Reviews

Organometallic Chemistry in the Flowing Afterglow: A Review

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The flowing afterglow technique, among the various mass spectroscopic methods that have been used to study ions and ion−molecule reactions in the gas phase, has provided a number of interesting results in organometallic chemistry. The flowing afterglow technique is particularly suited for the investigation of thermally relaxed species, since ions and ion−molecule reactions are carried out in a pressure regime where multiple collisions with inert gases occur. Many of these studies are reviewed in this paper, with particular emphasis on anionic organometallic chemistry.

I. Introduction

The flowing afterglow (FA) method was introduced by Ferguson, Fehsenfeld, and Schmeltekopf in 1963 to study atmospheric ion chemistry.[1] From these beginnings have come an outpouring of publications whose subjects range from atomic physics to the ion−molecule chemistry of a wide variety of species, many of which cannot be studied under more conventional reaction conditions. This review focuses on the gas-phase ion−molecule chemistry of organometallics with short diversions into the realm of bare metal and metal−cluster species. Because of the importance of anionic species[2−7] in organometallic chemistry and the relative paucity of anionic mass spectral studies, negative ion work is emphasized in this review, although some aspects of positive ion chemistry will be considered. Major emphases will be placed on the gas-phase (1) reaction chemistry of organometallics in ion−molecule reactions, (2) preparation of unusual species, both ionic and neutral, and (3) thermochemical properties obtained or derived from such ions and neutrals. While the FA technique has been an important source of such information, other gas-phase methods, typically in lower pressure regimes, have been used extensively to obtain complementary information. Such information will not be detailed here, although some references to important, complementary studies will be provided when appropriate.

A flowing afterglow (FA) instrument in its basic form is a flow tube (glass or stainless steel) attached to a mass spectroscopic detector for ion analysis.[8−11] Ions are generated in the flow tube by a variety of means, after which they are differentially pumped to the detector region. Attached to a typical flow tube are various inlets for handling, purifying, and metering gases. Large mechanical pumps maintain the carrier gas flow (helium typically), and an electronics center guides system operation, data collection, and data refinement. A flowing afterglow instrument is represented in Figure 1.[12] The flowing afterglow method has various features that have contributed to its impact in gas-phase studies. Ion−molecule reactions[13] are carried out at pressures near 1 Torr, thus thermalizing ions by multiple collision with the inert carrier gas, whereas in lower pressure regimes such ions might otherwise decompose. A number of modifications of the basic instrument have introduced flexibility in ion preparation and experimental design. As flowing afterglow instrumentation has evolved, new features that provide such versatility have been incorporated; among these modifications are (1) specialized introduction of reactive intermediates, (2) specific ion separation by tandem selected ion flow tube (SIFT) techniques, (3) tandem selected ion flow tube−drift field (SIFT-drift) technology, (4) tandem SIFT−triple-quadrupole technology, and (5) variable-temper-

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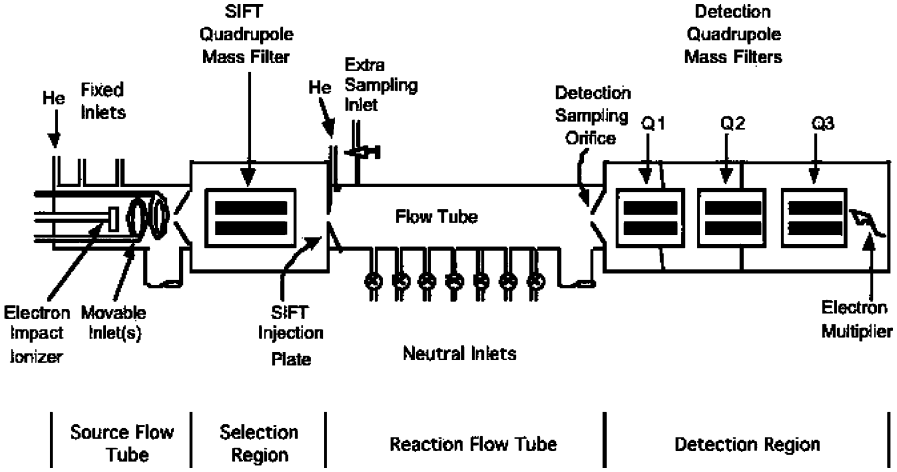

Figure 1. Schematic drawing of triple-quadrupole flowing afterglow instrument.

ature FA. Progressive FA instrumental design changes have been well documented.[8−11,14−18] The operation of a typical FA instrument is briefly described with reference to the tandem SIFT−triple-quadrupole schematic drawing shown in Figure 1. (1) Ions are produced by electron impact in the source flow tube region by introducing various precursors near an electron gun through fixed or moving inlets; such arrangements allow for flexibility in ion production. (2) Ions are then selected by the SIFT quadrupole mass filter in the selection region and injected into the reaction flow tube as they are entrapped in a flow of helium gas at a pressure where collisions cause the ions to be collisionally stabilized (thermalized). In this so-called second flow tube, a variety of neutral inlets allow complicated ion−molecule reactions to be carried out. (3) Ions then enter the triple-quadrupole detection region, in which not only simple *m*/*z* identity can be made but also experiments such as energy-resolved collision-induced dissociation (CID) (vide infra) can be accomplished.[17,19]

The first application of FA to metallic chemistry was a study by Ferguson and Fehsenfeld in 1968 of the atmospheric metal ion chemistry of Fe^+, Mg^+, Ca^+, Na^+, and K^+ with ozone and dioxygen.[20−22] No further metal-related FA investigations were undertaken until the late 1970s, when Bohme and co-workers studied the S_N2 reactions of silane and methane with a variety of anions.[23] DePuy, Bierbaum, and co-workers reported the reactions of organosilanes with various anions in 1980.[24] Their discovery that fluoride ion and certain organosilanes yield gas-phase carbanions has led to the preparation of a number of interesting gas-phase carbanions (vide infra).[24−30] The presumed intermediacy of pentacoordinate silicon anions (siliconates hereafter) in such reactions stimulated a number of exploratory studies. These and the large number of other FA studies of metal-containing species are the basis of this review.

A. Thermochemical Properties. Flowing afterglow techniques have been used in measuring a variety of thermochemical properties of neutral species, among them (1) electron affinities (EA), (2) acidities (typically ΔH_{acid}), and (3) bond dissociation energies (BDE). Central to these studies are various thermochemical cycles that link known and unknown thermochemical properties.[31,32] One often used cycle links the acidity of an acid R−H (eq 1) with the bond dissociation energy

$$\text{R-H} \rightarrow \text{R} + \text{H} \quad \text{BDE} \tag{1a}$$

$$\text{R} + e^- \rightarrow \text{R}^- \quad -\text{EA} \tag{1b}$$

$$\text{H} \rightarrow \text{H}^+ + e^- \quad \text{IE} \tag{1c}$$

$$\text{R}-\text{H} \rightarrow \text{R}^- + \text{H}^+ \quad \Delta H_{\text{acid}} = \text{BDE} - \text{EA} + \text{IP} \tag{1}$$

(BDE) of R−H (eq 1a),[33,34] the electron affinity (EA)[35]

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of R (eq 1b), and the ionization energy (IE) of H (eq 1c). Other thermochemical properties of both neutrals and anions (e.g. heats of formation and anion affinities) also are accessible in negative ion gas-phase experiments under favorable circumstances and will be discussed in context.[36] In many recent studies, such cycles are completed by using thermochemical data that are obtained in high-level computational studies. It is important to emphasize that the interplay between experiment and computation has not only benefited our understanding of gas-phase studies when thermochemical data are scarce or structural information is limited but also brought a greater appreciation of the scope and power of modern computational methods.

B. Non-Organometallics: Metal-Containing Species and Clusters. Flowing afterglow techniques coupled with various ionization methods that produce metal cations have allowed the study of the population of the excited states of various metal cations. Rare-gas ions and metastable rare-gas ions react (by different processes) with both metals and metal salts to give a variety of metal cations in a variety of electronic states.[37−40] These studies mainly have been undertaken to probe the lasing properties of metals such as Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Ti, and Cu.

In studies spearheaded by Lineberger and co-workers, numerous homonuclear diatomic and triatomic anions as well as mixed cluster anions have been generated by FA techniques. Electron detachment measurements (eq 2) using either threshold or photoelectron spectroscopy techniques have led to a dramatic increase in the number of accurately known EAs of the corresponding neutral element clusters.[35,41] Among these are Cr_2, Re_2, Fe_2, Co_2, Ni_2, Pd_2, Pt_2, Ni_3, Pd_3, Pt_3, Cu_n ($n = 1-10$), NiCu, NiAg, $NiAg_2$, and Ni_2Ag as well as the salts LiCl, NaF, NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, and CsCl.[42−51] That FA conditions produce thermalized (collisionally relaxed) ions has contributed immensely to these studies. Studies in which the reactivities of metal clusters such as Nb_n^- ($n = 2-7$) have been reported as well.[52]

$$R^- + h\nu \rightarrow R + e^- \qquad (2)$$

Although a few studies of the reaction chemistry of transition-metal cations with hydrocarbons have been carried out using FA techniques,[53−55] the most important work in this area is that of Armentrout and coworkers using other experimental techniques. These studies recently have been reviewed.[56,57]

FA studies of uranium-containing species that were initiated by Streit and Newton in 1980 by reacting UF_6 and various anions (F^-, Cl^-, Br^-, I^-, and SF_6^-) all give the electron-transfer product UF_6^-.[58] The relative electron-transfer rate constants for F^-, Cl^-, Br^-, I^-, and SF_6^- are 1.9, 1.6, 1.4, 1.1, and 1.0. The authors suggest that long-range electron transfer is less likely to UF_6 than to the rare-gas ions previously studied by Su and Bowers.[59,60] An EA of about 5 eV for UF_6 is consistent with this work. Later studies of UF_6 explore other anion reactions with O^- and O_2^- in which the first gas-phase examples of uranium bonded to a heteroatom other than fluorine are reported, namely UOF_5^- and UOF_4^-.[61] In addition, several reactions with positive ions mainly lead to fragmentation products, UF_n^+ with $n = 1-6$. Among the more interesting products is a cluster cation, $(UF_5-Kr)^+$, formed by reaction with Kr^+. More complex uranium clusters, $U_2F_n^+$, where $n = 9-11$, are also reported in the ion−molecule reactions of UF_n^+ ($n = 3-5$) and UF_6. Uranium tetraborohydrate ($U(BH_4)_4$) undergoes several interesting transformations in the FA.[62] Fragmentation occurs by charge transfer from He^+ and N_2^+, the more energetic He^+ causing greater "damage". Many interesting uranium-containing cations result: for He^+, $U(B_nH_m)^+$ cations with m values from 2 to 6 are observed for $n = 1$, cations with m values of 2−4, 7, and 8 are observed for $n = 2$, and cations with m values of 11−13 are observed for $n = 3$. Somewhat similar results are reported with N_2^+ fragmentation, although here only $n = 4$ and $m = 14$, 15 ions are observed. Many ions result from the expulsion of BH_3 and H_2. Not only F^- and Cl^- but also SF_6^- gave the adducts $[U(BH_4)_4X]^-$. A very rough fluoride affinity for $U(BH_4)_4$ was reported (Table 1). Uranocene ($U(\eta^8\text{-}C_8H_8)_2$) also undergoes fragmentation in the FA by He^+ to give $U(C_8H_8)^+$ and $U(C_6H_6)^+$ predominantly and by

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Table 1. Experimental Anion Affinities

compd	anion	affinity (kcal/mol)
$U(BH_4)_4$	F^-	$\sim$37−53[62]
$CH_3CHO \rightarrow BF_3$	H^-	$\sim$106[69]
CH_3CHO	H^-	$\sim$40[185]
BH_3	H^-	$\sim$74[70]
$(CH_3CH_2)_3B$	H^-	$\sim$69[70]
B_2H_6	H^-	$\sim$74[70]
BH_2CN	H^-	$\sim$96[70]
$(CH_3CH_2)_3Al$	H^-	$\geq$85
SiO	H^-	$\sim$49[143]
CO	H^-	$\sim$8[185]
$Cr(CO)_6$	H^-	$\sim$44[185]
$Mo(CO)_6$	H^-	$\sim$44[185]
$W(CO)_6$	H^-	$\sim$44[185]
$Fe(CO)_4$	I^-	$\sim$39[181]
$Fe(CO)_4$	Br^-	$\sim$47[181]
$Fe(CO)_4$	Cl^-	$\sim$54[181]
$Fe(CO)_5$[a]	H^-	$\sim$56[2,185]
$Fe(CO)_5$	HO^-	$\leq$61[2,157]
		$\geq$53[2,157]
$Fe(CO)_5$	CH_3O^-	$\leq$51[2,157]
		$\geq$39[2,157]
$Fe(CO)_5$	F^-	$\sim$41[2,157]
$Fe(CO)_5$	Cl^-	$\sim$14[2,157]
$Fe(CO)_5$	$CH_3CO_2^-$	$\leq$30[2,157]

[a] A large number of other anion affinities of $Fe(CO)_5$ have been reported; see ref 181 for a compilation.

less energetic N^+/N_2^+ to give $U(C_8H_8)_2^+$ and $U(C_8H_8)^+$.[63] Thermal electron capture is observed, giving $U(C_8H_8)_2^-$, but there is no electron transfer to uranocene with an assortment of anions including O^-, O_2^-, and SF_6^-, each of which has an EA value $\leq$1.5 eV.

II. Organometallics: Group 13 Ion−Molecule Chemistry

A few FA studies of group 13 species have been reported that mainly concern the Lewis acid−base properties of boron complexes, the chemistry of boron hydride species, and the reactivity of dimethylaluminum oxide.

A. Boron Anions. α-C−H acidity is enhanced greatly over the uncomplexed species in borane−Lewis acid complexes such as $BH_3 \leftarrow SMe_2$, $BH_3 \leftarrow NMe_3$, $BH_3 \leftarrow PMe_3$, and $BH_3 \leftarrow PEt_3$.[64,65] For example, the C−H acidity of $BH_3 \leftarrow SMe_2$ can be determined in bracketing experiments of $BH_3 \leftarrow S(CH_3)CH_2^-$ with reference acids.[66] (Typical bracketing experiments[67] are carried out by assessing the nonreaction or reaction of a ionic species with a set of reference compounds. In the case of acidity studies such as those discussed here, the reactivity of an anion with reference acids is studied. Most simply, the gas-phase acidity is assigned a value between that of an acid that reacts and the next laddered one that does not. Having a series of reference acids whose acidities are closely spaced leads to the best estimate of gas-phase acidity. Such a measure of gas-phase acidities is kinetic, not thermodynamic, in nature.)

Determination of the structure of the conjugate base, which could be either $BH_3 \leftarrow S(CH_3)CH_2^-$ or $CH_3SCH_2BH_3^-$, is based on both collision-induced dissociation (CID) and H/D exchange experiments. In the latter, reactions with D_2O and CH_3OD give a maximum of five H/D exchanges, which is consistent with the $BH_3 \leftarrow S(CH_3)CH_2^-$ formulation. This H/D exchange demonstrates that all the acidic H atoms are exchanged in a process that, while endothermic, is energetically driven by the complexation energy between the anion and D_2O.[4] Authentic $CH_3SCH_2BH_3^-$, prepared from $CH_3SCH_2^-$ and diborane, did not undergo H/D exchange. A further structural confirmation results from addition and substitution reactions of $BH_3 \leftarrow S(CH_3)CH_2^-$ with CO_2, BEt_3, and CS_2. Authentic $CH_3SCH_2BH_3^-$ is inert to these reagents, but $BH_3 \leftarrow S(CH_3)CH_2^-$ is not. The gas-phase acidity, ΔH_{acid}, of $BH_3 \leftarrow SMe_2$ is determined to be $\sim$373 kcal/mol, showing that $BH_3 \leftarrow SMe_2$ is a stronger C−H acid than SMe_2 by $\sim$20 kcal/mol (corresponding to $\sim 10^{15}$ in terms of its acid dissociation constant). High-level G2(MP2) acidity computations give a closely similar result. Both $BH_3 \leftarrow NMe_3$ and $BH_3 \leftarrow PMe_3$ give analogous results, as their C−H acidities ($\Delta H_{acid} = 393$ and 374 kcal/mol) are enhanced markedly over NMe_3 and PMe_3 ($\Delta H_{acid} = >404$ and 391 kcal/mol). The acidity measurement of $BH_3 \leftarrow NMe_3$ is made possible in the FA because $BH_3 \leftarrow N(CH_3)_2CH_2^-$ is stable while $(CH_3)_2NCH_2^-$ is not. Thus, the "solvent" BH_3 is stabilizing the carbanionic structure when the corresponding unsolvated carbanion ($(CH_3)_2NCH_2^-$) is unstable with respect to electron loss (the EA of $(CH_3)_2NCH_2$ is <0). Solvent-stabilized gas-phase anionic species are common.[68] Analysis of the ΔH_{acid}/EA/BDE/IE thermochemical cycle (see section IA) for $BH_3 \leftarrow SMe_2$ reveals that the enhancement of its acidity over that of Me_2S is overwhelmingly the result of differences in the EA values of the corresponding radicals. Thus, the EAs of the $BH_3 \leftarrow S(CH_3)CH_2$ and $S(CH_3)CH_2$ radicals indicate that $BH_3 \leftarrow S(CH_3)CH_2^-$ is 18 kcal/mol more stable than $CH_3SCH_2^-$. In addition to the Lewis base coordination effect, other reactivity enhancements of the borane complexes are reported, with one example being the elimination reaction of $BH_3 \leftarrow PEt_3$ to give $(CH_3CH_2)_2PBH_3^-$. Because complexes of $(CH_3)_2S$ and BF_3 are considerably weaker (S−B bond energies of 5−10 kcal/mol) than those with BH_3, measuring the ΔH_{acid} value of $BF_3 \leftarrow SMe_2$ was difficult and could only be roughly estimated as $\Delta H_{acid} = 371$ kcal/mol. Computational studies accompanying these experiments convincingly demonstrate why the less stable $BH_3 \leftarrow S(CH_3)CH_2^-$, which is formed experimentally, cannot convert to the more stable isomers $CH_3SCH_2BH_3^-$ and $CH_3CH_2SBH_3^-$, since computed barrier heights are $\geq\sim$28 kcal/mol.[65]

Surprisingly, BF_3 complexes with carbonyl compounds are C−H superacidic.[69] Using a combination of experimental measurements and computations, the critical thermochemical parameters that give the acidity of the acetaldehyde$\rightarrow BF_3$ complex ($\Delta H_{acid} = \sim 316$ kcal/mol) have been determined. Direct estimates at various computational levels are virtually identical with experiment for $CH_3CHO \rightarrow BF_3$; other acidity calculations for

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$CH_3C(O)CH_3{\rightarrow}BF_3$ and $CH_3C(O)CF_3{\rightarrow}BF_3$ show that each is superacidic, in range of the strongest acids known. An estimate of the pK_a value of an aqueous solution of $CH_3CHO{\rightarrow}BF_3$ is -7, near that of HBr. Another consequence of the carbonyl→BF_3 complexation is the extremely high gas-phase hydride affinity of $CH_3CHO{\rightarrow}BF_3$, which is ~106 kcal/mol. This apparently is the highest hydride affinity known, greater by far than that of uncomplexed aldehydes and ketones, whose hydride affinities range from 38 to 45 kcal/mol. A number of anion affinities are compiled in Table 1. Related to this is another study of hydride binding in various boranes, in which the hydride affinities of BH_3, Et_3B, B_2H_6, and BH_2CN are determined to be ~74, 69, 74, and 96 kcal/mol.[70] Such experiments typically are carried out by measuring the threshold collision energy for transfer of H^- to a suitable acceptor whose hydride affinity is well established (from BH_4^- to CO_2, for example). When the threshold energy and established hydride affinity are combined, the unknown hydride affinity can be determined. The very large hydride affinity of BH_2CN is consistent with the lowered reducing power of BH_3CN^-.

A host of boron hydride anions can be produced in the FA by adding B_2H_6 just downstream of H_2N^-.[71] Many of these anions have been prepared previously in ion cyclotron experiments, but a few, such as $B_2H_3^-$, were not known previously. Individual anions can be separated from this complex mixture by selected-ion flow tube (SIFT) techniques; in this way, $B_2H_3^-$, which is interesting because of its relationship to its conjugate acid B_2H_4, could be studied in detail. The anion is quite unreactive, despite its electron deficiency. The gas-phase acidity of B_2H_4 was determined to be 375 kcal/mol, but the anion did not undergo H/D exchange with a variety of deuterated reagents. It reacts with CXY reagents ($X = Y = O$, S and $X = O$, $Y = S$) to give both $B_2H_3X^-$ and $B_2H_3Y^-$. Computational studies of $B_2H_3^-$ $B_3H_2^-$, and $B_3H_4^-$ give a number of interesting structures. The lower energy ones in each case were cyclic and maximize hydrogen bridging of the B−B bond. Positive ion studies in the FA also have been reported.[72,73] In these, BH_2^+ as well as the remarkable ion BH_6^+ are detailed experimentally and computationally. The BH_6^+ deserves some comment, because it is the conjugate acid of BH_5, which is a weakly bound complex of BH_3 and dihydrogen.[74] Its relationship to isoelectronic CH_6^{2+} also is of interest. The BH_6^+ ion is very stable in the FA. Given the pressure regime of the FA, any species detected would have to be bound by at least 8−10 kcal/mol; such a species in solvent would undoubtedly be dissociated by dihydrogen loss. Computational studies suggest that BH_6^+ is bound by a good deal more than 10 kcal/mol. The lowest energy structure obtained computationally is best thought of as a BH_2^+ bound to two dihydrogen molecules.

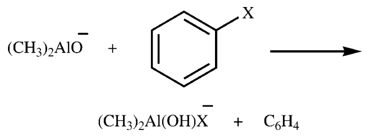
B. Aluminum Anions. The trimethylaluminum dimer is a rich source of aluminum anions in the FA, as shown in eq 3.[75−77] Dimethylaluminum oxide, $(CH_3)_2AlO^-$, the dimethylaluminum carbanion, $(CH_3)_2AlCH_2^-$, and a variety of aluminates, $(CH_3)_3AlX^-$, have been prepared in the first flow tube in various FA-SIFT experiments. Other simple aluminum oxides, CH_3AlO^- and AlO^-, can also be prepared by CID. The chemistry represented in eq 3 is explained by hydroxide addition to the aluminum atom of the dimer, followed by loss of trimethylaluminum and formation of the intermediate $(CH_3)_3AlOH^-$. This aluminate (1) can be cooled by collisional stabilization (eq 3a) and (2) undergoes methide cleavage and proton abstraction from the pendant OH (eq 3b) in a process suggested to be analogous to the reaction of hydroxide and tetramethylsilane, which will be considered shortly. The final product (eq 3c) may be formed either in a separate proton abstraction process or from the intermediate $(CH_3)_3AlOH^-$.

$$[(CH_3)_3Al]_2 + HO^- \xrightarrow{5\%} (CH_3)_3AlOH^- + Al(CH_3)_3 \quad (3a)$$

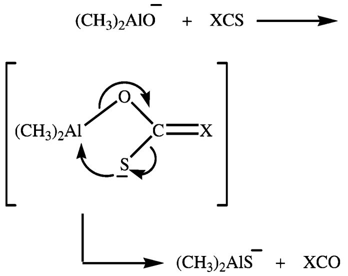
$$\xrightarrow{80\%} (CH_3)_2AlO^- + CH_4 + Al(CH_3)_3 \quad (3b)$$

$$\xrightarrow{15\%} (CH_3)_2AlCH_2^- + H_2O + Al(CH_3)_3 \quad (3c)$$

Dimethylaluminum oxide, $(CH_3)_2AlO^-$, has a rich chemistry, particularly with halogen-containing and other related neutrals. An interesting and representative example is shown in eq 4 (for X = F, Cl, methoxy).[75,76] Such β-elimination reactions have been considered as concerted processes that proceed through a complex in which a proton is abstracted by anionic oxygen as X adds to aluminum. In the cases illustrated, the neutral product is benzyne. Carboxylic acids react with $(CH_3)_2AlO^-$ not only by this pathway but also in other ways (CH_3CO_2H gives $CH_2{=}C{=}O$, but also $CH_3CO_2^-$ and $(CH_3)_2Al(OH)OC(O)CH_3^-$). $(CH_3)_2AlO^-$ reacts with XCS (X = O, S), as illustrated in eq 5.



(4)



(5)

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Table 2. Computational Anion Affinities of Aluminum-Containing Species

X^-	X^-affinity of $(CH_3)_3Al$ (kcal/mol)	Cl^-affinity of $(CH_3)_2AlX$ (kcal/mol)	CH_3^- affinity of $(CH_3)_2AlX$ (kcal/mol)
H	70[77] (exptl ~85)[a,81]	50[77]	81[77]
CH_3	80[77]	50[77]	80[77]
NH_2	84[77]	43[77]	73[77]
OH	84[77]	49[77]	79[77]
F	82[77]	55[77]	86[77]
SiH_3	50[77]	58[77]	91[77]
PH_2	53[77]	56[77]	89[77]
SH	53[77]	54[77]	88[77]
Cl	50[77]	59[77]	93[77]

[a] exptl denotes the experimental value.

A question that previously has not been addressed directly is how unknown anions can be characterized in ion−molecule reactions in mass spectral studies when the only datum on a product ion is its mass-to-charge ratio (m/z). Among the tools that gas-phase chemists use are (1) chemical intuition based on the m/z value and analogous chemical precedents, (2) reactivity studies with standard neutral reactants, (3) collision-induced dissociation (CID) experiments, and (4) computational studies. Emphasis is given here to (1) and (2), where the reactions of two standard reactants, OCS and CS_2, with $(CH_3)_2AlO^-$ give an m/z value that is well accommodated by the mechanism shown leading to $(CH_3)_2AlS^-$ (eq 5). Other examples of these characterization tools will be presented throughout this review.

Four-coordinate aluminates are readily prepared (eq 6) and react with a variety of acids, both organic and mineral.[77] These lead to the formation of HY or methane

$$[(CH_3)_3Al]_2 + Y^- \rightarrow (CH_3)_3AlY^- + Al(CH_3)_3 \quad (6)$$

by dissociative (eqs 7a and 7b) and associative processes (eqs 7c and 7d). Attempts to use this reaction to estimate

$$(CH_3)_2AlY^- + HA \rightarrow (CH_3)_3Al + A^- + HY \quad (7a)$$

$$\rightarrow (CH_3)_2AlY + A^- + CH_4 \quad (7b)$$

$$\rightarrow (CH_3)_3AlA^- + HY \quad (7c)$$

$$\rightarrow (CH_3)_2AlY(A)^- + CH_4 \quad (7d)$$

the Y^- affinities of trimethylaluminum (by analogy with studies of Hajdasz and Squires on the hydride affinity of silanes)[78,79] failed, largely because of the complexity of the reactions. High-level MP2/6-31++G(d,p)//6-31G(d) computations provide (1) X^- affinities for $(CH_3)_3Al$, (2) the Cl^- affinity for $(CH_3)_2AlX$, and (3) the CH_3^- affinity for $(CH_3)_2AlX$, with X = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl (see Table 2).[77] Although these affinities range between 43 and 93 kcal/mol, the higher ones generally are for the CH_3^- affinity of $(CH_3)_2AlX$ (73−93 kcal/mol) and the lower ones are for the Cl^- affinities of $(CH_3)_2AlX$ (43−59 kcal/mol). The X^- affinities of $(CH_3)_3Al$ range more widely (50−84 kcal/mol) and exhibit trends similar to the X^- affinities of silanes in that the anion affinities for second-row elements (CH_3, NH_2, etc.) are greater than for third-row elements (SiH_3, PH_2, etc.) (Table 3). At comparable levels of theory, the H^-, CH_3^-, and F^- affinities are 18, 32, and 29 kcal/mol for CH_3SiH_3 and 70, 80, and 83 kcal/mol for $(CH_3)_3Al$. In each case, the anion affinities with third-row anions such as SiH_3^-, PH_2^-, HS^-, and Cl^- are considerably smaller.[80] That the X^- bonding to aluminum is stronger than to silicon is likely the consequence of the more electropositive character of aluminum and the electron deficiency of $(CH_3)_3Al$. These computations also have provided some rationalization for the complex reactivity shown in eq 7.[77] Experimental measurements by Nibbering and co-workers set the lower limit for the hydride affinity of trimethylaluminum at 85 kcal/mol (Table 1).[81]

Table 3. Computational Anion Affinities[a] of Simple Silicon-Containing Species[99]

X^-	X^- affinity of SiH_4 (kcal/mol)	X^- affinity of CH_3SiH_3 (kcal/mol)
H	23.3[b] (16.7)[c]	17.8 (18.2)
CH_3	31.0 (54.1)	24.9 (32.4)
NH_2	29.8	23.0
OH	30.9 (29.9)	23.4
F	23.8 (29.1)	15.4 (29.0)
SiH_3	−3.4 (−0.2)	−6.9
PH_2	18.8	15.1
SH	16.8 (4.0)	12.9
Cl	12.3 (4.5)	8.5

[a] Ab initio values are given in parentheses. [b] MNDO computations were carried out in the MOPAC suite of programs with revised silicon parameters. [c] Optimizations of molecular structures were carried out using restricted Hartree−Fock (RHF) SCF computations with a 6-31G(d) basis followed by single-point RHF/6-31++G(d,p) computations for the ab initio studies.

III. Organometallics: Group 14 Ion−Molecule Chemistry

Because of the importance of organosilicon chemistry in its synthetic, structural, and mechanistic aspects,[82−84] a great deal of attention has been given to understanding organosilicon species in the gas phase.[36,85−88] Reactions between various anions and neutral silanes can be generalized in terms which, although simplified, form the basis of most of the following discussion of silicon negative ions (Scheme 1). Path a illustrates the formation of stable siliconates. Although a large number of silicon reactions involve nucleophilic substitution, which path b exemplifies, those cases that lead to stable carbanions have had a more important impact on gas-phase chemistry and only these will be considered in

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detail. Paths c (alkyl, aryl, and vinyl cleavage from silicon) and d (proton abstraction from a C−H group bonded to silicon) come into play under conditions when paths a and b are less likely. Other important aspects of negative ion silicon chemistry, namely the chemistry of silyl anions, hypocoordinate silicon anions, and multiply bonded silicon anions that are not accommodated by Scheme 1 will be considered as well. Several reviews of organosilicon chemistry provide important background.[82−84,89−95]

Scheme 1

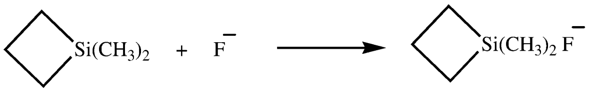
$$\begin{aligned} R_3SiA + Y^- &\xrightarrow{a} R_3Si(A)(Y)^- \\ &\xrightarrow{b} R_3SiY + A^- \\ &\xrightarrow{c} R_2SiAY + R^- \\ &\xrightarrow{d} (R-H)R_2SiA^- + HY \end{aligned}$$

A. Path a to Stable Siliconates. Pentacoordinate silicon has a storied past in both condensed- and gas-phase studies.[82−84,91,92,96] Generally, siliconates are considered as unstable intermediates in the gas-phase reactions of neutral four-coordinate silanes and nucleophiles; such intermediates can lead to important negative ion chemistry that will be discussed later. An early FA study of nucleophilic substitution at silicon compares the reactivity of trimethylchlorosilane and methyl iodide, showing that their behaviors with nucleophiles of widely varying basicities are strikingly different in substitution reactions.[97] Such dramatically divergent results show that different displacement mechanisms are at play and indicate that the trimethylchlorosilane reactions take place through an unstable pentacoordinate intermediate.

Stable siliconates are rarer in the gas phase, although many studies have been reported in solution.[82,92,98] Although first obtained in ion−molecule studies as early as 1970, they were not studied in detail until the early 1980s.[36] The direct method of preparing stable siliconates consists of adding negative ions to four-coordinate silanes (eq 8). Detailed experimental and computational studies of such addition reactions indicate that successful reaction in the gas phase generally occurs under conditions where (1) the four-coordinate silane lacks a good leaving group, (2) the energy of bonding between the anion and neutral can be dissipated by collisional stabilization, and (3) the anion neither abstracts a proton from the silane nor cleaves a C−Si bond (eq 8a).[36,99−101]

$$(CH_3)_3SiX + Y^- \longrightarrow (CH_3)_3SiXY^- \qquad (8a)$$

$$RSiH_3 + H^- \longrightarrow RSiH_4^- \qquad (8b)$$



(8c)

Even though (3) above might suggest it impossible, Squires and co-workers[78,79] have shown that very basic hydride adds to alkylsilanes with great specificity (eq 8b), not unlike condensed-phase studies yielding hydridosiliconates.[96] Conditions for efficient fluoride addition to silacyclobutanes have been reported, even though silacyclobutanes are sensitive to ring-opening reactions (eq 8c).[17] Deuterium labeling experiments coupled with CID analysis demonstrates that in some cases (addition of methoxide to methoxytrimethylsilane, for example) small amounts of products that are likely to be weak (ion−dipole) complexes form as well as the corresponding siliconate.[102] There have been a large number of condensed-phase studies of the properties and reactivity of siliconates.[96,103]

Sometimes direct addition fails and other means such as the “soft-transfer” method, in which the exothermicity of reaction is less, can be used to prepare siliconates.[17,78,79,99,104] Although the parent siliconate, SiH_5^-, is unstable with respect to loss of dihydrogen, it has a fairly high barrier to such loss. It has not been made by direct addition, yet it has been prepared by Squires and co-workers by soft transfer (eq 9).[78,79] Hydroxysiliconates have been difficult to synthesize in reasonable concentrations until recently, when Krouse and Wenthold reported that solvated HO^- can be added directly to phenyltrifluorosilane (eq 10).[105] Solvated HO^- reacts as shown in contrast to HO^- itself, which gives $C_6H_5SiF_2O^-$ and HF.

$$RSiH_4^- + SiH_4 \rightarrow SiH_5^- + RSiH_3 \qquad (9)$$

$$C_6H_5SiF_3 + HO(H_2O)_n^- \rightarrow C_6H_5Si(OH)F_3^- \qquad (10)$$

Squires and co-workers have shown in elegant experiments that protonolysis of siliconates can be used to determine silane hydride affinities, which cannot be

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Table 4. Experimental Anion Affinities of Silicon-Containing Species

compd	anion	affinity (kcal/mol)
$C_6H_5SiF_3$	H^-	$\sim 64^{105}$
$C_6H_5SiF_3$	F^-	$\sim 79^{105}$
$C_6H_5SiF_3$	CH_3O^-	$\sim 77^{105}$
dimethylsilacyclobutane ($(CH_2)_3Si(CH_3)_2$)	F^-	$\sim 40^{17}$

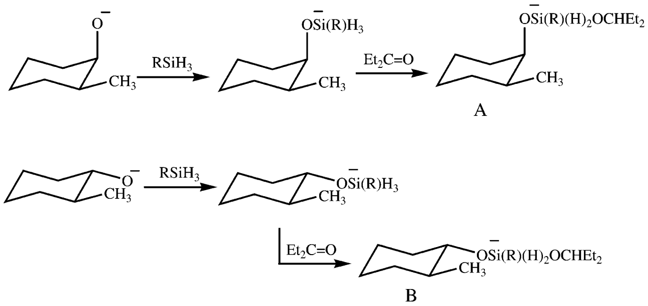
measured directly (eq 11).[79] The utility of this reaction

$$RSiH_4^- + HB \rightarrow RSiH_3 + B^- + H_2 \qquad (11)$$

depends on having (1) a low reaction barrier and (2) a variety of reference acids whose gas-phase acidities are accurately known in the range where reaction occurs (bracketing). Both conditions are met for the siliconates studied, although not for the aluminates discussed earlier. The hydride affinities of SiH_4 and alkylsilanes ($RSiH_3$) obtained using this method are all about 20 kcal/mol, which is consistent with independent computational studies.[79] In a combination of experimental and computational approaches, the fluoride affinity of phenyltrifluorosilane has recently been reported as ~79 kcal/mol.[105] This value is very large, greater than that of SiF_4, and, as the authors suggest, reflects a significant phenyl substitution effect (Table 4). Both the hydride and methoxide affinities of phenyltrifluorosilane also are much larger than for other silanes. Additional silane anion affinities that were determined by non-FA methods have been reported.[36,106,107] A collection of anion affinities of silanes is presented in Tables 3 and 4.

Hydridosiliconates add to a number of neutral molecules readily in the gas phase (CO_2, OCS, CS_2, $Cr(CO)_6$, triethylborane, and aliphatic aldehydes and ketones)[79] as well as in solution.[103] Extensive use of CID methods has allowed Ho and Squires to analyze both the diastereoselectivity of various carbonyl hydride additions and the regioselectivity of 1,2- versus 1,4-addition to α,β-unsaturated carbonyl compounds.[108,109] It turns out that CID of the alkyl-substituted dialkoxysiliconates, $[RSi(H)_2(OR)(OR')]^-$, yields both RO^- and $R'O^-$, but in amounts that vary with the structural characteristics of R and R′. The RO^- to $R'O^-$ ratio can be used to evaluate diastereoselectivity in carbonyl reduction by hydridosiliconates. Thus, *tert*-butylcyclohexanone, 2-methylcyclohexanone, and 3,3,5-trimethylcyclohexanone were examined, as is illustrated for 2-methylcyclohexanone in Scheme 2. The independently prepared cis and trans alkoxides in Scheme 2 yield A and B, which each can undergo CID to provide the $C_7H_{13}O^-$ to $C_5H_{11}O^-$ ratio. Reduction of 3-pentanone was shown to yield the most sensitive siliconates for subsequent CID measurements (R is *n*-hexyl throughout). Collisional dissociation of A gave a ratio of ~3.2, while the ratio for the trans isomer B was ~1.4, indicating that the large $C_7H_{13}O^-$ is more readily lost in A and B (the control experiment). Application of this knowledge to the hydride reduction of an “unknown” was accomplished by preparing and mass selecting $RSi(H)_3OCHEt_2^-$ and then reducing 2-methylcyclohexanone. CID of the resulting siliconate, $[RSi(H)_2(OCHEt_2)(C_7H_{13}O)^-]$, followed by data analysis based on the control experimental CIDs demonstrates that hydride reduction occurs ~68% in the axial position. Approximately 99 and 9% axial reductions are reported for *tert*-butylcyclohexanone and 3,3,5-trimethylcyclohexanone. The last result is easily explained, because approach of the bulky siliconate on the axial side of the carbonyl group is blocked by the “axial” 3-methyl substituent. These gas-phase results are consistent with solution experiments of $LiAlH_4$ and $NaBH_4$ reductions, indicating that solvent effects in such reductions are not of great consequence. Applications of similar techniques demonstrate that 1,4-hydride addition predominates in reactions of hydridosiliconates and acrolein (70% 1,4), methyl vinyl ketone (72% 1,4), and cyclohex-2-one (100% 1,4).[109] In solution, Corriu and co-workers have shown that hydridosiliconates are active as reducing agents.[82]

Scheme 2

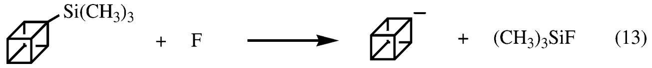


B. Path b to Stable Carbanions from Siliconates. Silanes undergo a very important reaction with fluoride that can lead to stable carbanions.[24,25] The first application of this reaction led to the specific syntheses of the $C_3H_3^-$ insomers, which cannot be prepared individually by deprotonation of propyne (eq 12). The isomeric $C_3H_3^-$

$$CH_3C{\equiv}CSi(CH_3)_3 + F^- \rightarrow CH_3C{\equiv}C^- + (CH_3)_3SiF \qquad (12a)$$

$$HC{\equiv}CCH_2Si(CH_3)_3 + F^- \rightarrow HC{\equiv}CCH_2^- + (CH_3)_3SiF \qquad (12b)$$

species were distinguished by their differential reactivity with dioxygen. This fluorodesilylation reaction has been beautifully applied, particularly by Kass and coworkers, in preparing and studying a number of otherwise difficult to obtain species such as acetyl,[30] cubyl[26] (eq 13), dodecahedryl,[27] thiomethyl,[15] *cis*- and *trans*-β-formylcyclopropanyl,[110] and (*E*)- and (*Z*)-vinyl[111]anions as well as the benzocyclobutadiene radical anion.[28] These anions have provided important gas-phase data on such unusual species (acidities, other thermochemi-



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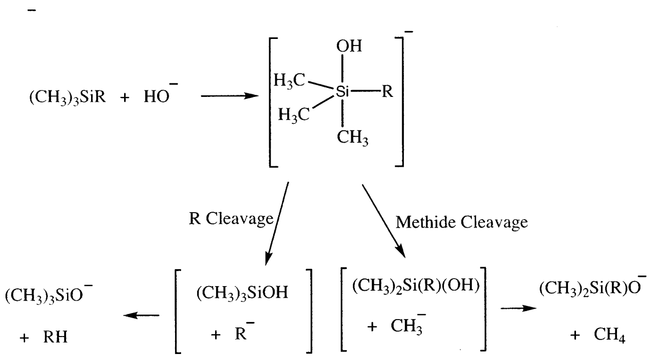
(108) Ho, Y.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 10961−10963.

(109) Ho, Y.; Squires, R. R. *Org. Mass Spectrom.* **1993**, *28*, 1658−1664.

(110) Baschky, M. C.; Peterson, K. C.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 7218−7224.

(111) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 4357−4359.

Scheme 3



cal data, configurational stability, etc.). Less stable, but no less important, are alkyl carbanions that have been observed by Graul and Squires in CID experiments of alkylcarboxylates in the FA.[112−114] These experiments have particular relevance to the alkyl cleavage work described in the next section, since carbanions with small EAs have been observed (e.g. neopentyl) in the CID studies.

C. Paths c and d to Alkyl Cleavage and Proton Abstraction. Intermediate siliconates react by other pathways that depend differently on the nature of the silane and the added anion. In many cases, strongly basic anions (such as hydroxide or amide) react with simple alkylsilanes, giving Si−alkyl cleavage followed by proton abstraction from the added, hydrogen-bearing anion (eq 14) (path c).[24,115,116] Here, the intermediate

$$(CH_3)_4Si + HO^- \rightarrow (CH_3)_3SiO^- + CH_4 \qquad (14)$$

siliconate that forms as shown in Scheme 3 undergoes methide cleavage and subsequent removal[117] of the H−O hydrogen to give methane and $(CH_3)_3SiO^-$ and/or R^- cleavage if $R \neq CH_3$.[118−120] This reaction has been used to prepare many structurally varied siloxides whose gas-phase acidities have been reported.[121] Other bases such as amide react by both cleavage (eq 15a) and direct proton abstraction (eq 15b) (paths c and d in Scheme 1) channels. Whereas hydroxide and amide

$$(CH_3)_4Si + H_2N^- \rightarrow (CH_3)_3SiNH^- + CH_4 \qquad (15a)$$

$$\rightarrow (CH_3)_3SiCH_2^- + NH_3 \qquad (15b)$$

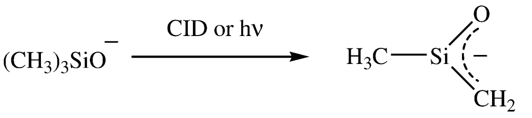
generally react these ways, less basic F^- is more versatile. Not only is the expected carbanion formation exhibited (section IIIB) in reactions of silanes with good leaving groups but also siliconate formation and anion cleavage reactions can occur (phenyltrimethylsilane reacts with fluoride to give a siliconate (65%), phenide (20%), and benzene cleavage (15%)).[24] When basic anions have no abstractable hydrogen atom (e.g. CH_3O^- versus HO^-), yet another pathway can be taken (eq 16a) in non-FA experiments in which methide cleaves from the intermediate siliconate but reacts at the OCD_3 carbon before leaving the collision complex.[122,123]

$$(CH_3)_4Si + CD_3O^- \rightarrow (CH_3)_3SiO^- + CD_3CH_3 \qquad (16a)$$

$$\rightarrow (CH_3)_2Si(OCD_3)CH_2^- + CH_4 \qquad (16b)$$

The reactions of hydroxide with silanes having more than one cleavable group (Scheme 3) have been used to determine the gas-phase acidity of a variety of hydrocarbons.[26,27,86,87,115,116,124] This kinetic acidity method has provided estimates of the acidity of a number of hydrocarbons, including some that cannot be measured by direct acidity methods because their corresponding carbanions are unstable with respect to electron loss (e.g. ethyl and *tert*-butyl).[112−116] Recent applications of this method include determinations of the gas-phase acidities of cubane and dodecahedrane.[26,27] While this method of determining hydrocarbon acidities has been an important tool, various factors (steric, configurational) can limit its application.[26,27,118]

Another interesting consequence of the alkyl cleavage reaction giving $(CH_3)_3SiO^-$ is its use in preparating silaacetone enolate by CID or photolysis (eq 17).[125,126]



$$(CH_3)_3SiO^- \xrightarrow{\text{CID or hv}} H_3C-Si(\cdots O)(\cdots CH_2)^- \qquad (17)$$

Although these studies were carried out using Fourier transform mass spectrometry, they have particular relevance not only as indicators of the importance of the cleavage reaction, showing that they can be carried out under quite different gas-phase conditions, but also for the discussion of multiply bonded species in Section IIIE.

D. Three-Coordinate Species. It was mentioned in Section IIB that since mass spectroscopic detection provides no structural information about the anions produced in anion−molecule reactions, additional means need to be used for characterization. Some mention already has been made of standard reagent reactions, CID, and computational studies (others will follow) that help evaluate structural questions. However, the tool used most frequently to assess structure in silicon studies has been the reaction of anions with simple,

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(112) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607−608.

(113) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 892−899.

(114) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2506−2516.

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(116) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973.

(117) There has been some debate about the concertedness of the alkyl cleavage/proton transfer in Scheme 3. See refs 118−120 for further details.

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(121) Damrauer, R.; Simon, R.; Krempp, M. *J. Am. Chem. Soc.* **1991**, *113*, 4431−4435.

(122) Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519−529.

(123) Hayes, R. N.; Bowie, J. H.; Klass, G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1167−1173.

(124) Wenthold, P. G.; Squires, R. R. *J. Mass Spectrom.* **1995**, *30*, 17−24.

(125) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863−6864.

(126) Tumas, W.; Salomon, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541−2546.

highly reactive reagents (typically OCS, CS_2, CO_2, and N_2O, the so-called standard reagents)[36,85,88,127] in what in many ways is a throwback to the days when "structure determination" was done using chemical reactivity studies and little or no spectroscopy.

An illustration of their use comes in a final, but important, aspect of the reactions of bases and neutral silanes and involves competition between C−H and Si−H acidities in methylsilanes (eq 18).[36,127,128] These

$$(CH_3)_3SiH + H_2N^- \rightarrow (CH_3)_3Si^- + NH_3 \qquad (18a)$$

$$\rightarrow (CH_3)_2Si(H)CH_2^- + NH_3 \qquad (18b)$$

isomeric anions can be distinguished on the basis of their characteristic chemistry with CS_2, CO_2, and/or N_2O (eqs 19−21), since differences in mass-to-charge

$$\underset{m/z\,=\,73}{(CH_3)_2Si(H)CH_2^-} + CS_2 \rightarrow \underset{m/z\,=\,91}{(CH_3)_2Si(H)S^-} + CH_2CS \qquad (19a)$$

$$\underset{m/z\,=\,73}{(CH_3)_3Si^-} + CS_2 \rightarrow \underset{m/z\,=\,105}{(CH_3)_3SiS^-} + CS \qquad (19b)$$

$$\underset{m/z\,=\,73}{(CH_3)_2Si(H)CH_2^-} + CO_2 \rightarrow \underset{m/z\,=\,75}{(CH_3)_2Si(H)O^-} + CH_2CO \qquad (20a)$$

$$\underset{m/z\,=\,73}{(CH_3)_3Si^-} + CO_2 \rightarrow \underset{m/z\,=\,89}{(CH_3)_3SiO^-} + CO \qquad (20b)$$

$$\underset{m/z\,=\,73}{(CH_3)_2Si(H)CH_2^-} + N_2O \rightarrow \underset{m/z\,=\,75}{(CH_3)_2Si(H)O^-} + CH_2N_2 \qquad (21a)$$

$$\underset{m/z\,=\,73}{(CH_3)_3Si^-} + N_2O \rightarrow \underset{m/z\,=\,89}{(CH_3)_3SiO^-} + N_2 \qquad (21b)$$

ratios (*m*/*z*) in each case distinguish the product.[129] Silyl anions such as $(CH_3)_3Si^-$ also can be prepared by reaction of H_2N^- and F^- with disilanes.[127,130−132]

A systematic study of SiH_4, CH_3SiH_3, $(CH_3)_2SiH_2$, $(CH_3)_3SiH$, and $(CH_3)_4Si$ gives all the possible Si−H and C−H acidities, although, because there are often not enough closely spaced bracketing acids, these values are not finely tuned. These acidities allow the estimation of previously unknown electron affinities for CH_3SiH_2, $(CH_3)_2SiH$, $(CH_3)_3Si$, $(CH_3)_3SiCH_2$, and $C_6H_5SiH_2$. Related studies by Brauman, Ellison, and their co-workers have measured the EAs of related silicon-containing species.[130,131,133−136] A small sampling of silicon- and carbon-centered EAs showing the profound stabilization of silicon substitution on the EAs of both carbon and silicon radicals is presented in Table 5.[137]

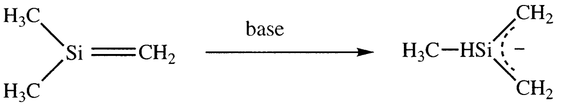
Table 5. Electron Affinities (EA) of Silicon- and Carbon-Centered Radicals

Si-centered radical	EA (kcal/mol)	C-centered radical	EA (kcal/mol)
Si	$\sim 32^{35}$	C	$\sim 29^{35}$
SiH	$\sim 29^{35}$	CH	$\sim 29^{35}$
SiH_2	$\sim 26^{35}$	CH_2	$\sim 15^{35}$
SiH_3	$\sim 32^{35}$	CH_3	$\sim 2^{35}$
CH_3SiH_2	$\sim 28^{35}$	CH_3CH_2	$\sim -6^{a,116}$
$(CH_3)_2SiH$	$\sim 25^{35}$	$(CH_3)_2CH$	$\sim -10^{a,116}$
$(CH_3)_3Si$	$\sim 22^{131}$	$(CH_3)_3C$	$\sim -6^{a,116}$
$C_6H_5SiH_2$	$\sim 33^{35}$	$C_6H_5CH_2$	$\sim 21^{35}$
$(CH_3)_3SiSiH_2$		$(CH_3)_3SiCH_2$	$\sim 22^{35}$
$[(CH_3)_3Si]_2SiH$	$\sim 45^{35}$	$[(CH_3)_3Si]_2CH$	$\sim 36^{35}$
$CH_2{=}SiH$	$\sim 46^{35,140}$	$CH_2{=}CH$	$\sim 15^{35}$

[a] These values were computed from the thermochemical cycle shown in eq 1.

E. Hypocoordinate and Multiply Bonded Silicon Negative Anions. A challenging aspect of organosilicon chemistry in the last quarter century has been the search for organosilicon species in which silicon either (1) lacks a full complement (octet) of electrons (hypocoordinate) or (2) is multiply bonded.[82−84] One particular challenge has been the isolation of stable species such as silylenes (divalent silicon), silenes (silicon−carbon double bond), disilenes (silicon−silicon double bond), silanones (silicon−oxygen double bond), and silaacetylenes (silicon−carbon triple bond). These problems also have been addressed in limited negative ion FA studies, particularly using collisionally induced dissociation (CID), photolytic, and pyrolytic technniques.

Pyrolysis of the standard precursors to dimethylsilene and dimethylsilylene into a carrier gas stream containing a strong base yields their corresponding conjugate bases (eqs 22 and 23), from which bracketing acidity studies have yielded the gas-phase acidities of dimethylsilylene and dimethylsilene.[138,139] The conjugate base



(22)

$$(CH_3)_2Si \xrightarrow{\text{base}} CH_3SiCH_2^- \qquad (23)$$

of dimethylsilene reacts more sluggishly than that of its carbon analogue, the M − 1 anion of 2-methylpropene (isobutene). Its greater stability also is reflected in the acidity of dimethylsilene being greater than that of 2-methylpropene. The chemistry of dimethylsilylene has been probed, revealing not only its acidity near that of methanol but also information about its rearrangement to $CH_3(H)Si{=}CH_2$.[139] The latter was studied by adding F^- at the exit of the pyrolysis tube followed by N_2O characterization downstream. As the pyrolysis

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(127) DePuy, C. H.; Damrauer, R. *Organometallics* **1984**, *3*, 362−365.

(128) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637−640.

(129) Under the conditions used in ref 127, amide ion and silane did not react at Si−H. Later, in ref 128, it was reported that Si−H reactivity could be observed.

(130) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304−8310.

(131) Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835−3841.

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(136) Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522−6529.

(137) For a more extensive discussion of related EA references, see refs 125, 126, and 144.

(138) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T. *Organometallics* **1986**, *5*, 2050−2054.

(139) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T. *Organometallics* **1986**, *5*, 2054−2057.

temperature increased, these reactions demonstrated the presence of $CH_3(H)Si{=}CH_2$.

Bengali and Leopold have prepared $[Si,C,H_3]^-$ in an FA and measured the EAs of CH_3Si and $CH_2{=}SiH$ to be 19.6 and 46.4 kcal/mol (Table 5). Estimates of ΔH_{acid} for CH_3SiH (372 ± 3 kcal/mol) and $CH_2{=}SiH_2$ (360 ± 5 kcal/mol) were derived (eq 1) using computational values for the BDEs.[140]

A number of other multiply bonded and hypocoordinate silicon anions have been prepared in the FA (e.g., $HSi({=}O)NH^-$, $CH_3OSi({=}O)CH_2^-$, $HSiO^-$, CH_3OSiO^-, $HSiS^-$, $HSiNH^-$, $HCSi^-$).[36,141−145] The most thoroughly studied is the conjugate base of silaformaldehyde, namely $HSiO^-$, which is prepared by CID of H_3SiO^- (eq 24) and undergoes a number of characteristic reactions of hypocoordinate silicon anions (e.g., eqs 25a−c).[143]

$$H_3SiO^- \xrightarrow{CID} HSiO^- + H_2 \qquad (24)$$

$$HSiO^- + C_6F_6 \xrightarrow{0.25} FSiO^- + C_6F_5H \qquad (25a)$$

$$\xrightarrow{0.50} HF_2SiO^- + C_6F_4 \qquad (25b)$$

$$\xrightarrow{0.25} C_6F_5^- + HFSiO \qquad (25c)$$

Determination of the acidity of silaformaldehyde by bracketing studies of $HSiO^-$ demonstrates the greatly enhanced acidity of its corresponding conjugate acid ($H_2Si{=}O$ or HSiOH) compared with that of formaldehyde. The ion−molecule chemistry of $HSiO^-$ is rich. Its reaction with CO_2 reveals, for example, both its oxidizing and reducing tendencies (eq 26). These studies also

$$HSiO^- + CO_2 \xrightarrow{55\%} HSiO_2^- + CO \qquad (26a)$$

$$\xrightarrow{45\%} SiO + HCO_2^- \qquad (26b)$$

allow a determination of the hydride affinity of SiO (∼49 kcal/mol) and an estimation of the heat of formation of $HSiO^-$ and its parent compound (∼−38 and −36 kcal/mol). The large hydride affinity of SiO, much larger than that of CO (∼8 kcal/mol), indicates a greater "willingness" of SiO to disturb its π-bonding (Table 1). More recent computational studies of proton-transfer reactions of $HSiO^-$ and CO_2 have been reported.[146,147]

The silaacetone anion (eq 17), although not studied in the FA, is also of interest because the the chemical reactivity and property comparisons with acetone enolate.[125,126] An example is its reaction with CO_2, in which $CH_3SiO_2^-$ and ketene are formed. The proton affinities of silaacetone anion and acetone enolate are similar (∼366 and 368 kcal/mol). Despite the proton affinity similarities, silaacetone anion and acetone enolate have very different H/D exchange behaviors, the former being unreactive and acetone enolate undergoing five H/D exchanges. An estimate of ∼62 kcal/mol has been made for the π-bond energy of the Si═O bond in silaacetone.[126]

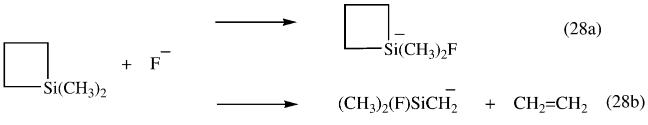
A final example of hypocoordination/multiple bonding in silicon anions illustrates a feature of FA that has not been emphasized up to now. When methylsilane is introduced into the FA, as many as 20 different anions are produced by electron impact and secondary reactions with the neutral.[145] The silaacetylide anion, $HC{\equiv}Si^-$ (m/z 41), can be mass-selected for further study and characterized by its reactions with neutral reagents, which demonstrate that hydrogen is bound to carbon, not silicon (eq 27). Computational studies indicate that

$$HC{\equiv}Si^- \xrightarrow{SO_2} HCSO^- + SiO \qquad (27a)$$

$$\xrightarrow{OCS} HCCS^- + SiO \qquad (27b)$$

the H−C isomer is considerably more stable than the Si−H isomer. Proton affinity measurements of $HC{\equiv}Si^-$ reveal that its conjugate acid is much more acidic than acetylene, but the structure of the conjugate acid is unknown, although it is clear from computational studies that $H_2C{=}Si$ is more stable than $HC{\equiv}SiH$.[145,148] Schmidt and Gordon indicate that $HCSi^-$ is best characterized as triply bonded.[148] Their computational study of the reactions with CO_2, OCS, and SO_2 reveals that the formation of products from a cycloadduct does not occur spontaneously, as had been proposed in the experimental paper. Instead, the cycloadduct undergoes stepwise ring opening. Examination of the potential surface for the reaction of $HC{\equiv}Si^-$ and CS_2 indicates a high barrier to product formation by a pathway similar to the OCS reaction. This result is consistent with the experimental work, in which no reaction is observed. Another computational study of $[H,C,Si]^-$ species in which proton-transfer reactions have been examined has been reported.[149]

F. Miscellaneous Silicon Negative Anion Studies. One of the earliest FA silicon studies involved nucleophilic additions to cyclic silanes, in which it was shown that (1) F^- addition to dimethylsilacyclobutane (DMSCB) yielded both a siliconate and a ring-opened product (eq 28), (2) F^- addition to dimethylsilacyclohexane yielded only a siliconate, and (3) $(CH_3)_4SiF^-$ soft-transferred F^- to DMSCB to form the siliconate shown in eq 28a.[104] The fluoride affinity of DMSCB and other



silacyclobutanes was shown to be ∼40 kcal/mol, in sharp contrast to smaller values for normal alkylsilanes such as silacyclohexane and tetramethylsilane, a result which presumably reflects the favorable pentacoordinate geometry of the four-membered ring (Tables 3 and 4). A

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(140) Bengali, A. A.; Leopold, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 9192−9194.

(141) Hankin, J. A.; Krempp, M.; Damrauer, R. *Organometallics* **1995**, *14*, 2652−2663.

(142) Damrauer, R.; Krempp, M. *Organometallics* **1990**, *9*, 999−1004.

(143) Gronert, S.; O'Hair, R. A. J.; Prodnuk, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 997−1003.

(144) Damrauer, R.; Krempp, M.; O'Hair, R. A. J. *J. Am. Chem. Soc.* **1993**, *115*, 1998−2005.

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(146) Shimizu, H.; Gordon, M. S.; Damrauer, R.; O'Hair, R. A. J. *Organometallics* **1995**, *14*, 2664−2671.

(147) Rusho, J. A.; Gordon, M. S.; Damrauer, N. H.; Damrauer, R. *J. Am. Chem. Soc.* **1998**, *120*, 2124−2130.

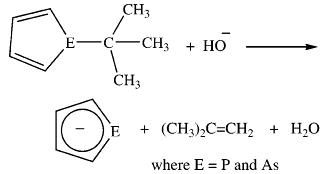
(148) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5244−5248.

(149) Rusho, J. A.; Gordon, M. S.; Damrauer, N. H.; Damrauer, R. *Organometallics* **1998**, *17*, 3401−3404.

subsequent study related to using N_2O as a characterization reagent for anions revealed that what had been thought to be exclusively the siliconate (eq 28a) was a mixture of it and $CH_3CH_2CH_2Si(F)CH_2^-$.[127] The latter is formed by ring opening of the energy-rich siliconate adduct (from Si−F bond formation). It forms in greater amounts unless the concentration (flow) of DMSCB is increased, in which case the siliconate is formed by soft F^- transfer from $(CH_3)_2(F)SiCH_2^-$. A more recent study showcased the SIFT and triple-quadrupole capabilities of our FA instrument.[17] Here the siliconate can be isolated in the first quadrupole and allowed to undergo increasingly energetic collisions with argon in the second. The result is ethylene loss and the clean formation of $(CH_3)_2(F)SiCH_2^-$. The cyclic anion $(CH_2)_3Si(CH_3)CH_2^-$ can be prepared by both HO^- and H_2N^- reactions with DMSCB. It is shown to have intact silacyclobutane and α-silylcarbanion moieties by CID. The C−H, S−H, and O−H acidities of the cyclic species DMSCB, $(CH_2)_3Si(CH_3)SH$, and $(CH_2)_3Si(CH_3)OH$ have been measured in bracketing experiments of the corresponding anions and shown to be unremarkable, indicating that the strained silacyclobutane ring has no effect on exocyclic X−H acidity. Recently, siliconates of silacyclobutanes have been revisited in an unexpected way in a computational study in which the electron affinities of silicon-containing species are addressed.[150]

IV. Organometallics: Group 15 Ion−Molecule Chemistry

Various aspects of gas-phase organophosphorus anion chemistry, including both FA and other gas-phase methods, have been reviewed recently,[88,151,152] but FA studies of other group 15 organometallics are lacking, with one exception.[153] Ashe, Squires, and co-workers reported an FA investigation of the phospholide and arsolide anions and a computational investigation of the phospholide and pyrrolide anions. The anions were prepared for FA study by elimination of 2-methylbutene by HO^- (eq 29). The proton affinity of each was measured to be 338 kcal/mol; however, the identity of the corresponding acid, in these cases being fairly strong acids, cannot be determined in such experiments. Computational studies of various phospholes combined with the experimental work on both the phospholide and arsolide anions were used to explore the reasonable possibilities for the parent acids, phosphole and arsole. The 1-H, 2-H, and 3-H isomers of phosphole have relative energies determined at the MP3/6-311+G(d)//6-31+G(d) level of computation to be 7.8, 0.0, and 3.8 kcal/mol. The barrier between the 1-H and 2-H isomers has been computed to be ∼16 kcal/mol by Bachrach[154] and that between the 2-H and 3-H isomers to be ∼27 kcal/mol. On the basis of these and other solution- and gas-phase data, it appears that the phospholide anion is protonated at phosphorus but that ready rearrangement occurs to the 2-H isomer. This is consistent with FA experiments, in which two H/D exchanges occur in $C_4H_4P^-$ with FCH_2CO_2H.[153] In contrast, no exchange of either $C_4H_4N^-$ or $C_4H_4As^-$ occurs, leading the authors to posit that the conjugate acid of arsolide is 1-H-arsole.



where E = P and As

(29)

V. Organometallics: Transition-Metal Ion−Molecule Chemistry

A number of papers on the behavior of transition-metal organometallic species in the FA were published during the 10 year period from 1984 to 1993. Part of this work was superbly reviewed in 1987 by Squires.[3] The reader is directed to that review, which not only covers FA studies but also discusses in detail work using other gas-phase mass spectroscopic techniques in negative ion transition-metal chemistry. The first FA work in transition-metal chemistry was reported almost simultaneously by McDonald and Squires and their respective co-workers. These research groups dominated the exploration of anion transition-metal FA studies, doing so in their unique styles, with McDonald more generally investigating the reaction chemistry of transition-metal anions and Squires generally concentrating on the reactivity of transition-metal neutrals and related thermochemical properties (bond strengths, acidities, etc.). To organize this extensive work, we will survey the reaction chemistry of anions in terms of their electron count, followed by examination of the reaction studies of neutral transition-metal species. Some emphasis also will be given to important thermochemical quantities derived from these experiments.

A. 17-Electron Anions. The 17-electron anion radical $Fe(CO)_4^-$ was prepared by dissociative electron detachment (electron impact of $Fe(CO)_5$).[155] Neutral halomethanes of the type XCF_3 (where X = Br, I) react by a major X abstraction pathway, giving $Fe(CO)_4X^-$. Minor products, such as $Fe(CO)_3(X)CF_3^-$ and $Fe(CO)_2(X)CF_3^-$, in which one or two CO ligands have been displaced are observed as well. Carbon tetrachloride and $BrCCl_3$ only undergo abstraction, and CH_3I and $ClCF_3$ are unreactive. The rate constants for the reactions leading to $Fe(CO)_4X^-$ are roughly governed by the strength of the C−X bond in concert with a proposed mechanism that involves rate-limiting X abstraction. A complex of $Fe(CO)_4X^-$ weakly bound to CF_3 is proposed to explain the formation of $Fe(CO)_4X^-$ and the other products; however, we will see this will be found to be too simple a view. Lower limit estimates of the Fe−X BDE in $Fe(CO)_4X^-$ are reported for I, Br, and Cl (Table 6).[3,155] $Fe(CO)_4^-$ is unreactive with dihydrogen but gives $Fe(CO)_3H^-$ (16-electron) and $Fe(CO)_3^-$ (15-electron) when hydrogen atoms are added to the FA.[156] In turn,

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Table 6. Bond Dissociation Energies (BDE) of Neutral and Anionic Transition-Metal Species

compd	BDE (kcal/mol)	compd	BDE (kcal/mol)
$Fe(CO)_4{-}CO$	$\sim$42	$Cr^-(CO)_2{-}CO$	$\sim$44[189]
$Cr(CO)_5{-}CO$	$\sim$37	$Mn^-(CO)_4{-}CO$	$\sim$41[189]
$Mo(CO)_5{-}CO$	$\sim$40	$Mn^-(CO)_3{-}CO$	$\sim$41[189]
$W(CO)_5{-}CO$	$\sim$46	$Mn^-(CO)_2{-}CO$	$\sim$28[189]
$Fe(CO)_3{-}CO$	$\sim$28[188]	$Co^-(CO)_3{-}CO$	$\sim$40[189]
$Fe(CO)_2{-}CO$	$\sim$29[188]	$Co^-(CO)_2{-}CO$	$\sim$38[189]
$Fe(CO){-}CO$	$\sim$37[188]	$Fe(CO)_4{-}CHO^-$	$\sim$90
$Fe{-}CO$	$\sim$8[188]	$Cr(CO)_5{-}CHO^-$	$\sim$73
$Ni(CO)_2{-}CO$	$\sim$28[188]	$Mo(CO)_5{-}CHO^-$	$\sim$77
$Ni(CO){-}CO$	$\sim$47[188]	$W(CO)_5{-}CHO^-$	$\sim$82
$Ni{-}CO$	$\sim$40[188]	$Fe^-(CO)_4{-}CHO$	$\sim$41
$Fe^-(CO)_3{-}CO$	$\sim$42[188]	$Cr^-(CO)_5{-}CHO$	$\leq$32
$Fe^-(CO)_2{-}CO$	$\sim$42[188]	$Mo^-(CO)_5{-}CHO$	$\leq$38
$Fe^-(CO){-}CO$	$\sim$36[188]	$W^-(CO)_5{-}CHO$	$\leq$43
$Fe{-}CO$	$\sim$34[188]	$CpV(CO)_2{-}CO^-$	$\sim$42[191]
$Ni^-(CO)_2{-}CO$	$\sim$38[188]	$CpV(CO){-}CO^-$	$\sim$44[191]
$Ni^-(CO){-}CO$	$\sim$43[188]	$CpCr(CO)_2{-}CO^-$	$\sim$48[191]
$Ni^-{-}CO$	$\sim$32[188]	$CpMn(CO){-}CO^-$	$\sim$47[191]
$V^-(CO)_5{-}CO$	$\sim$31[189]	$CpMn{-}CO^-$	$\sim$28[191]
$V^-(CO)_4{-}CO$	$\sim$31[189]	$CpFe(CO){-}CO^-$	$\sim$45[191]
$V^-(CO)_3{-}CO$	$\sim$40[189]	$CpCo(CO){-}CO^-$	$\sim$24[191]
$V^-(CO)_2{-}CO$	$\sim$36[189]	$CpCo{-}CO^-$	$\sim$56[191]
$Cr^-(CO)_4{-}CO$	$\sim$41[189]	$CpCo^-$ (Co−Cp)	$\sim$39[191]
$Cr^-(CO)_3{-}CO$	$\sim$40[189]		

these primary products react with dihydrogen to produce $Fe(CO)_3H_3^-$ (18-electron) and $Fe(CO)_3H_2^-$(17-electron). Labeling studies with D_2 help establish the identity of these products and lead to mechanistic insights. It is clear from this study that when a coordinatively unsaturated anion can add two 1-electron ligands (such as two H atoms), it reacts readily. The addition of dihydrogen then can be used as a tool to probe the saturated versus unsaturated nature of these metal anions. Another 17-electron anion, (η^2-1,3-cyclohexadiene)$Fe(CO)_3^-$, reacts with hydrogen atoms to give three products, $Fe(CO)_3H^-$ (16-electron), $Fe(CO)_3^-$ (15-electron), and (η^4-1,3-cyclohexadiene)$Fe(CO)_2H^-$ (18-electron) (75/20/5). Assignments of these are based on their reactivity with dihydrogen, in concordance with the discussion above. The addition of a hydrogen atom to (η^2-1,3-cyclohexadiene)$Fe(CO)_3^-$ takes place at the Fe atom, in contrast to hydride addition, which occurs at carbon.[157]

The 17-electron species $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$ were shown by Squires and co-workers to undergo slow reaction with dioxygen, yielding an array of products that depend on the dioxygen flow rate.[158] These are generally of two types: $M(CO)_x(O)_y^-$ with x, $y = 1, 2$ for Fe, with $x = 3$ and $y = 1, 2$ for Cr, and with $x = 3, 4$ and $y = 2$ for Mo; $M(O)_z^-$ with $z = 2-4$ for Fe, $z = 2-5$ for Cr, and $z = 3-5$ for Mo. No product with greater than a single metal atom was detected. The primary and secondary Fe and Cr products arise by dioxygen addition and CO and CO_2 loss but differ from $Mo(CO)_5^-$, which adds dioxygen with the loss of only CO. The radical nature of these reactions is contrasted with the lack of reactivity of the 18-electron species $Mn(CO)_5^-$ and $Co(CO)_4^-$, although the slowness of the reactions of the 17-electron species is emphasized. The reaction of dioxygen with $CpCo(CO)_2^-$ yields $CpCoO^-$, which, although formally a 17-electron anion, is very reactive.[159] It is important to recognize that so-called ring slippage can change the hapticity of the metal, thus dramatically increasing its reactivity. $CpCoO^-$ displays high reactivity with Brønsted acids (NH_3, H_2O, ROH, RCO_2H, H_2S, and RSH) in a series of addition−dehydration steps (eq 30). Isotopic and CID experiments

$$CpCoO^- + HA \rightarrow CpCo(OH)A^- \rightarrow CpCoA_2^- \rightarrow CoA_3^- \quad (30)$$

with water and alcohols demonstrate that in the early stages these reactions are sequential insertions into O−H. H/D exchange studies with H_2O/D_2O make it clear that reversible hydroxide exchange occurs at the metal center rather than proton exchange at oxygen.

A more comprehensive look at the reactions of 17-electron transition-metal anions and haloalkanes by McDonald in 1989 considered the metal carbonyl anions $Mn(CO)_4X^-$ ($X =$ Br, Cl), $Re(CO)_4X^-$ ($X =$ Br, Cl), (η-C_3H_5)$Mn(CO)_3^-$, (η-C_3H_5)$Re(CO)_3^-$, $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$. Two others studied, $Mn(CO)_3X^-$ ($X =$ Br, Cl), although formally 15-electron anions, behaved in both rate and reactivity studies in a manner similar to the 17-electron anions, suggesting to the authors that Cl and Br are 3-electron donors in $Mn(CO)_3X^-$.[160] The rates of these reactions vary widely but do not correlate with C−X BDEs. All fast reactions give two products (illustrated for $Ni(CO)_3^-$): the abstraction product, $Ni(CO)_3X^-$, and a product associated with CO loss, $Ni(CO)_2X^-$. The branching ratios leading to these products are thought to be dependent on the vibrational energy content of $[Ni(CO)_3X^-]^*$ and the efficiency with which the vibrationally excited species can be collisionally deactivated before losing CO. Formally 16-electron $Ni(CO)_2X^-$ does not undergo further reaction with excess RX in the flow tube, suggesting that X is a 3-electron ligand. Only $Fe(CO)_4^-$ yielded products that lost two COs (with CF_3X, where $X =$ Br, I). These reactions were originally interpreted to be governed by halogen atom abstraction,[156] but because this approach fails for other transition-metal anions, various electron transfer mechanisms were subsequently considered.[160] Correlations with the EAs of RX and with the C−X BDEs of the RX^- radical anions also fail, but the rate constants give a log−log linear plot with the thermal-energy electron attachment rate constants for RX, which correspond to vertical electron transfers. The details of the electron-transfer mechanism for the reactions of $Ni(CO)_3^-$ and $Fe(CO)_4^-$ with CCl_4 are discussed, revealing a consistent pattern in which differences in the vertical EAs of $Ni(CO)_3$ and $Fe(CO)_4$ control the very different rates of their reactions.

Two other detailed 17-electron ligand substitution studies deal with a number of other transition-metal anions: $Fe(CO)(NO)_2^-$, $Co(CO)_2(NO)^-$, (η^3-C_3H_5)-$Co(CO)_2^-$, $(C_3H_5)Co(CO)_3^-$, $CpCo(CO)_2^-$, $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mn(CO)_4H^-$.[161,162] Their reactions with phosphines, NO, SO_2, olefins, ketones, O_2, CO, CO_2, and

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COS were studied. The chemistry is complex and difficult to summarize succinctly. Major reactivity trends suggest that these 17-electron species balance adduct formation with ligand substitution in complicated ways that depend on the energetics of ion−molecule collision complexes, on the nature of the ligands and their ability to adjust hapticity, and on the collisional stabilization conditions. For example, $Fe(CO)_4^-$ undergoes reaction with PF_3 to give the 17-electron ligand substitution product $Fe(CO)_3(PF_3)^-$. Other anions studied react with PF_3 to give ligand substitution and adduct formation ($Fe(CO)(NO)_2^-$, $Co(CO)_2(NO)^-$, (η^3-C_3H_5)$Co(CO)_2^-$, and $CpCo(CO)_2^-$); still others give only ligand substitution ((C_3H_5)$Co(CO)_3^-$) or do not react at all ($Cr(CO)_5^-$ and $Mn(CO)_4H^-$). None of the 17-electron transition-metal anions studied react with trimethylphosphine. Reactions of these 17-electron anions with dioxygen also are complex, proton-transfer reactions leading to a variety of oxide anions and ligand displacements.[158,161,162] For example, $Fe(CO)(NO)_2^-$ undergoes CO substitution, CO and NO displacement, and loss of CO_2, all believed to arise from the η^1-superoxide intermediate $Fe(CO)(NO)_2$-(O−O)$^-$. The complexity of the many anions and reactions studied, although leading to interesting reaction chemistry, yields only limited thermochemical data. Values for the EAs of (η^3-C_3H_5)$Co(CO)_3$, $CpCo(CO)_3$, (η^3-C_3H_5)$Co(CO)_2$, $Co(CO)_2(NO)$, and $Fe(CO)(NO)_2$ as well as $Cr(CO)_3$, $Mo(CO)_3$, and $W(CO)_3$ have been reported.[161,163]

B. Fewer Than 17-Electron Anions. The reaction of carbon monoxide (^{13}CO) with 16-electron $Mn(CO)_4^-$ reveals that both addition and substitution reactions occur very slowly. The slow reactions are attributed to spin-forbidden curve crossings of the triplet $Mn(CO)_5^-$, whose multiplicity is based on isoelectronic $Fe(CO)_4$, which undergoes slow addition of CO.[164] The reactions of $Mn(CO)_4^-$ with propene, 1,3-butadiene, cyclopentadiene, and benzene have also been studied.[165] Each of these gives exclusive η^2-addition, while allene and acetylene give η^4-addition and ligand-substitution products, addition being favored. That the reactions of $Mn(CO)_5^-$ consistently are slower than similar reactions of $Fe(CO)_3^-$ again is attributed to a change in spin multiplicity of the manganese anion from reactant to product (high-spin triplet to 18-electron singlet). The 15-electron anion $Fe(CO)_3^-$ can be prepared by electron impact of $Fe(CO)_5$ at energetically higher emission currents (~5 mA).[166] It is substantially more reactive than the 17-electron anions, undergoing reactions with dihydrogen, dinitrogen, carbon monoxide, propene, and allene as as well as displacement reactions (eqs 31−33).

$$Fe(CO)_3^- + H_2 \rightarrow Fe(CO)_3H_2^- \qquad (31)$$

$$Fe(CO)_3^- + CH_2{=}C{=}CH_2 \rightarrow Fe(CO)_3(C_3H_4)^- + Fe(CO)_2(C_3H_4)^- + CO \qquad (32)$$

$$Fe(CO)_3^- + CH_3Br \rightarrow Fe(CO)_3Br^- + CH_3 + Fe(CO)(Br)CH_3^- + 2CO \qquad (33)$$

In related work probing the mechanism of addition, the addition/substitution reactions of 15-electron $Fe(CO)_3^-$ with ^{13}CO have been studied.[167] This reaction is spin allowed and is considerably faster than that of $Mn(CO)_4^-$, although the addition/substitution branching ratio is similar. The results suggest the formation of a vibrationally excited adduct, $[Fe(CO)_3(^{13}CO)^-]^*$, that can either be stabilized by collision with the helium buffer gas or lose CO. Finally, both $Mn(CO)_4^-$ and $Fe(CO)_3^-$ react with silanes and germanes to give adducts that are believed to be M_{14}−H insertion products, where M_{14} stands for these group 14 elements.[168] As illustrations, $Mn(CO)_3^-$ and germane react to give $Mn(CO)_3({=}Ge)^-$ and 2 equiv of H_2, but $Mn(CO)_3(H)(\equiv SiH)^-$ is obtained with silane. Reaction 33 demonstrates the greater reactivity of $Fe(CO)_3^-$ over $Fe(CO)_4^-$, which does not react with methyl bromide. The second primary product in reaction 32, $Fe(CO)_2(C_3H_4)^-$, undergoes further reaction with allene, giving $Fe(CO)_2(C_3H_4)_2^-$, suggesting that allene is a 2-electron donor.[169] Reactions with acetylene are consistent with it being a 4-electron donor with $Fe(CO)_3^-$.[166] The 15-electron species (η^4-C_4H_6)Fe-(CO)$^-$, prepared at high emission currents from (η^4-C_4H_6)$Fe(CO)_3$ and considered as a model for homogeneous hydrogenation catalysts, reacts with dihydrogen and dideuterium, affording a 17-electron adduct.[170] The reaction with D_2 reveals that as many as four H/D exchanges occur, undoubtedly in the terminal positions of η^4-butadiene.

The reactions of coordinatively unsaturated $Fe(CO)_2^-$ (13-electron) and $Mn(CO)_3^-$ (14-electron) (prepared using high emission currents) have been used to investigate whether these anionic species behave in ways similar to those of unsaturated transition-metal complexes that have been so important in homogeneous catalysis, CH activation, etc.[171−177] Their reactions with dihydrogen, water, hydrogen sulfide, ammonia, and phosphine provide examples of diverse reactivity, particularly in view of the simplicity of the neutral reactants. Both react with dihydrogen to yield adducts (either $M(H_2)(CO)_x^-$ or $M(H)_2(CO)_x^-$, where M = Fe and $x = 2$ or M = Mn and $x = 3$) with no isotope effects, while reaction with water leads to the ligand-substitu-

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tion products $M(CO)_y(H)(OH)^-$ (where M = Fe and y = 1 or M = Mn and y = 2). The reactions of $Fe(CO)_2^-$ with hydrogen sulfide, ammonia, and phosphine appear to involve insertion into the heteroatom−H bond; $Mn(CO)_3^-$ behaves similarly, except for its reaction with ammonia, in which addition but no ligand substitution occurs.[172] Reactions of these anions with silanes and germanes have also been reported.[168]

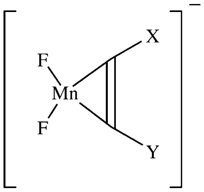
It was determined that a tertiary C−H is more reactive than a secondary C−H, which in turn is more reactive than a primary C−H in a C−H activation study of $Mn(CO)_3^-$.[173] This report was expanded in comprehensive work examining the reactivity of $Mn(CO)_3^-$ and $Fe(CO)_2^-$ with a wide variety of unstrained alkanes[176] and cyclopropane.[177] Only $Fe(CO)_2^-$ reacts with methane and 2,2-dimethylpropane, in each case giving the C−H insertion adduct $Fe(CO)_2(H)(R)^-$, although the methane reaction is very slow. Product characterization was made by analogy with the neopentane reaction in which the adduct, $[Fe(CO)_2(H)(CH_2C(CH_3)_3)]^-$, was characterized by single H−D exchange with dideuterium and by reaction with hydrogen sulfide, giving $[Fe(CO)_2(SH)(CH_2C(CH_3)_3]^-$. Many other alkanes undergo reaction with both $Mn(CO)_3^-$ and $Fe(CO)_2^-$, typically giving products of the general formula adduct−H_2. The reactions of $Mn(CO)_3^-$ have been more thoroughly characterized in the alkane study.[176] What is thought to be a π-complex in the reaction with ethane (eq 34) has been characterized by H−D exchange with

$$Mn(CO)_3^- + C_2H_6 \rightarrow Mn(CO)_2(\pi\text{-}C_2H_4)^- + H_2 \quad (34)$$

dideuterium (up to four H/D exchanges), by ethylene displacement with SO_2, and by the identical reactivity of an independently prepared sample. Longer alkanes react to give what are suggested to be intermediate π-complexes that subsequently rearrange to η^3-anions (eq 35). The latter are 18-electron species whose lack of

$$Mn(CO)_3^- + C_3H_8 \rightarrow Mn(CO)_3(H)(\eta^3\text{-}C_3H_5)^- + H_2 \quad (35)$$

reactivity provides credence to the structural proposal. Rate and exchange studies indicate the complexity of these alkane reactions. The reactions of $Mn(CO)_3^-$ and $Fe(CO)_2^-$ with cyclopropane yield two products for each: an adduct and adduct−H_2.[177] Their structural characterizations were based on studies with a series of reagents including dideuterium, trimethylsilane, and hydrogen sulfide. The adduct and adduct−H_2 pair prepared from $Mn(CO)_3^-$ are inert to further reactions, an indication that $Mn(CO)_3(H)_2(C_3H_4)^-$ and $Mn(CO)_3(C_3H_4)^-$ are saturated species, although their structures are uncertain.[178] The adduct structure favored for the $Fe(CO)_2^-$ reaction is the 15-electron C−H insertion product $Fe(CO)_2(H)(\eta^1\text{-}C_3H_5)^-$, but the adduct−$H_2$ structure favored is the 15-electron $Fe(CO)_2(\pi\text{-}C_3H_4)^-$ rather than the isomeric cyclopropylidene anion. Both $Mn(CO)_3^-$ and $Fe(CO)_2^-$ react with propene, giving $M(CO)_x(H)(\eta^3\text{-}C_3H_5)^-$, where x = 2 for M = Fe and x = 3 for M = Mn.[165] The identity of these products is based on their lack of reactivity with D_2 and other reagents. This suggests that they are saturated, a 17-electron species in the case of $Fe(CO)_2(H)(\eta^3\text{-}C_3H_5)^-$. Both $Mn(CO)_3^-$ and $Fe(CO)_2^-$ react with benzene to give $M(CO)_x(\eta^4\text{-}C_6H_6)^-$ adducts in which η^4 coordination is suggested, again based on the lack of further reactivity of the products. With 1,3-butadiene, both of these anions give two products: an adduct and an adduct−CO anion. Both are suggested to be derived from an excited $\eta^4\text{-}C_4H_6$ intermediate. Exhaustive reactions of $Mn(CO)_3^-$ and $Fe(CO)_2^-$ with acetylene yielded $M(C_2H_2)_x^-$, with x = 2 for M = Fe and x = 3 for M = Mn. Their inertness indicates their saturated state. Competition between O−H and C−H reactivity with $Mn(CO)_3^-$ is revealed by two product channels in its reaction with CH_3OH: a 29% pathway leading to $Mn(CO)_2(H)(OCH_3)^-$ by O−H insertion and CO loss and a 71% pathway leading to $Mn(CO)_3(H_2CO)^-$ plus H_2.[174] The latter structure is likely an η^2-bound formaldehyde. Rate studies with isotopically labeled methanol indicate that two independent pathways with the excited species $Mn(CO)_3(H)(OCH_3)^-$ and $Mn(CO)_3(H)(CH_2OH)^-$ lead to products. Despite the typically large BDE of the C−F bond, both $Mn(CO)_x^-$ species (x = 3, 4) undergo a series of extremely interesting reactions with fluorinated alkenes ($F_2C{=}CF_2$, $F_2C{=}CHF$, and $FHC{=}CHF$).[175] In all its reactions with the fluoroalkenes, $Mn(CO)_3^-$ gives $Mn(F_2)(C_2XY)^-$ products, where X and Y can be H and F. Studies of these products with SO_2 establish the likelihood of two Mn−F bonds and strongly suggest that **1** is the proper structure. Reaction with CF_3CF_3 affords the same product.



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C. Reactions of Anions with Neutral Transition-Metal Complexes: Squires and co-workers have studied the reactions of various anions with neutral transition-metal complexes, particularly $Fe(CO)_5$. It and other 18-electron metal carbonyls such as $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ undergo fast reaction with HO^- and $HO(H_2O)_n^-$ by distinctly different paths: substitution for n = 0 and addition for n = 1−4 (eq 36).[157,179−185]

$$\begin{aligned} Fe(CO)_5 + HO(H_2O)_n^- &\xrightarrow{n=0} Fe(CO)_3OH^- + 2CO \quad (36)\\ &\xrightarrow{n=1-4} Fe(CO)_5OH^- + nH_2O \end{aligned}$$

Because of the saturated nature of these reactants, the likely addition products are ones in which hydrated hydroxide has reacted at carbon, giving an acyl product

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(178) The structures of many of the transition-metal anions are not certain, because the experimental work generally was carried out before the routine use of companion computational studies. As a result, there are many examples of interesting problems for the computational chemist.

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($[Fe(CO)_4CO_2H]^-$ in the $Fe(CO)_5$ case). This structural supposition is amply verified in reactivity studies, where single H−D exchanges occur with various deuterated acids. An isomeric formate structure would not undergo exchange. A possible strongly bound ion-induced dipole complex, $[HO^- \cdots Fe(CO)_5]$, is ruled out for $Fe(CO)_5OH^-$, since no exchange reactions of HO^- occur with highly polar neutral molecules that would be expected to make stronger ion-induced dipole complexes. It has also been shown that no $^{18}O/^{16}O$ exchange occurs once the initial product has formed, which suggests that HO^- addition is irreversible and/or that no internal proton transfer occurs. The authors point out that the gas-phase stability of $Fe(CO)_4CO_2H^-$ argues against its intermediacy in the alkaline, metal-catalyzed water-gas shift reaction. In fact, collision-induced dissociation of $Fe(CO)_4CO_2H^-$ occurs by CO loss, in contrast to the necessary decarboxylation of the water-gas shift reaction. The energetics and mechanism of decarboxylation of $Fe(CO)_4CO_2H^-$ have been studied as well.[186] That hydrated hydroxides with as many as $n = 4$ water molecules react at nearly collision rates with $Fe(CO)_5$, but with loss of the waters, indicates that C−OH bond formation is highly exothermic and that hydroxide reactivity is not significantly attenuated by several waters of hydration, as can sometimes be the case.[105,157] A rough estimate of the lower limit of the C−OH BDE in $Fe(CO)_4CO_2H^-$ was reported (Table 6).[179]

The full range of reactivity of $Fe(CO)_5$ has been examined with various anions (An^-).[181,182] Lane, Sallans, and Squires have shown that three main reaction channels are possible in An^- addition reactions (eq 37).

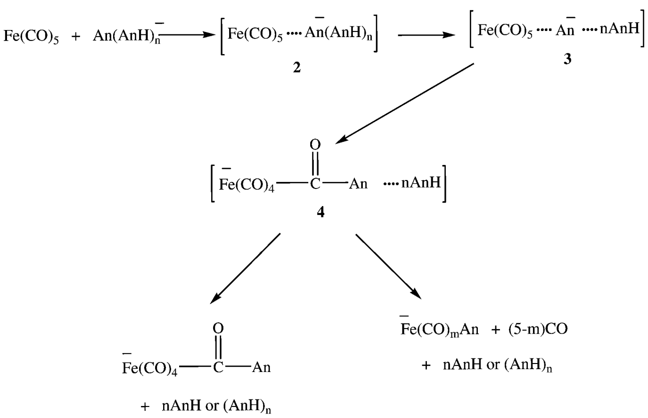
$$Fe(CO)_5 + An^- \rightarrow Fe(CO)_3An^- + 2CO \quad (37a)$$

$$\rightarrow Fe(CO)_4An^- + CO \quad (37b)$$

$$\rightarrow Fe(CO)_4C(O)An^- \quad (37c)$$

Their relative importance depends on several factors, including basicity. The strongly basic anions H^-, H_2N^-, and HO^- each react to give primary products in which displacement of one or two carbon monoxide ligands occurs (eqs 37a and 37b). Although secondary reactions between 16-electron products and $Fe(CO)_5$ can lead to dinuclear products, the 18-electron species $Fe(CO)_4H^-$ is inert to further reaction. Each of these reactions occurs on nearly every collision. A series of less basic alkoxide ions reveal not only the acyl−adduct pathway (eq 37c) but also show double CO loss (eq 37a) and a hydride transfer pathway only open to those alkoxides bearing a hydrogen atom β to oxygen, namely that yielding $Fe(CO)_4C(O)H^-$. Thus, *tert*-butoxide, *tert*-amyloxide, and $CF_3CH_2O^-$ give exclusively the [adduct − 2CO] product, $Fe(CO)_3OR^-$, while CH_3O^- (by α elimination), $CH_3CH_2O^-$, and $CH_3OCH_2CH_2O^-$ afford $Fe(CO)_3OR^-$ and $Fe(CO)_4C(O)H^-$. *tert*-Butoxide, *tert*-amyloxide, and $CF_3CH_2O^-$, which bear no β-hydrogen, thus are unable to undergo hydride transfer; for different reasons (steric and lowered basicity), they are not good candidates for the acyl−adduct pathway (eq 37c); therefore, they only react by pathway 37a. Among the other anions studied (thiolates, enolates, carboxylates, carbanions, nitriles, nitrocarbanions, azides, and halides), the thiolates and carbanions deserve brief comment. Thiolates, whose basicities are low, give exclusive acyl−adduct formation (eq 37c) without any secondary reactivity, but the more basic carbanions studied give a wider range of products. Phenide ($C_6H_5^-$) with a basicity close to that of hydride behaves identically, giving products resulting from the loss of one and two COs (eqs 37a and 37b). Less basic carbanions such as allyl and cyclohexadienyl yield $Fe(CO)_4^-$ by dissociative electron transfer, as well as other products. Some carbanions give H^- transfer as well.

Scheme 4



A more comprehensive study of $Fe(CO)_5$ with a variety of partially solvated anions presents a special window on reactivity by exploring in detailed fashion the relationship between gas- and condensed-phase reactivity.[182] The so-called homoconjugate clusters studied are $HO^-(H_2O)_n$ ($n = 0-4$) (see above),[179] $RO^-(R_2O)_n$ (R = Me, $n = 0-4$), $RO^-(R_2O)_n$ (R = Et, $n = 0-2$), $RO^-(R_2O)_n$ (R = t-Bu, $n = 0-2$), $RO^-(R_2O)_n$ (R = $MeOCH_2CH_2$, $n = 0-2$), $RO^-(R_2O)_n$ (R = *tert*-amyl, $n = 0-2$), $RO^-(R_2O)_n$ (R = *sec*-hexyl, $n = 0-2$), $RO^-(R_2O)_n$ (R = CF_3CH_2, $n = 0-2$), $HS^-(H_2S)_n$ (n = 0, 1), $EtS^-(EtSH)_n$ (n = 0, 1), $CH_3CO_2^-(CH_3CO_2H)_n$ ($n = 0-2$), and $NH_2^-(NH_3)_n$ (n = 0, 1). With the exception of the acetate and amide, the other clusters react with $Fe(CO)_5$ rapidly and efficiently to give an acyl adduct, $Fe(CO)_4C(O)An^-$ (An denotes the anions shown above). Acetate hydrates do not react, while the amide ammonylate, $NH_2^-(NH_3)$, affords the acyl anion and products of single and double CO loss, $Fe(CO)_{3,4}NH_2^-$.

These reactions have been analyzed in terms of the general mechanistic patterns shown in Scheme 4. Anion **2** may have as much as 30 kcal/mol of excess energy that will be distributed to various rotational and vibrational modes, depending on the structure and solvation of An^-. As the excess energy is so distributed, solvent molecules may be shed in what is localized heating in particular modes. This leads to anion **3**, in which solvent is more loosely bound to An^-, but ultimately to **4**, where the $Fe(CO)_4C(O)$−An bond energy is deposited. Since solvent "boils off" in the process, the C(O)−An bond formation drives the loss of solvent because the metal ion−solvent binding energies are small. A careful analysis of the hydroxide and amide

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(183) Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6403−6404.

(184) Lane, K. R.; Sallans, L.; Squires, R. R. *Organometallics* **1985**, *4*, 408−410.

(185) Lane, K. R.; Squires, R. R. *Polyhedron* **1988**, *7*, 1609−1618.

(186) Sunderlin, L. S.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 337−343.

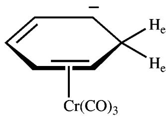
reactions makes clear why CO loss only occurs in the amide case. Earlier studies showed that CO loss from iron acyl anions requires about 34 kcal/mol.[181] Thus, for **4** to take the lower right-hand path in Scheme 4, enough energy has to be captured in its formation to overcome the barrier to CO loss. While this is true for the monosolvate of amide, it is not so for $HO^-(H_2O)$.[182] An energy analysis of the reaction of naked H_2N^- and HO^- demonstrates that the unhydrated anion in both cases is higher in energy than its hydrated counterpart ($HO^- + H_2O + Fe(CO)_5$ versus $HO^-(H_2O) + Fe(CO)_5$ and the corresponding species for H_2N^-). This results in a large enough excess energy content when $Fe(CO)_4C(O)-An^-$ is formed that the barrier to CO loss is readily overcome. Estimates of the thermochemical parameters of the reactions of H_2N^-, HO^-, CH_3O^-, and $CH_3CO_2^-$ to form the acyl adducts reveal other interesting features of these solvated reactions. Enthalpy changes for higher solvated states of hydroxide ($n = 3, 4$) and methoxide ($n = 3$) are shown to be unfavorable, although these reactions take place. The favorable free energies are possible because of large compensating entropy driven changes accompanying desolvation.

The binding of simple anions (An = H^-, HO^-, F^-, $CH_3CO_2^-$, Cl^-) to $Fe(CO)_5$ to produce the acyl derivative $[Fe(CO)_4C(O)An]^-$ has been used to obtain a relative anion affinity scale for $Fe(CO)_5$ (Table 1).[157] The anion affinities are measured using bracketing techniques with a series of neutral compounds that have known An affinities and are quantified in terms of eq 38.[187]

$$Fe(CO)_4C(O)An^- \rightarrow Fe(CO)_5 + An^- \qquad (38)$$

The anion affinities so obtained vary over a ~40 kcal/mol range, from weakly bound HS^- (~23 kcal/mol) to RO^- (~40−45 kcal/mol), HO^- (~53 kcal/mol), and H^- (~56 kcal/mol). In the case of $Fe(CO)_5$, the bracketed values correlate well with the proton affinities of the corresponding anions and with the heterolytic bond energies of $CH_3C(O)-An$ compounds (that is, to An^- and $CH_3C(O)^+$). These correlations were tested by calculating the chloride affinity of $Fe(CO)_5$ before measuring it. The experimental value of 13.9 ± 3 kcal/mol compared favorably with 14.0 and 14.5 kcal/mol predicted from the two correlations. What this suggests is that very dissimilar species (H^+, $CH_3C(O)^+$, and $Fe(CO)_5$)), with very different electronic and steric properties, behave in remarkably similar ways in binding An^-. Once either the proton or acetyl cation affinity of any An^- is known, its binding energy to $Fe(CO)_5$ can be determined and, as a result, the heat of formation of $Fe(CO)_4C(O)An^-$ can be calculated. This analysis has provided a number of such heats of formation as well as thermochemical information on some iron-containing anions believed to be important in homogeneous catalysis. In separate studies the hydride affinity of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_5$, were determined, as well as important bond energies and heats of formation.[184,185] The hydride affinities of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_5$ are compiled in Table 1. Estimates of the BDEs of $Fe(CO)_4-CHO^-$, $Cr(CO)_5-CHO^-$, $Mo(CO)_5-CHO^-$, $Fe^-(CO)_4-CHO$, $W(CO)_5-CHO^-$, $Cr^-(CO)_5-CHO$, $Mo^-(CO)_5-CHO$, and $W^-(CO)_5-CHO^-$ are given in Table 6.

Although 18-electron systems are generally unreactive in ion−molecule reactions, $C_6H_6Cr(CO)_3$ undergoes rapid reaction with H^- to yield a proton abstraction product, $C_6H_5Cr(CO)_3^-$, and a novel 14-electron hydride, $HCr(CO)_3^-$, in roughly equal amounts.[183] The formation of $HCr(CO)_3^-$ is believed to occur by hydride addition to coordinated benzene to give **5**, followed by transfer of H^- to chromium and subsequent loss of benzene. Reaction with D^-gave a ~7:1 ratio of $HCr(CO)_3^-$ to $DCr(CO)_3^-$, which suggests that H/D exchange in **5** may occur before benzene is expelled. Mechanisms in which H^- adds directly to Cr or to C−O are not credible in view of the D^- reaction. The 14-electron species $HCr(CO)_3^-$ undergoes facile reactions with Brønsted acids, HX, to give dihydrogen and $XCr(CO)_3^-$ (e.g. H_2O, NH_3, and ROH). It undergoes H/D exchange with dideuterium as well as insertion/elimination reactions with propene and other alkenes bearing allylic C−H (giving dihydrogen and $Cr(CO)_3(\eta^3\text{-}C_3H_5)^-$.



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Bond strengths in metal carbonyls also have been measured using energy-resolved CID. Squires, Sunderlin, and Wang have carried out a series of energy-resolved collision-induced dissociation (CID) studies of simple metal carbonyls.[188,189] These involve isolating an anion in the second quadrupole (Q2) of a flowing afterglow triple-quadrupole instrument (Figure 1).[9] Also present in Q2 is a constant pressure of a rare gas (Rg), which undergoes collisions with the selected anion. The conditions are manipulated so that single anion−Rg collisions occur as the energy of the collisions is varied. The anions ultimately undergo dissociation when the collision energy is sufficient. The energy at which dissociation occurs (threshold energy) can be correlated with bond dissociation enthalpies.[190] The transition-metal carbonyls of the first transition series (V, Cr, Mn, Fe, Co, and Ni) have provided a wealth of thermochemical information, only some of which will be detailed (Table 6).[188,189] The M−CO bond strengths of the first transition series metal carbonyl anions, $M(CO)_n^-$, show several trends. The bond strengths for $n \geq 3$ generally are in the narrow range of 36−44 kcal/mol, which leads the authors to suggest that any energetic effects due to electron promotion are unimportant once several CO molecules are bonded; however, the bond energies of some anions with $n \geq 3$ are weak ($V^-(CO)_n$ for $n = 4, 5$ at ~31 kcal/mol). In contrast, some of the carbonyl anions with $n \leq 3$ have smaller M−CO bond energies (Fe^-−CO at ~34 kcal/mol); in fact, a linear relationship

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(187) A large number of anion affinities have been obtained by a variety of workers, McMahon, Kebarle, Beauchamp, and their co-workers chief among them. These studies are abundantly referenced in the papers by Squires and co-workers.

(188) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788−2796.

(189) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12060−12070.

(190) The details of data collection and manipulation as well as thermochemical analysis are complicated. The interested reader is referred to these papers and earlier ones referenced by Squires and co-workers.

between $D(M^- - 2CO)$ and the $s^2d^{n-2} \rightarrow sd^{n-1}$ promotion energy suggests the necessity of promotion from an atomic to a hybridized state for bonding of the first two CO molecules. Where comparison of isoelectronic species (cation, neutral, anion) can be made, the data reveal that the M−CO bond strength orders as anion ≥ neutral ≥ cation. This is consistent with the degree of $d\pi-\pi^*$ back-bonding. There has been a wealth of bond energy and derived thermochemical data reported for anions and neutrals in these studies.[188,189] These and other studies, particularly those of Armentrout and co-workers using beam techniques on positive ions, should be consulted for additional details.[57]

Related work with $CpM(CO)_x$, where M = V, Cr, Mn, Fe, Co, examines why the Mn−CO bond energy in neutral $CpMn(CO)_3$ (~55 kcal/mol) is substantially greater than that of the simple 18-electron metal carbonyls $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ (~37, 42, and 22 kcal/mol).[191] That is, does cyclopentadienyl bonding increase the M−CO bond strengths in various accessible anions? Energy-resolved CID studies of $CpV(CO)_3^-$, $CpV(CO)_3^-$, $CpV(CO)_2^-$, $CpCr(CO)_3^-$, $CpMn(CO)_2^-$, $CpMn(CO)^-$, $CpFe(CO)_2^-$, $CpCo(CO)_2^-$, $CpCo(CO)^-$, and $CpCo^-$ yield several M^-−CO bond energies that are near 40 kcal/mol, two that are nearer 47 kcal/mol ($CpCr(CO)_3^-$ and $CpMn(CO)_2^-$), and two that are less than 30 kcal/mol ($CpCo(CO)_2^-$ and $CpMn(CO)^-$) (Table 6). In addition, $CpCo(CO)^-$ preferentially loses the cyclopentadienyl anion on CID, not CO. All the other anions lose one or two CO molecules more readily than Cp^-. The more ready loss of CO from $CpCo(CO)_2^-$ and $CpMn(CO)^-$ than from the other anions studied is discussed in terms of Cp bonding patterns in $CpCo(CO)_2^-$ (η^5, η^4, and η^3); weakened Co−CO bonding would be expected in each case, and so, the CID experiments do nothing to address any structural questions of Cp bonding. The weak Mn−CO bond in $CpMn(CO)^-$ is attributed to a mismatch in the electronic structures of $CpMn^-$ and $CpMn(CO)^-$, where it is proposed that the promotion energy required for CO bonding in $CpMn^-$ must be large. The preferential loss of Cp^- in $CpCo(CO)^-$ is surprising, in view of its 17-electron configuration. The corresponding CpCo−CO bond in $CpCo(CO)^-$ is believed to be near 55 kcal/mol, which easily makes it the strongest M−CO bond studied, although the authors do not comment on this (Table 6). The original rationale for this study was to determine if the Cp ligand increased the M−CO bond strengths. On average, it does so by 3−4 kcal/mol.

Conclusion

The application of flowing afterglow techniques to anionic organometallic chemistry has highlighted the importance of this method in studying unusual species and reaction chemistry and in obtaining thermochemical information that is otherwise often difficult to gather. A number of examples of both main-group and transition-metal species have been presented.

Acknowledgment. I wish to express thanks to Dr. Shuji Kata for allowing the use of the schematic diagram (Figure 1) of one of the current Boulder flowing afterglow instruments. In addition, a great deal of the work described was funded by grants to R.D. from the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp., for which thanks are given. A number of wonderful collaborators participated in this work and are acknowledged for their insights and hard work. Particularly, the long and wonderful collaboration with Chuck DePuy and Ronnie Bierbaum made the flowing afterglow work a constant source of excitement and wonder. Finally, in rereading so much of the truly elegant work of Bob Squires, I was overwhelmed at what a great loss his early death was to the chemical community, not to mention the personal loss to his family and so many of his friends.

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[191] Sunderlin, L. S.; Squires, R. R. *Int. J. Mass Spectrom.* **1999**, *182/183*, 149−161.