nonmolecular compounds $Ca(OH)_2$,[6] $Mg(OH)_2$ (brucite),[6] $Ca(OR)_2$,[7] $Sr(OR)_2$,[7] and $Ba(OR)_2$[7] (R = Me, Et) all possess the CdI_2 structure.

In order to develop a reasonable structural model that correlates n and CN_{av} for various $[Ca(OCH_2CH_2OMe)_2]_n$ oligomer sizes, we make the following assumptions. First we assume that oligomers will adopt a CdI_2 core geometry. Thus, calcium atoms will arrange in a close-packed manner with each Ca_3 triangle capped by one μ_3 alkoxide, each Ca_2 edge bridged by one μ_2 alkoxide, and each remaining alkoxide occupying a terminal position. We also assume that each ether oxygen will participate in one Ca–O dative bond. We may then readily calculate CN_{av} as a function of n (see Figure 3). According to this model an aggregate with $n = 9$ produces a CN_{av} of 6.67, as was found in **1**, and as n decreases, so does CN_{av}. Similarly, as n increases above 9, CN_{av} increases above 6.67 (to a point).

Two opposing thermodynamic factors likely determine the observed aggregate size: (1) the enthalpic gains (per metal atom) resulting from coordinative saturation through internuclear bridge (dative-bond) formation and (2) the translational entropy losses (per metal atom) resulting from oligomerization. Typical coordination numbers for calcium(II) are 6–9, with 8 being most predominant.[8] Thus the n observed for **1** likely reflects a compromise between the preferences for a larger CN_{av} and for a larger number of independent particles. Because **1** is among the smallest aggregates able to satisfy the coordination requirements of calcium, Bradley's structural theory obtains.[9]

We propose that the competition between the enthalpic and entropic factors cited above provides the basis for Bradley's empirical argument.[3] Because the enthalpic benefits of forming internuclear dative bonds should drop off after the coordination requirements of a metal atom are satisfied, oligomerization should proceed only to the point of coordinative saturation. Thus, in cases uncomplicated by M–M bonds or directional M–L bonding such as the group 2 alkoxides, Bradley's theory should hold.

Soluble and volatile alkoxides of calcium(II), strontium(II), and barium(II) are presently sought for the preparation of high-T_c superconductors by sol–gel and CVD techniques.[1,10] However, group 2 alkoxides with conventional, monodentate alkoxide ligands are generally nonvolatile and poorly soluble in nondonor solvents,[11] probably as a result of nonmolecular, CdI_2-like structures.[7] Bidentate alkoxide ligands may reduce molecularities sufficiently to allow soluble derivatives (such as **1**) to be obtained. A simple extension of the reasoning above suggests that appropriate *tridentate* alkoxide ligands may produce molecularities as low as $n = 2$ (with a CN_{av} of 7.0), perhaps inducing volatility as well.

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Supplementary Material Available: Description of experimental details and listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** (14 pages); listing of observed and calculated structure factors for **1** (30 pages). Ordering information is given on any current masthead page.

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Carbene/Anion Complexes. Unusual Structural and Thermochemical Features of α-Halocarbanions in the Gas Phase

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Recent advances in experimental techniques for generating and detecting singlet carbenes have led to a wealth of new information concerning the structures, thermochemical properties, and reactivity of these important organic intermediates.[1-18] We recently

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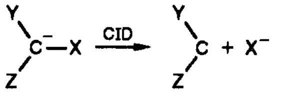
Table I. Halide Dissociation Energies of α-Halocarbanions

			ΔH (eq 1), kcal/mol	
$CXYZ^-$	X^-	CYZ	expt	theor[a]
CCl_3^-	Cl^-	CCl_2	30 ± 3[b]	30.9
$CFCl_2^-$	Cl^-	CFCl	24 ± 3	23.7
CF_2Cl^-	Cl^-	CF_2	<8.0	9.3
CF_3^-	F^-	CF_2	55 ± 3[b]	50.2
$MeOCHCl^-$	Cl^-	MeOCH	<8.5	11.5[c]

[a] ΔE(MP3/6-31+G(d)//6-31+G(d)) + ΔZPE; corrected to ΔH_{298}. [b] Reference 19. [c] Cl^- binding energy for structure illustrated in Figure 1B.

described a new general method for obtaining heats of formation for singlet carbenes in the gas phase from collision-induced dissociation (CID) threshold energy measurements with a flowing afterglow–triple quadrupole device.[19] The method relies on the accurate determination of an activation energy for the dissociation of a halide ion from a thermalized α-halocarbanion that has been subjected to low-energy collisional activation (eq 1). In cases



(1)

where the heat of formation of the precursor halocarbanion is known or can be determined from gas-phase acidity measurements, the heat of formation of the neutral singlet carbene fragment can be derived from the measured activation energy and a simple thermochemical cycle.

In the course of our investigation of a series of substituted carbenes with this technique, we discovered an unusual class of halocarbanion precursors that exhibit exceptionally labile carbon–halide ion bonds: so labile, in fact, that these ions are better viewed as gas-phase carbene–halide ion complexes rather than true carbanions in the conventional sense. Herein we describe combined experimental and computational studies of the structures and energetics of these novel species, along with a simple correlation model that provides verifiable predictions of the existence of additional examples.

Reaction between OH^- and the series of fluoro-, chloro-, and mixed chlorofluoromethanes in the helium flow reactor of the flowing afterglow produces variable yields of α-halocarbanions, along with both free and monohydrated ions from competing S_N2 displacement and α-elimination reactions.[20] Collisional activation of the mass-selected α-halocarbanions with argon target gas under single-collision conditions in the triple quadrupole analyzer results in efficient dissociation of halide ion; in all mixed chlorofluoromethyl anions, only the chloride ion fragment is observed. Careful monitoring of the dissociation yield as a function of the center-of-mass collision energy gives rise to an ion appearance plot from which the threshold dissociation energy can be obtained by an analysis procedure that we have described previously.[21]

The measured halide ion dissociation energies for the four $CF_nCl_m^-$ ($n + m = 3$) ions expose a remarkable trend (Table I). Replacement of Cl by F in CCl_3^- reduces the carbon–chloride bond energy by about 6 kcal/mol. Replacement of *two* Cl atoms by F as in CF_2Cl^- diminishes the chloride binding energy to a much greater extent, as indicated by the rapidly rising Cl^- yield from CID of CF_2Cl^- at collision energies less than ca. 0.3 eV (7 kcal/mol) in the center-of-mass frame. The extraordinary lability of the Cl^- ligand in CF_2Cl^- is further verified by the occurrence of rapid Cl^- transfer from this ion to both CO_2 ($D[CO_2-Cl^-] = 8.0 \pm 0.1$ kcal/mol)[22] and c-C_5H_{10} (D[c-$C_5H_{10}-Cl^-$] = 8.5 ± 0.5 kcal/mol)[23] under near-thermal conditions in the triple quadrupole collision cell.

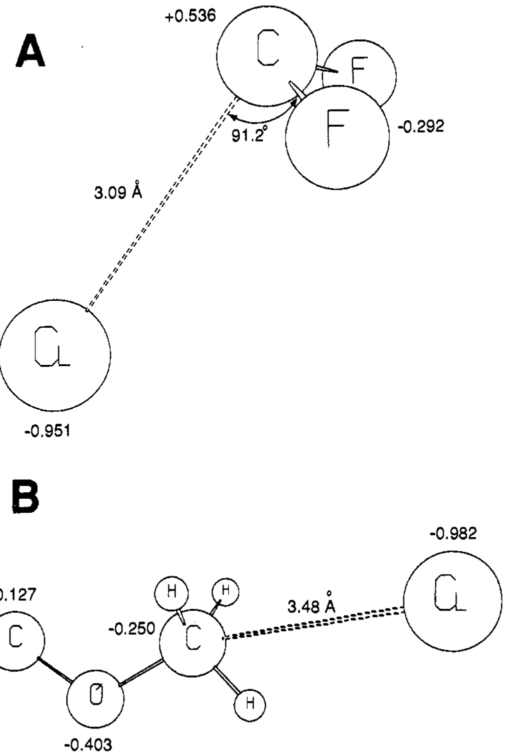


Figure 1. Computed structures and charge distributions at the 6-31+G(d) level for (A) the CF_2Cl^- ion and (B) deprotonated CH_3OCH_2Cl.

The reduced Lewis acidity of CF_2 toward Cl^- that is indicated by our experimental results is dramatically manifested in the computed structure and charge distribution for CF_2Cl^- obtained from ab initio SCF calculations with a 6-31+G(d) basis set (Figure 1A).[24] An extraordinarily long carbon–chlorine bond distance of 3.0 Å is obtained for CF_2Cl^-, with the chlorine atom situated at a nearly perfect 90° angle from the plane of a CF_2 moiety that closely resembles a free difluorocarbene molecule. Moreover, the Mulliken charges expose substantial positive charge at carbon and a nearly full −1 charge at chlorine. These are precisely the structural and electronic features that one would expect for a complex composed of a halide ion engaged in a weak Lewis acid–base (dative) interaction with the empty p orbital of the highly stabilized singlet CF_2.[25] Single-point energy calculations at the MP3/6-31+G(d) level with corrections for zero-point energy differences give a final calculated Cl^- binding energy (ΔH_{298}) for singlet CF_2 of 9.3 kcal/mol, in good agreement with our experimental results.

A methoxy group also strongly stabilizes singlet states of carbenes[26,27] and, therefore, should have a similar attenuating effect

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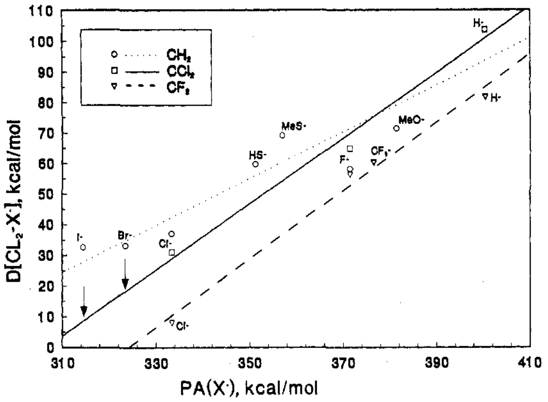

Figure 2. Correlation of proton affinities and singlet carbene binding energies for negative ions.

on the Lewis acidity of the carbene carbon. Reaction between CH_3OCH_2Cl and OH^- in the flow tube yields several products, among which is an $[M - H]^-$ ion. Exclusive deprotonation at the chloromethyl group is indicated by the absence of any $[M - D]^-$ product in the analogous reaction with CD_3OCH_2Cl. The CH_3OCHCl^- ion exhibits a Cl^- appearance plot from CID that closely resembles that for CF_2Cl^-, and it is observed to undergo exothermic transfer of Cl^- to c-C_5H_{10} and CS_2 ($D[CS_2-Cl^-]$ = 11.7 kcal/mol).[28] Low-level (4-31G) optimization of the geometry of CH_3OCHCl^- yields a C_1 "carbanion" structure with an unusually long C-Cl bond (2.6 Å). However, this carbanion structure is unstable at higher levels of theory with respect to Cl^- loss and rearrangement to the minimum energy geometry shown in Figure 1B. This remarkable structure incorporates a free carbene moiety and a Cl^- ion electrostatically bound to the backside of the methoxy group in a manner reminiscent of gas-phase S_N2 intermediates.[29] The computed Cl^- binding energy (ΔH_{298}) for this structure at the MP3/6-31+G(d)//6-31+G(d) and MP2(full)/6-31+G(d)//MP2(full)6-31+G(d) levels is 11-12 kcal/mol, in good agreement with our experimental results.

The Cl^- binding energies of singlet carbenes provide a direct measure of their relative Lewis acidities. We[30] and others[31] have previously noted the good linear correlations that often can be found between the binding energies of a series of negative ions to specific neutral Lewis acids and to the proton, i.e., between their Lewis and Bronsted basicities. Figure 2 illustrates a set of such correlations for singlet carbenes, where the requisite thermodynamic data for the various carbanions (CL_2X^-), negative ions (X^-), and carbenes (CL_2) are taken from results from our laboratory[19] or established literature data.[32] The linear relationship between $PA(X^-)$ and $D[CL_2-X^-]$ for singlet CH_2, CF_2, and CCl_2 extends over a wide range of anion basicities and provides a predictive capability for identifying additional candidates for gas-phase carbene/anion complexes. Thus, one predicts from the correlations that neither Br^- nor I^- will exhibit any binding other than weak electrostatic attraction to singlet CF_2. Moreover, Br^- should possess a ca. 20 kcal/mol bond strength toward singlet CCl_2, whereas I^- should have a CCl_2 bond energy of about half as much. After formulating these predictions, we generated a sample of the CCl_2Br^- ion in the flowing afterglow by deprotonating $CHCl_2Br$ and carried out energy-resolved CID studies. An appearance energy for Br^- of 0.9 eV (21 kcal/mol) was obtained, in excellent agreement with the predicted $D[CCl_2-Br^-]$ value from the correlation.

We are currently examining the gas-phase reactions of these unusual species with olefins and other reagents in pursuit of further evidence for their carbene character.

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Electron-Transfer Reaction of Cytochrome *c* Adsorbed on Carboxylic Acid Terminated Alkanethiol Monolayer Electrodes

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Protein electron-transfer (ET) kinetics is a topic of intense current interest.[1] Recent experimental progress has been due largely to the use of donor-acceptor species for investigating diffusionless intramolecular ET reactions.[1,2] Significant developments have also been reported for self-exchange reactions[1,3] and for direct electrochemical ET reactions.[4] Recently it has become clear that the ET kinetics of strongly adsorbed native proteins can be investigated from an *intramolecular* perspective using voltammetry, as shown for cytochrome *c* (cyt *c*) (sub)monolayers on tin oxide[5] and bis(4-pyridyl) disulfide modified gold.[6] This type of voltammetric approach is well suited for probing fundamental kinetic aspects of ET reactions[7] and was recently used to determine the reorganization energy of cyt *c* adsorbed on tin oxide.[5d] A highly desirable goal in this regard would be the development of electrode/adsorbed protein systems of controllable

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