycloaddition of CrO$^+$ and the double bond.

The present results exhibit interesting similarities to condensed-phase alkene oxidations by oxometal reagents. The observation of allylic hydrogen abstraction by CrO$^+$ parallels several studies of alkene oxidation by heterogeneous metal oxide catalysts.[20,21] The formation of metallacycle intermediates has

analogies in the mechanism proposed for reactions of CrO$_2$Cl$_2$ with alkenes in solution.[22] In the gas phase, CrO$^+$ oxidizes alkenes via both pathways, bridging the gap between the heterogeneous metal oxide catalysts and other solution-phase oxometal reagents. Observation of such varieties of oxidation pathways from a simple diatomic metal oxide ion is quite surprising and suggests that even mechanistically complex heterogeneous allylic oxidation processes might be interpreted in terms of rather simple reactions involving specific active sites.

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Reactions of Transition-Metal Ions with Methylsilanes in the Gas Phase. The Formation and Characteristics of Strong Transition Metal–Silylene Bonds

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Abstract: Reactions of transition-metal ions (Ti$^+$, V$^+$, Cr$^+$, Fe$^+$, Co$^+$, and Ni$^+$) with organosilanes are investigated in the gas phase with an ion beam apparatus. Co$^+$ and Ni$^+$ react with silane to yield metal silylenes as exothermic products. Collision-induced dissociation studies of the product CoSiH$_2^+$ and nascent CoSiH$_4^+$ adducts provide additional information concerning the product structure and reaction mechanisms. Reactions with methylsilanes lead to formation of metal silylenes as major reaction channels, along with several other processes including hydride abstraction, dehydrogenation, and methane loss. Reactions with hexamethyldisilane are also investigated, with major products indicating Si–Si bond cleavage. An examination of the reaction enthalpies for the observed metal silylene products provides estimates for metal ion–silylene bond energies, which include $D°(\text{M}^+ - \text{SiH}_2) = 67 ± 6$ kcal mol^{-1} (M = Co, Ni). Correlation between the metal ion–silylene bond energies and the electronic structure of the metal ions supports a bonding scheme in which silylene donates its nonbonding lone pair electrons to an empty 4s orbital of the metal center. For Co$^+$ and Ni$^+$, back-donation of paired 3d electrons from the metal into the empty 3p orbital on silicon is suggested to account for the stronger bond deduced for these metals.

Studies of molecular transformations involving the reactions of silicon compounds at transition-metal centers are numerous. Hydrosilation, for example, which results in the addition of Si–H bonds to unsaturated hydrocarbons, is catalyzed by transition-metal complexes.[3–5] However, catalytic hydrosilations are often very complex, and their mechanisms are not well understood. Oxidative addition of a Si–H bond to the metal center is presumed to be an obligatory step in the hydrosilation process, and direct evidence for this reaction is provided by several spectroscopic studies at low temperatures.[6,7] Nevertheless, relatively little is known about the nature, strengths, and specific reactions leading to the formation and rupture of single and multiple bonds between transition metals and silicon.

Recent studies of the reactions of transition-metal ions with small organic molecules in the gas phase have been very successful

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Table I. Lower Electronic States of Transition-Metal Ions and Their Relative Populations

metal ion	state[a]	config	energy,[b] eV	filament temp, K	population, %
Ti^+	X^4F	$3d^24s$	0.00	2290	62
	^4F	$3d^3$	0.11		36
	^2F	$3d^24s$	0.56		2
	^2D	$3d^24s$	1.05		<1
V^+	X^5D	$3d^4$	0.00	2290	81
	^5F	$3d^34s$	0.34		19
	^3F	$3d^34s$	1.08		<1
Cr^+	X^6S	$3d^5$	0.00	2000	100
	^6D	$3d^44s$	1.52		<1
Fe^+	X^6D	$3d^64s$	0.00	2560	74
	^4F	$3d^7$	0.25		25
	^4D	$3d^64s$	0.98		1
	^4P	$3d^7$	1.64		<1
Co^+	X^3F	$3d^8$	0.00	2560	78
	^5F	$3d^74s$	0.43		22
	^3F	$3d^74s$	1.21		<1
Ni^+	X^2D	$3d^9$	0.00	2490	98
	^4F	$3d^84s$	1.09		2
	^2F	$3d^84s$	1.68		<1

[a] Data from ref 22. [b] State energies cited are averaged over J states.

in providing valuable information concerning the reaction mechanisms[8-13] and thermochemistry of organometallic fragments in the absence of complicating solution phenomena.[14-18] In the present work, we have examined reactions of several first-row transition-metal ions with a series of methylsilanes in the gas phase. A surprising observation, with no precedent in condensed phase chemistry, is prevalent formation of transition-metal silylenes as major products. The silicon center in organosilanes completely dominates the observed reactions, which are very different from the reactions of transition-metal ions with alkanes in the gas phase.[9,10,16] These differences can be attributed to the special stability of metal silylenes. Correlation of metal–silicon bond energies with the electronic structures of the metal ions provides interesting insights into the nature of transition metal–silylene bonds.

Experimental Section

The ion-beam apparatus used for these investigations is described in detail elsewhere.[19] Briefly, transition-metal ions, Ti^+, V^+, Cr^+, Fe^+, Co^+, and Ni^+, are generated from organic compounds, $TiCl_4$, $VOCl_3$, $Cr(CO)_6$, $FeCl_3$(anhydrous), $CoCl_2$(anhydrous), and $NiCl_2$(anhydrous), respectively, by surface ionization. Ions are extracted from the source, mass and energy selected, and allowed to interact with the target gas in a collision chamber. Product ions scattered in the forward direction are focused into a quadrupole mass filter and detected with a channeltron electron multiplier operated in a pulse counting mode. Ion signal intensities are corrected for the mass discrimination of the quadrupole mass filter. The surface ionization source minimizes the production of excited state metal ions which can often react differently from ground state species.[17,20,21] The relative populations of the electronic states[22] of metal

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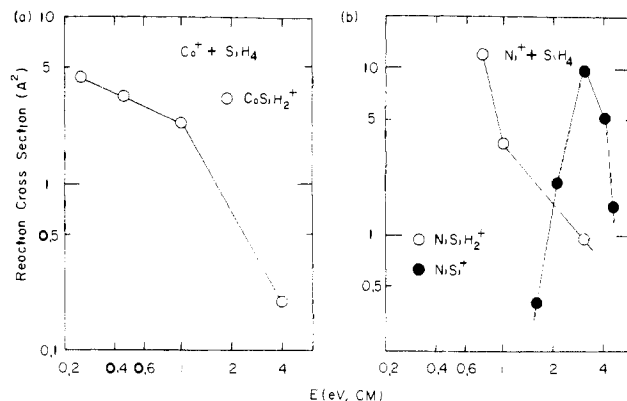

Figure 1. Variation in experimental cross section with center of mass kinetic energy for (a) the reaction of Co^+ with silane and (b) the reaction of Ni^+ with silane.

ions are estimated by assuming a Boltzmann distribution at the source temperature employed 2000–2600 K (Table I). CH_3SiH_3, CH_3SiD_3, and $(CH_3)_2SiD_2$ were prepared by reducing CH_3SiCl_3 and $(CH_3)_2SiCl_2$ with $LiAlH_4$ and $LiAlD_4$.[23] The other silicon compounds were obtained commercially and used without further purification. One sample of CH_3SiD_3 was kindly provided by Professor F. S. Rowland (U. C. Irvine).

Collision-induced dissociation (CID) studies[24-26] were performed on nascent $CoSiH_4^+$ adducts as well as $CoSiH_2^+$ to probe their structures and fragmentation processes. These studies were performed with a reverse geometry double focusing mass spectrometer (VG Instruments ZAB-2F).[24] Cobalt ions were formed from 150 eV electron impact on $Co(CO)_3NO$. Metal–silane adducts were formed in a high-pressure source operated typically at <3 × 10^{-3} Torr of total pressure. Under these conditions metal–silane clusters were formed and extracted from the source before undergoing subsequent collisions. The source was operated under nearly field-free conditions to avoid imparting translational energy to the reactant species. Ions exited the source, were accelerated to 8 kV, and were mass selected. Products resulting from collision-induced dissociation of mass selected ions in the second field-free region between the magnet and electric sectors were detected by scanning the energy of the electric sector. CID experiments used He as the target admitted into the collision cell situated at the focal point between the magnetic and electric sectors until 50% attenuation of the main beam intensity was observed.

It is important to point out that neutral products are not detected in these experiments. However, except where noted below, the identity of these products can usually be inferred without ambiguity. In addition, these experiments provide no direct structural information about the ionic products. The CID studies in addition to thermochemical arguments can often distinguish possibilities for isomeric structures.

Results and Discussion

In the present study, the transition-metal ions, Ti^+, V^+, Cr^+, Fe^+, Co^+, and Ni^+, are reacted with silane, the methylsilanes, and hexamethyldisilane in the gas phase. Reactions observed in these systems are considered in the following section, along with plausible mechanisms. In general, Ni^+ and Co^+ are observed to be most reactive toward organosilanes, followed by Ti^+, V^+, and Fe^+. The specific reactions of Ti^+ and V^+ distinguish these ions from the late transition metals. Cr^+ is unreactive with organosilanes, as is the case with hydrocarbons.[27] This is followed by an examination of reaction thermochemistry in which several transition metal–silylene bond energies are bracketed. Finally, these bond energies are related to the electronic structures of the metal ions

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Table II. Low Energy Product Distributions for Reactions of Transition-Metal Ions with Silicon Compounds[a]

metal ion	Neutral Reactant					
	SiH$_4$	SiH$_3$Me	SiH$_2$Me$_2$	SiHMe$_3$	SiMe$_4$	Si$_2$Me$_6$
Ni$^+$	[17][b] H$_2$ (100)[c]	[34] H$_2$ (100)	[126] H$_2$ (95) CH$_4$ (5)	[120] H$_2$ (9) CH$_4$ (30) NiH (61)	[110] NiMe (100)	[370] SiHMe$_3$ (66) SiMe$_4$ (34)
Co$^+$	[3.7] H$_2$ (100)	[117] H$_2$ (100)	[64] H$_2$ (95) CH$_4$ (5)	[190] H$_2$ (12) CH$_4$ (33) CoH (55)	[47] CoMe (100)	[300] SiHMe$_3$ or CoMe (97) SiMe$_4$ (3)
Fe$^+$	n.r.	n.r.	[43] H$_2$ (100)	[23] H$_2$ (40) CH$_4$ (60)	n.r.	[180] SiHMe$_3$ (15) SiMe$_4$ (85)
Cr$^+$	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
V$^+$	n.r.	[1.9] H$_2$ (100)	[17] H$_2$ (45) CH$_4$ (55)	[7.6] H$_2$ (100)	[2.7] H$_2$ (10) CH$_4$ (90)	[280] H$_2$ (23) 2H$_2$ (8) CH$_4$ (10) CH$_4$, H$_2$ (20) SiC$_2$H$_8$ (10) SiC$_3$H$_{10}$ (29)
Ti$^+$	[0.8] H$_2$ (100)	[57] H$_2$ (94) CH$_4$ (6)	[95] H$_2$ (58) CH$_4$ (42)	[133] H$_2$ (95) CH$_4$ (5)	[44] H$_2$ (66) CH$_4$ (34)	[310] H$_2$ (18) 2H$_2$ (5) CH$_4$ (17) CH$_4$, H$_2$ (31) SiC$_2$H$_8$ (11) SiC$_3$H$_{10}$ (18)

[a] Only the neutral products are listed. No reaction indicated by n.r. The product distribution was measured at 0.5 eV center of mass kinetic energy. [b] Approximate total cross section, Å^2. Estimated uncertainty ±50% due to discrimination in measuring reactant and product ion intensities. [c] % of total reaction.
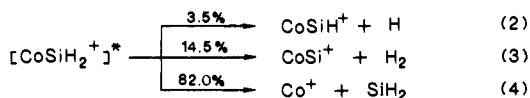
to deduce a favorable bonding scheme for transition-metal silylenes.

Silane. The products observed in the exothermic reactions with organosilanes are shown in Table II. Both Co$^+$ and Ni$^+$ dehydrogenate silane at low energies (reaction 1). Experimental reaction cross sections for these products are characteristic of exothermic processes, decreasing with increasing kinetic energy as shown in Figure 1. V$^+$, Cr$^+$, and Fe$^+$ are all unreactive with

$$M^+ + SiH_4 \rightarrow MSiH_2^+ + H_2 \ (M = Ni, Co) \quad (1)$$
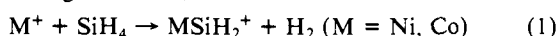
silane. Ti$^+$ undergoes an exothermic reaction with silane (eq 1). The maximum experimental cross section at low energy is very small ($\sigma < 0.8$ Å^2) in this instance.
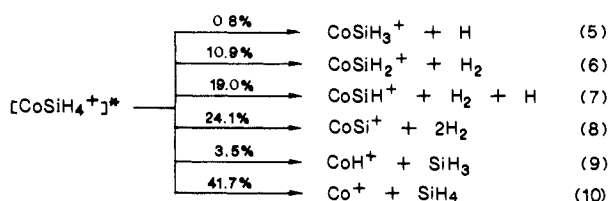
Collision-induced dissociation (CID) of CoSiH$_2^+$, formed in reaction 1, yields reactions 2–4. The small amount of CoSiH$^+$ and CoSi$^+$, processes 2 and 3, suggests that the structure of

$$[CoSiH_2^+]^* \begin{cases} \xrightarrow{3.5\%} CoSiH^+ + H & (2) \\ \xrightarrow{14.5\%} CoSi^+ + H_2 & (3) \\ \xrightarrow{82.0\%} Co^+ + SiH_2 & (4) \end{cases}$$
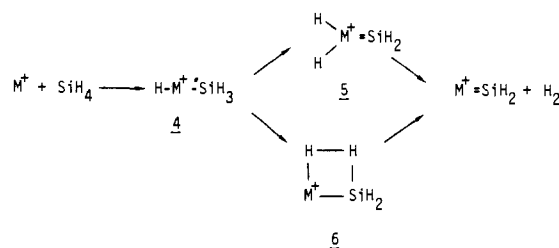
CoSiH$_2^+$ can be formulated as a cobalt–silylene complex, **1**. If the CoSiH$_2^+$ structure were better described by either **2** and **3**, then processes 2 and 3 would be expected to dominate. CID of
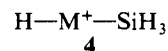
M$^+$—SiH$_2$ H—M$^+$—SiH   H\M$^+$—Si/H

1   **2**   **3**
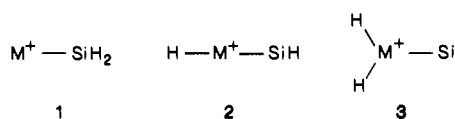
the nascent CoSiH$_4^+$ cluster yields processes 5–10. Processes

$$[CoSiH_4^+]^* \begin{cases} \xrightarrow{0.8\%} CoSiH_3^+ + H & (5) \\ \xrightarrow{10.9\%} CoSiH_2^+ + H_2 & (6) \\ \xrightarrow{19.0\%} CoSiH^+ + H_2 + H & (7) \\ \xrightarrow{24.1\%} CoSi^+ + 2H_2 & (8) \\ \xrightarrow{3.5\%} CoH^+ + SiH_3 & (9) \\ \xrightarrow{41.7\%} Co^+ + SiH_4 & (10) \end{cases}$$

Scheme I

5 and 9 may indicate competitive dissociations from intermediate **4**, which may be formed by insertion of Co$^+$ into a Si–H bond.

H—M$^+$—SiH$_3$
4

CoSiH$_3^+$, formed by process 5, probably dissociates further into CoSiH$^+$ and H$_2$ as indicated in process 7, and hence the yield of CoSiH$_3^+$ may actually be much higher. This suggests D° (Co$^+$ $-$ SiH$_3$) $\sim$ D° (Co$^+$ $-$ H) $=$ 52 kcal mol^{-1}.[9] With this bond energy, insertion of Co$^+$ into the silane Si–H bond is energetically favorable.

A mechanism for the dehydrogenation of silane is proposed in Scheme I and involves the insertion of a metal ion into the Si–H bond to form **4** as an initial step. This is then followed by an α-hydrogen transfer forming **5** which can eliminate H$_2$ to yield M—SiH$_2^+$ (M = Co, Ni).[28] Alternatively, dehydrogenation may proceed through the four-centered intermediate **6** in Scheme I. Such four-centered intermediates have been proposed in theoretical studies of the H/D exchange reaction of Cl$_2$MH (M = Sc, Ti, Ti$^+$) with D$_2$ with generalized valence bond methods.[29] In ad-

(28) We use M=SiH$_2^+$ in representing metal silylenes to be consistent with the valence of the silicon atom. However, this should not be interpreted as two σ-bonds between the metal and silicon, because, as discussed in the text, the metal–silylene bond is considered as σ-donation of a nonbonding lone-pair orbital of silylene to a metal and in some cases additional π-back-donation from metal to silicon.

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Table III. Thermochemical Data Used in the Text

	kcal mol⁻¹	ref		kcal mol⁻¹	ref
$D(H_3Si-H)$	90.3	a	$\Delta H_f(SiH_4)$	8.2	a
$D(H_3Si-Me)$	88	a	$\Delta H_f(SiH_3Me)$	-7	a
$D(Me_3Si-SiMe_3)$	80.5	a	$\Delta H_f(SiH_2Me_2)$	-23	a
$\Delta H_f(CH_4)$	-17.9	b	$\Delta H_f(SiHMe_3)$	-39	a
$\Delta H_f(C_2H_6)$	-20.2	b			
$\Delta H_f(C_2H_4)$	12.5	b	$\Delta H_f(SiMe_4)$	-55.4	a
$\Delta H_f(CH_2)$	93.7	e	$\Delta H_f(SiMe_6)$	-87	b
			$\Delta H_f(SiH_2)$	69	a
			$\Delta H_f(SiHMe)$	53	c
			$\Delta H_f(SiMe_2)$	37	c
			$\Delta H_f(CH_2{=}SiMe_2)$	7	a
			$\Delta H_f(CH_2{=}SiH_2)$	39	a
			$\Delta H_f(SiH_3{}^+)$	234.1	d

a Reference 31. *b* Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: Sussex, 1977. *c* Estimated from the values of ref 31. *d* Reference 41. *e* Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem., Ref. Data. Suppl.* 1977, 6.

dition, Watson[30] has recently observed an interesting methane exchange reaction which may proceed through a four-centered transition state.

The metal ions which dehydrogenate silane do not undergo a similar reaction with methane. The reaction enthalpy[31] for process 11 forming silylene from silane is only 61 kcal mol⁻¹ (Table III). This can be compared with carbene formation from methane, reaction 12, which requires 112 kcal mol⁻¹, rendering 1,1-dehy-

$$SiH_4 \rightarrow SiH_2(^1A_1) + H_2 \qquad (11)$$

$$CH_4 \rightarrow CH_2(^3B_1) + H_2 \qquad (12)$$

drogenation a very demanding process in the corresponding reactions of metal ions with methane.[32] Theory and experiment[33-35] suggest that the reverse of reaction 11 has a very low activation energy (<2 kcal mol⁻¹).
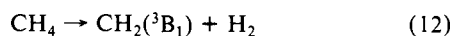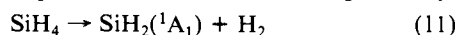
The variation of product abundances as a function of kinetic energy for reactions of Co⁺ and Ni⁺ with silane is shown in Figure 1. For the cobalt system only a decrease in the Co=SiH₂⁺ product is observed with increasing energy, and no other products are detected ($\sigma < 0.3$ Å²). For the nickel system, however, NiSi⁺ is observed at higher energy as an endothermic product. This result suggests that dehydrogenation of Ni=SiH₂⁺ is more facile than that of Co=SiH₂⁺.

Methyl-Substituted Silanes. Ni⁺, Co⁺, and V⁺ undergo exothermic reactions with CH_3SiH_3 to yield $M(SiCH_4)^+$ and H_2 (reaction 13). An examination of these reactions with CH_3SiD_3

$$M^+ + CH_3SiH_3 \rightarrow MSiCH_4{}^+ + H_2 \quad (M = Ni, Co, V) \qquad (13)$$

$$M^+ + CH_3SiD_3 \rightarrow MSiDCH_3{}^+ + D_2 \quad (M = Co, V) \qquad (14)$$
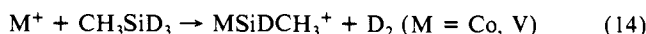
results in D₂ loss for Co⁺ and V⁺, indicating exclusively a 1,1-dehydrogenation process (reaction 14).[36] The observed 1,1-

(29) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* 1984, 106, 308.

(30) Watson, P. L. *J. Am. Chem. Soc.* 1983, 105, 6491.

(31) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246. We have recently determined a new value for $\Delta H_f(SiH_2)$ of 69 ± 3 kcal mol⁻¹ by studying the deprotonation of $SiH_3{}^+$ with a series of *n*-donor bases (Shin, S. K.; Beauchamp, J. L. *J. Phys. Chem.* 1986, 90, 1507). This is in good agreement with recent ab initio calculations [Ho, P.; coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* 1985, 89, 4647] which give a value of 68.1 kcal mol⁻¹. Several of Walsh's recommended heats of formation accordingly require revision.

(32) The 1,1-dehydrogenation process is not observed in the gas-phase reactions of the first-row transition-metal ions with methane or with larger hydrocarbons.

(33) (a) Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* 1983, 105, 5557. (b) Blomberg, M. R. A.; Siegbahn, P. E. M.; Bauschlicher, C. W. *J. Chem. Phys.* 1984, 81, 1373.

(34) Sax, A.; Olbrich, G. *J. Am. Chem. Soc.* 1985, 107, 4868.

(35) (a) Viswanathan, R.; Thompson, D. L.; Raff, L. M. *J. Chem. Phys.* 1984, 80, 4230-4240. (b) Jasinski, J. M. *J. Phys. Chem.* 1986, 90, 555-557. (c) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* 1986, 108, 2191-2199.
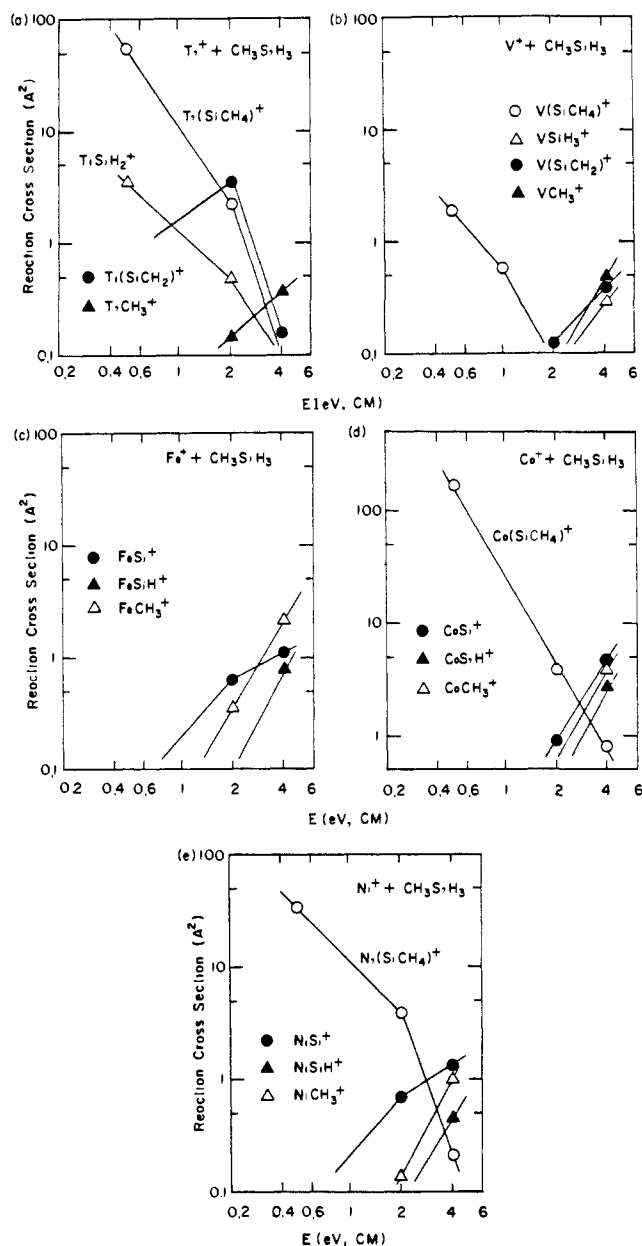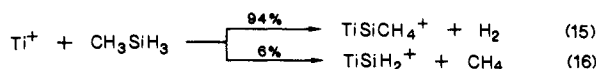

Figure 2. Variation in experimental cross section with center of mass kinetic energy for the reactions of (a) Ti⁺ with methylsilane, (b) V⁺ with methylsilane, (c) Fe⁺ with methylsilane, (d) Co⁺ with methylsilane, and (e) Ni⁺ with methylsilane. Lines drawn through single data points are extrapolated to smaller experimentally determined cross sections.

dehydrogenation process suggests that the product is a metal silylene (M=SiDCH₃⁺). Formation of the other isomers such as a metal–silaethylene complex [M(SiH₂=CH₂)⁺] and metal-silylmethylene [M=CH(SiH₃)⁺] would be expected to yield HD and H₂ losses, respectively.[37] Ti⁺ reacts with methylsilane to yield both H₂ and CH₄ losses (reactions 15 and 16). In the same reaction with CH_3SiD_3, D₂, and CH₃D losses are observed. This

$$Ti^+ + CH_3SiH_3 \xrightarrow[\substack{94\% \\ 6\%}]{} \begin{cases} TiSiCH_4{}^+ + H_2 & (15) \\ TiSiH_2{}^+ + CH_4 & (16) \end{cases}$$
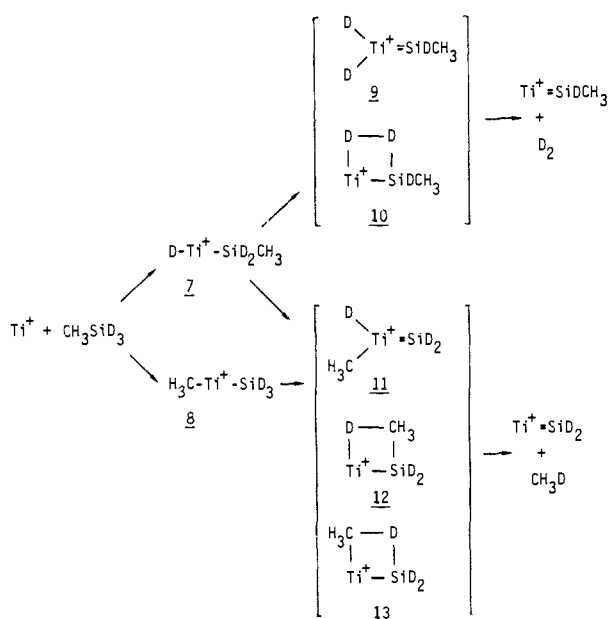
is again consistent with the formulation of product structures as metal silylenes, Ti=SiDCH₃⁺ and Ti=SiD₂⁺. Fe⁺ and Cr⁺ do not undergo exothermic reactions with methylsilane.

(36) Ni⁺ was not included in this study because of the limited amount of CH_3SiD_3 available for the experiment.

(37) The energy difference between methylsilylene and silaethylene is controversial. The data in Table III suggest that the latter is more stable by ~14 kcal mol⁻¹. Theoretical results are not generally in accord with this result; however, see, for example: Schaefer, H. F. *Acc. Chem. Res.* 1982, 15, 283.

Scheme II

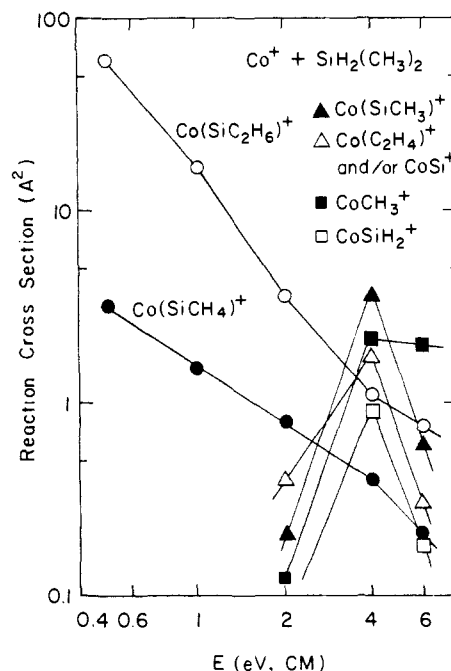**Figure 3.** Variation in experimental cross section with center of mass kinetic energy for the reaction of Co⁺ with dimethylsilane.

The observed processes can be rationalized by the mechanisms proposed in Scheme II with the reactions of Ti⁺ as an example. Ti⁺ may first insert into a Si–D bond of CH₃SiD₃ to form an intermediate 7. Then, D₂ loss can result from either α-D transfer to the metal center (9) or, alternatively, the dissociation of a four-centered intermediate (10). 7 may either undergo α-methyl transfer (11) or form a four-centered intermediate 12 to eliminate CH₃D. Initial insertion of Ti⁺ into a Si–Me bond can also be postulated, with loss of CH₃D occurring via intermediate 11 or 13.

Products observed at different collision energies in the reactions with methylsilane are shown in Figure 2. Most of the metal ions except Cr⁺ react with methylsilane at high energies to yield minor products of endothermic reactions. Although Fe⁺ does not yield products involving exothermic reactions with methylsilane, several products are observed at high energies, including FeSi⁺, FeSiH⁺, and FeCH₃⁺. Similar products are observed for Co⁺ and Ni⁺ at high energies, including MSi⁺, MSiH⁺, and MCH₃⁺ (M = Co, Ni), illustrating very similar reactivities between Fe, Co, and Ni. On the other hand, Ti⁺ and V⁺ yield quite different high-energy products from those of the late transition metals. The double dehydrogenation product M(SiCH₂)⁺ is unique for M = Ti and V. Metal silicides (MSi⁺) are not produced from these metals. A common high-energy product for all of these metals is MCH₃⁺ (M = Ti, V, Fe, Co, and Ni), which might be expected to be formed by the dissociation of a Si–C bond insertion intermediate (8 in Scheme II) via an endothermic bond cleavage at high energies. Considering that MSiH₃⁺ is not produced except for V, this could imply $D°(M^+-CH_3) > D°(M^+-SiH_3)$. Alternatively, this observation could also imply that the bond cleavage product M⁺–SiH₃ further dissociates to yield other products, as indicated by the formation of MSi⁺ and MSiH⁺ (M = Fe, Co, and Ni) at high energies. The reaction of V⁺ yields comparable amounts of VCH₃⁺ and VSiH₃⁺. Assuming that the structure is V⁺–SiH₃, $D°(V^+-SiH_3) \sim D°(V^+-CH_3) = 49$ kcal mol⁻¹ is implied.[21]

It is interesting to compare the reactions of methylsilane and those of ethane. Reaction of Ti⁺ with methylsilane, for example, yields Ti=SiH₂⁺ and Ti=SiHCH₃⁺, the metal silylenes. On the other hand, reaction of Ti⁺ with ethane yields the metal–ethylene complex Ti(CH₂=CH₂)⁺, and the corresponding metal–carbene species Ti=CHCH₃⁺ is not produced.[10] This is confirmed by the reaction of Ti⁺ with CH₃CD₃, which eliminates predominately HD in a 1,2-dehydrogenation process.[38] It has been suggested that M=CHCH₃⁺ (M = Fe, Co) species readily rearrange to the

corresponding M(ethene)⁺ isomer.[39]

Reactions of Ti⁺, V⁺, Co⁺, and Ni⁺ with dimethylsilane yield H₂ and CH₄ loss as exothermic products. Reaction of Fe⁺ exhibits H₂ loss as the only product channel. Both exothermic and endothermic products formed in the reaction of Co⁺ with dimethylsilane are shown as an example in Figure 3. The exothermic products include Co(SiC₂H₆)⁺ and Co(SiCH₄)⁺ (reactions 17 and 18). These products can be rationalized by a mechansim

$$Co^+ + SiH_2(CH_3)_2 \xrightarrow{\text{95%}} Co(SiC_2H_8)^+ + H_2 \quad (17)$$
$$\xrightarrow{\text{5%}} Co(SiCH_4)^+ + CH_4 \quad (18)$$

analogous to Scheme II, which involves an initial insertion of Co⁺ into a Si–H of Si–C bond followed by an α-Me or α-H transfer. Assuming similar pathways for the reactions with methylsilane and dimethylsilane, the products M(SiC₂H₆)⁺ and M(SiCH₄)⁺ observed for Ti, V, Fe, Co, and Ni are assumed to be metal silylenes. This was confirmed in the reaction of Co⁺ with (CH₃)₂SiD₂, where the major product involved loss of D₂ (>85%) rather than HD or H₂. High-energy products in the reaction of Co⁺ with dimethylsilane include Co(SiCH₃)⁺, CoCH₃⁺, Co-(C₂H₄)⁺ and/or CoSi⁺, and CoSiH₂⁺. Formation of CoCH₃⁺ may result from direct bond cleavage of a Si–C insertion intermediate analogous to 8 in Scheme II. Formation of the other product may involve further molecular rearrangements in the high-energy intermediates.

Trimethylsilane shows somewhat different reactivity than mono- and dimethylsilanes. Reaction of Co⁺ with trimethylsilane, reactions 19–21, leads to formation of Si(CH₃)₃⁺ as the major product channel, along with methane loss and dehydrogenation.

$$Co^+ + SiH(CH_3)_3 \xrightarrow{\text{55%}} CoH + Si(CH_3)_3^+ \quad (19)$$
$$\xrightarrow{\text{33%}} Co(SiC_2H_8)^+ + CH_4 \quad (20)$$
$$\xrightarrow{\text{12%}} Co(SiC_3H_8)^+ + H_2 \quad (21)$$

These three product channels dominate the reaction, and only small amounts of Co(SiCH₄)⁺ and Co(SiH₂)⁺ are formed at high energies (Figure 4). The product Si(CH₃)₃⁺ results from hydride abstraction by Co⁺ to generate CoH as a neutral product (reaction 19). The hydride abstraction reaction is observed only for Co⁺ and Ni⁺, indicating $D°(M^+-H^-) > D°(SiMe_3^+-H^-)$ for these metals. This observation is consistent with the fact that heterolytic

(38) Tolbert, M. A. Ph.D. Thesis, California Institute of Technology, 1986.

(39) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

Reactions of Transition-Metal Ions with Methylsilanes
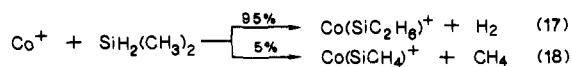
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Figure 4. Variation in experimental cross section with center of mass kinetic energy for the reaction of Co^+ with trimethylsilane.
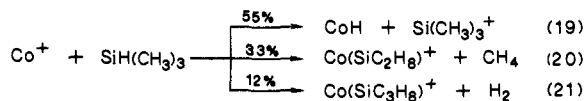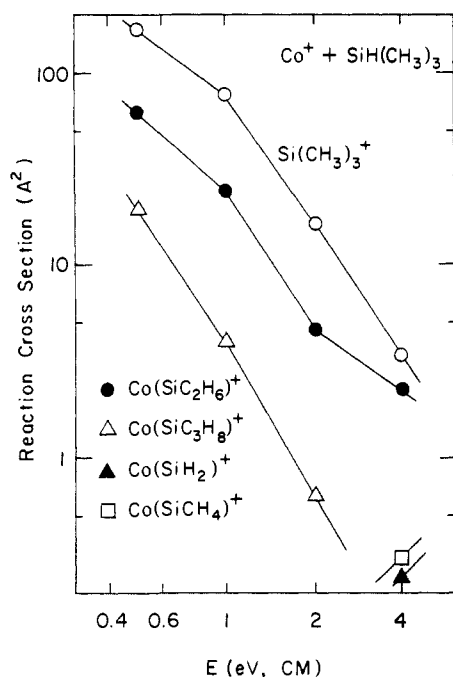
**Table IV.** Heterolytic M^+-H^- Bond Dissociation Energies[a]

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
$D°$ ($M^+ - H^-$), kcal mol^{-1}	163	178	178	179	196	194	206 >218[b]	214 >218[b]

[a] Reference 40. [b] This study.

M^+-H^- bond dissociation energy is higher for Ni and Co than for the other first-row transition metals[40] (Table IV). The $Me_3Si^+-H^-$ heterolytic bond dissociation energy of 218 kcal mol^{-1} is calculated with use of eq 22, with $AP(SiMe_3^+) = 10.20 \pm 0.03$ eV obtained from photoionization mass spectrometry measurements.[41] This value suggests somewhat higher values for the heterolytic bond dissociation energies for nickel and cobalt hydride than the values summarized in Table IV.

$$D°(Me_3Si^+-H^-) = AP(SiMe_3^+) - EA(H) \qquad (22)$$

Reaction 21, in which H_2 is eliminated, yields the ion product $Co(SiC_3H_8)^+$. The dehydrogenation process is observed to be the major channel in the reaction of Ti^+ and V^+. The structures of the ionic products $M(SiC_3H_8)^+$ (M = Ti, V, Fe, Co, and Ni) are not known. A metal–dimethylsilaethylene complex $[M(H_2C{=}SiMe_2)^+]$ may be thermodynamically feasible. Since formation of dimethylsilaethylene from trimethylsilane (reaction 23) requires 46 kcal mol^{-1} (Table III), the exothermic formation of M-$(H_2C{=}SiMe_2)^+$ would require a binding energy between the metal

$$SiHMe_3 \rightarrow H_2C{=}SiMe_2 + H_2 \qquad (23)$$
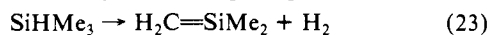
ion and dimethylsilaethylene greater than this value. The binding energy of Co^+ and the corresponding alkene, 2-methylpropene, is estimated to be ~50 kcal mol^{-1}.[8] For comparison, reactions with 2-methylpropane exhibit H_2 loss as a major process for all of these metals.[9,10,16] Isotope labeling has been used to confirm a 1,2-dehydrogenation of 2-methylpropane in several instances.[9b]

Reactions of Ni^+ and Co^+ with tetramethylsilane yield $SiMe_3^+$ as the only exothermic product. Cross-section data for the Ni system are shown in Figure 5. This product represents formal methyl anion abstraction from tetramethylsilane by Co^+ or Ni^+. As discussed in the case of trimethylsilane, a lower limit for
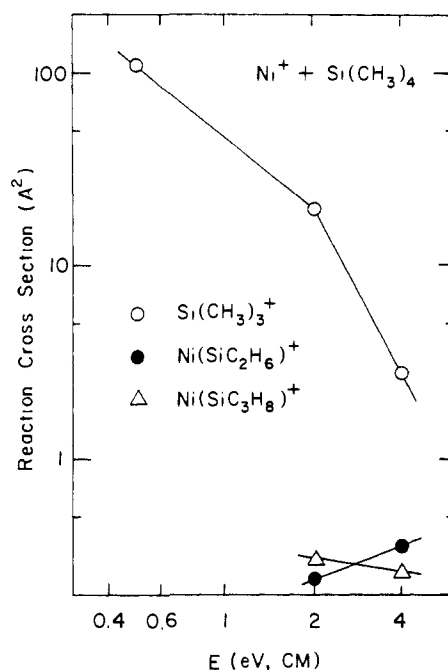

Figure 5. Variation in experimental cross section as a function of center of mass kinetic energy for the reaction of Ni^+ with tetramethylsilane.

Table V. Reaction Enthalpies for the Formation of Silylenes from Several Silicon Compounds (kcal mol^{-1})[a]

silicon compd	eliminated fragment			
	H_2	CH_4	C_2H_6	$Si(CH_3)_4$
SiH_4	61			
CH_3SiH_3	60	58		
$SiH_2(CH_3)_2$	60	58	72	
$SiH(CH_3)_3$		58	72	
$Si(CH_3)_4$			72	
$Si_2(CH_3)_6$				69

[a] Reference 31.

M^+-Me^- heterolytic bond dissociation energy can be estimated as $D°(M^+-Me^-) > D°(Me^--SiMe_3^+) = 229$ kcal mol^{-1} (M = Co, Ni).[42] Using this value, homolytic bond dissociation energies $D°(Ni-CH_3) > 55$ kcal mol^{-1} and $D°(Co-CH_3) > 50$ kcal mol^{-1} are derived.[43] Both Ti^+ and V^+ react with tetramethylsilane to cause loss of H_2 and CH_4. Although Fe^+ undergoes a facile reaction with 2,2-dimethylpropane to lose methane, no exothermic reaction is observed with tetramethylsilane.

Hexamethyldisilane. The reactions with hexamethyldisilane $(Me_3Si-SiMe_3)$ exhibit very large experimental cross sections for product formation, which indicates that these reactions are extremely facile. Fe^+, Co^+, and Ni^+ yield products of exothermic reactions which include $M(SiC_3H_8)^+$ and $M(SiC_2H_6)^+$ (M = Fe, Co, and Ni). Figure 6 presents cross-section data for the reaction of Ni^+ with hexamethyldisilane as an example of these late transition-metal systems. The observed products in these systems indicate that cleavage of the weak Si–Si bond (80.5 kcal mol^{-1})[31] completely dominates the reaction pathways. The reactions of Ti^+ and V^+, on the other hand, are distinguished from those of Fe^+, Co^+, and Ni^+, yielding a variety of products including dehydrogenation, methane loss, as well as Si–Si bond cleavage products.

Bond Energies. As is amply illustrated by the above results, metal silylenes are often observed as a major product in the

(40) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.*, to be published. See also: Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379.

(41) Cordermann, R. R. Ph.D. Thesis, California Institute of Technology, 1977.

(42) Calculated with $D(Me_3Si^+-Me^-) = AP(SiMe_3^+) - EA(Me)$; where the appearance potential of $SiMe_3^+$ from tetramethylsilane, $AP(SiMe_3^+)$, is 10.03 ± 0.04 eV from the following: Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085. $EA(CH_3) = 0.08$ eV from the following: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(43) Calculated with $D°(M-Me) = D°(M^+-Me^-) + EA(Me) - IP(M)$.

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Table VI. Transition Metal Ion–Silylene Bond Energies

metal ion	ground state electronic config (term)	bond energies, kcal mol^{-1}		
		$M^+ - SiH_2$	$M^+ - SiHCH_3$	$M^+ - Si(CH_3)_2$
Ni$^+$	d^9(^{2}D)	67 ± 6^{a,b}	>60^d	>69^e
Co$^+$	d^8(^{3}F)	67 ± 6^{a,b}	>60^d	>69^e
Fe$^+$	s^{1}d^6(^{6}D)	<72^b		>69^e
V$^+$	d^4(^{5}D)		>60^d	>60^f
Ti$^+$	s^{1}d^2(^{4}F)	>58^c	>60^d	>60^f

^{a} $M^+ + SiH_4 \rightarrow MSiH_2^+ + H_2$, $\Delta H < 0$. ^{b} $M^+ + SiH_2Me_2 \rightarrow MSiH_2^+ + C_2H_6$, $\Delta H > 0$. ^{c} $M^+ + SiH_3Me \rightarrow MSiH_2^+ + CH_4$, $\Delta H < 0$. ^{d} $M^+ + SiH_3Me \rightarrow MSiHMe^+ + H_2$, $\Delta H < 0$. ^{e} $M^+ + Si_2Me_6 \rightarrow MSiMe_2^+ + SiMe_4$, $\Delta H < 0$. ^{f} $M^+ + SiH_2Me_2 \rightarrow MSiMe_2^+ + H_2$, $\Delta H < 0$.
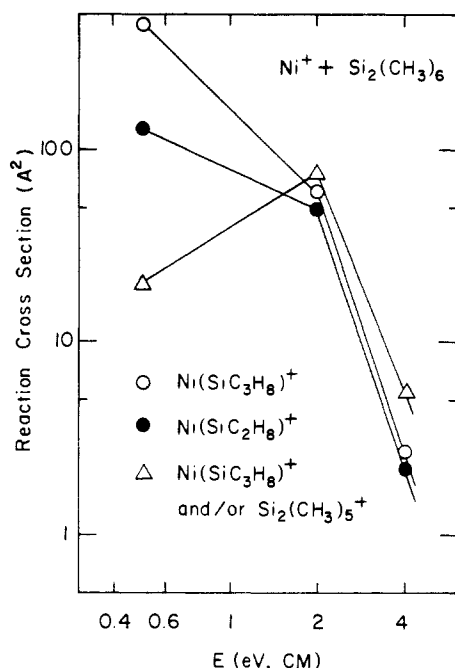

Figure 6. Variation in experimental cross section as a function of center of mass kinetic energy for the reactions of Ni$^+$ with hexamethyldisilane.

reactions of atomic metal ions with methylsilanes. By examining the reaction thermochemistry of the observed processes, limits on the dissociation energies of metal–silylene bonds can be obtained. For example, the reactions of Co$^+$ and Ni$^+$ with silane yield M=SiH$_2^+$ as an exothermic product reaction (reaction 1 and Figure 1). This provides a lower limit for the M$^+$–SiH$_2$ bond energy (M = Co, Ni) of 61 kcal mol^{-1} (Table VI). Similarly, a lower limit for the M$^+$–SiHCH$_3$ bond dissociation energy can be obtained from the exothermic formation of this species in the reactions with methyl silane (reaction 13). In several reactions with the methylsilanes and hexamethyldisilane, M(SiC$_2$H$_6$)$^+$ is produced as an exothermic product. On the condition that the structure is a metal silylene M=Si(CH$_3$)$_2^+$, this provides a lower limit for the metal–silylene bond energy (Table VI). Interestingly, the reactions with dimethylsilane yield M=SiH$_2^+$ as a *high energy product* for Fe$^+$, Co$^+$, and Ni$^+$. Cross sections for the formation of these products exhibit the typical behavior of an endothermic reaction, which is shown in Figure 4 for Co=SiH$_2^+$. Provided that no substantial energy barrier is present which might inhibit the formation of M=SiH$_2^+$ at low energy, the endothermicity of M=SiH$_2^+$ formation provides an upper limit of 72 kcal mol^{-1} for the M$^+$–SiH$_2$ bond energy (M = Fe, Co, and Ni). The bond dissociation energies estimated in this fashion are summarized in Table VI along with the reactions used to infer the various limits. Reaction enthalpies used in this determination may require additional attention. One of the important quantities in deriving these reaction enthalpies is the controversial heat of formation of SiH$_2$, for which several values have been previously reported, including 58[31] and 81 kcal mol^{-1}.[44] Considering the probable

experimental uncertainties in these measurements, we have chosen to use the value determined recently in our laboratory,[31] $\Delta H_f°(SiH_2) = 69$ kcal mol^{-1}.

The Nature of the Transition Metal–Silylene Bond. The present study shows two distinct features of transition-metal silylenes. First, the transition-metal silylenes are fairly stable, which often renders metal silylenes as major products in the reactions of transition-metal ions with the silanes. The stability of metal silylenes may be illustrated further by the enthalpy change of reaction 24, for which $\Delta H° = 46 ± 10$ kcal mol^{-1}.[45] Second,

$$NiSiH_2^+ + CH_2=CH_2 \rightarrow NiCH_2^+ + CH_2=SiH_2 \quad (24)$$

the metal–silylene bond is stronger for Ni$^+$ and Co$^+$ than the other transition-metal ions studied, as illustrated by the exothermic formation of M=SiH$_2^+$ (M = Ni and Co) from silane. These observations provide a basis to describe the bonding between transition-metal ions and silylene as follows.

Silylene has a singlet ground state (^{1}A$_1$) and a low-lying triplet excited state (^{3}B$_1$) at ~20 kcal mol^{-1}.[46] The ground-state silylene is expected to form a donor–acceptor type σ-bond to the metal ion by donating its nonbonding lone-pair electrons to the metal center. Hence, metal ions with an empty 4s orbital (ground state derived from a 3d^n valence electronic configuration) can make a strong metal–silylene bond by accepting the lone-pair electrons from silylene. Observation of the strong bond for Ni$^+$(3d^9) and Co$^+$(3d^8) supports this conjecture. In addition to accepting lone-pair electrons from silylene, both Ni$^+$ and Co$^+$ can also back-donate electrons from their paired 3d$_π$ orbital to the empty 3p$_π$ orbital of silicon, enhancing the transition metal–silylene bond strength.[47]

One way to test the validity of the bonding analysis for transition-metal silylenes described above is to apply this scheme to the other metal ions. Fe$^+$ and Ti$^+$ have 4s^{1}3d^n valence electronic configurations, and we expect that their metal–silylene bond strength is weakened due to the half-filled 4s orbital. This argument is supported by the absence of FeSiH$_2^+$ as well as a very small amount of TiSiH$_2^+$ formation from the exothermic reactions of Ti$^+$ with silane. Although the ground state of V$^+$ is derived from a 3d^4 electronic configuration with an empty 4s orbital, V$^+$ is unreactive toward silane. Comparing V$^+$ with Ni$^+$ and Co$^+$, V$^+$ has only singly occupied 3d orbitals. Hence, the amount of back-donation in the metal–silylene bond may be reduced for V$^+$ compared with Ni$^+$ or Co$^+$. Cr$^+$ has a stable 3d^5 valence electronic configuration and may not initiate reaction toward silane or methyl-substituted silanes by the insertion into a Si–H or Si–Me bond. We have previously found that the Cr$^+$ is unreactive toward alkanes for the same reason.[27]

Conclusion

The present results are the first experimental observation and bond energy determination of transition-metal silylenes. The metal silylenes are the major products from the reactions of transition-metal ions with the silanes, providing a contrast to the formation of metal–alkene complexes from the reactions of transi-

(44) Saalfeld, F. E.; McDowell, M. V. *Inorg. Chem.* **1967**, *6*, 96.

(45) $D°(Ni^+-CH_2) = 86 ± 6$ kcal mol^{-1} from ref 9a.

(46) Meadows, J. H.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 3998. Calvin, M. E.; Grev, R. S.; Schaefer, H. F., III; Bicerano, J. *Chem. Phys. Lett.* **1983**, *99*, 399.

(47) Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* **1983**, *258*, C1–C4.

tion-metal ions with alkanes. This difference in reactivity is attributed to the thermodynamically less demanding process of generating silylene from the silanes compard to carbene formation from the corresponding alkanes. Metal–silylene bond dissociation energies, estimated by examining the reaction thermochemistry associated with metal silylene formation, are stronger for Co^+ and Ni^+ than for the other metal ions. The bonding between transition-metal ions and silylene is described by σ-donation of nonbonding lone-pair electrons from the ground-state silylene to the metal center, and π-back-donation of paired 3d electrons from the metal into the empty 3p orbital of Si is invoked to account for the strengthened $Ni^+–SiH_2$ and $Co^+–SiH_2$ bonds.

Activation of Alkanes by Ruthenium, Rhodium, and Palladium Ions in the Gas Phase: Striking Differences in Reactivity of First- and Second-Row Metal Ions

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Contribution No. 7380 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received March 14, 1986

Abstract: The reactions of Ru^+, Rh^+, and Pd^+ with alkanes are studied in the gas phase by using an ion beam apparatus. The reactivity of the second row group 8–10 metal ions is shown to be dramatically different than that of their first-row congeners. Studies with deuterium labeled alkanes reveal that Ru^+, Rh^+, and Pd^+ all dehydrogenate alkanes by a 1,2-mechanism, in contrast to the 1,4-mechanism of Co^+ and Ni^+ and the combination of 1,2- and 1,4-processes for Fe^+. In most respects, Ru^+ and Rh^+ exhibit similar reactivity quite distinct from that observed for Pd^+. The reactions of Ru^+ and Rh^+ are dominated by the loss of one or more molecules of hydrogen, via mechanisms characterized by C–H bond insertions and β-H transfers. In contrast to the reactions of their first-row congeners, neither β-methyl transfers nor C–C bond insertions occur competitively at Ru^+ and Rh^+ centers. Furthermore, evidence is presented which indicates that the barriers for reductive elimination of H_2 and HR from $Rh–(olefin)^+$ complexes are much smaller than the corresponding barriers for the first row group 8–10 metal ions. These low barriers may result in the formation of internally excited products able to undergo a second exothermic elimination reaction. The differences in reactivity of the first and second row group 8 and 9 metal ions are proposed to be due to differences in the sizes and shapes of the orbitals used for bonding. Although the reactivity of Pd^+ appears in some ways to be quite similar to that of Ni^+, the mechanism by which alkanes are activated by Pd^+ may be quite different than for any of the first-row metal ions. It is proposed that the uniquely high Lewis acidity of Pd^+ results in hydride abstraction as a first step in the mechanism for C–H bond activation, leaving the hydrocarbon fragment with an appreciable amount of carbonium ion character in the reaction intermediate. This mechanism is supported by the fact that Pd^+ dehydrogenates n-butane by a 1,2-elimination across the central C–C bond exclusively. Palladium is the only metal ion studied to date which undergoes this selective elimination.

The determination of the mechanism by which alkanes are activated by transition-metal ions in the gas phase is an intriguing and challenging problem. The reaction mechanisms are necessarily complex, multistep processes. Furthermore, the reactions often result in the formation of many products. Fundamental for understanding the mechanisms of these reactions is a knowledge of the activation parameters for competing processes. What factors control C–C vs. C–H bond insertion? What determines the relative rates for β-hydrogen vs. β-alkyl transfers?

Clues to the puzzle of hydrocarbon activation by transition-metal ions have been obtained by using a variety of complementary techniques. The studies to date include the reactions of the entire first-row transition-metal series and several metal ions in the second-row series.[1–6] Ion beam and ion cyclotron resonance (ICR)

Table I. Homolytic and Heterolytic Bond Dissociation Energies for Group 8–10 Transition-Metal Ions in the Gas Phase

	bond dissociation energy (kcal/mol)					
	Fe	Co	Ni	Ru	Rh	Pd
$M^+–H$	53[a]	48[a]	39[a]	41[b]	42[b]	45[b]
$M^+–CH_3$	68[b]	61[c]	48[c]	54[b]	47[b]	59[b]
$M^+–H^-$	208[d]	218[d]	224[d]	208[d]	214[d]	231[d]

[a] Reference 10. [b] Reference 11. [c] Reference 32. [d] Reference 13.

techniques have been used successfully to identify the products of these reactions and to obtain thermochemical information. In addition, recent studies of product translational energy release distributions have probed the potential energy surfaces for elimination of H_2 and small hydrocarbons from ionic iron, cobalt, and nickel complexes.[7,8] By the use of these complementary tech-

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