carborane complex, and the microanalytical data suggested its molecular formula as $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$.[11] The crystal structure (see Figure 1) reveals that complex **1** has a 2-fold symmetry in which the rotation axis, parallel to *b*, passes through the atoms Mn(1), Li(1), and O(40) and bisects the angle Mn(2)-Mn(1)-Mn(2a) (plane 1).[12] Although the three Mn atoms form a central plane with the Mn-Mn distance of 2.682 (2) Å, the Mn(2)-Mn(2a) distance of 3.283 (2) Å and the Mn(2)-Mn(1)-Mn(2a) angle of 75.5 (1)° indicate that no direct bonding exists between the two terminal Mn atoms. However, the central manganese atom [Mn(1)] adopts an essentially $\eta^5$-bonding posture with respect to each of the $C_2B_3$ faces (plane 2), with the metal to cage distances ranging from 2.155 to 2.249 Å, which are significantly shorter than the Mn-$\eta^5$-carbon distance of 2.42 Å in the high-spin, polymeric, zigzag structure of $Mn(C_5H_5)_2$[4a,c] and slightly longer than those found in the low-spin, monomeric structure of $Mn(C_5Me_5)_2$.[4b]

The "butterfly" geometry of **1** is primarily due to bondings of the terminal manganese atoms to two adjacent borons of each of the central carborane ligands [Mn(2 or 2a)-B = 2.37-2.52 Å] as well as to the planar pentagonal faces (plane 3) of the terminal carborane ligands [Mn(2 or 2a)-Cnt(2) = 2.125 Å], each of which makes dihedral angles of 86.8° and 87.4° to the planes formed by the three Mn atoms and the C(1), C(2), B(3), B(4), and B(5) atoms of the central ligands, respectively (see Figure 1). Thus, compound **1** distinguishes itself from other structurally characterized trinuclear $\pi$-complex cluster systems such as $(\eta^5\text{-}C_5H_5)_3Mn_3(\mu_3\text{-NO})(\mu_2\text{-NO})_3$,[13] $[(\eta^5\text{-}C_5H_5)_3Mo_3(\mu_3\text{-S})(\mu_2\text{-S})_3]^+$,[14] and $[\{(C_2B_9H_9)(\text{4-methylisonicotinate})\}_3Cu_3(\mu\text{-H})_3]$,[15] all of which are based on an equilateral triangle of metal atoms. The bridging of two terminal carborane ligands by the $Li^+$(THF) moiety and bonding of each of the $Li^+$(TMEDA) groups to two adjacent borons of the respective cages form a zwitterionic cluster of **1** (see Figure S1, supplementary material). Since each carborane ligand bears a 2- charge and three $Li^+$ cations are present, the total formal oxidation states of three Mn atoms in **1** would be 5+. Because of a 2-fold symmetry, mentioned above,[12] it is expected that the two terminal Mn atoms would be identical and, therefore, would formally be in an oxidation state of either 2+ or 1+. Accordingly, the oxidation state of 1+ or 3+ could be assigned to the central metal Mn(1). In order to obtain more information regarding the oxidation states of the metals, magnetic measurements on a powdered sample of **1** were undertaken.

The magnetic susceptibility of **1** was measured in the temperature range 15-300 K using the Faraday method.[16] The room temperature effective magnetic moment of 8.3 $\mu_B$ for **1** is significantly less than the calculated spin-only value of 9.7 $\mu_B$ for the high-spin $Mn(II)_{terminal}$-$Mn(I)_{central}$-$Mn(II)_{terminal}$ trimer system. Therefore, it is most likely that cluster **1** consists of a trimer in which the central Mn could be formally in a 3+ oxidation state and bonded to two terminal Mn(I) atoms. The shorter Mn(1)-$C_2B_3$ cent(1) distance (1.708 Å) when compared to that of Mn(2)-$C_2B_3$ cent(2) (2.125 Å) strongly supports the assignment that **1** is a high-spin complex of the Mn(I)-Mn(III)-Mn(I) trimer system. Nevertheless, the magnetic moment decreases monotonically with decreasing temperature and reaches 6.2 $\mu_B$ at 15 K, indicating that a significant antiferromagnetic coupling exists between central Mn(1) and terminal Mn(2 or 2a) atoms. A significantly long distance of 3.283 (2) Å between the two terminal manganese atoms rules out the possibility of a direct coupling between Mn(2) and Mn(2a). There was no signal in the X-band EPR spectrum of **1** at room temperature.

The low-temperature EPR spectral measurements and theoretical expressions for the antiferromagnetic interactions of **1** are in progress. Investigations of the reaction chemistry of the zwitterionic **1** and other related sandwich cluster complexes are also currently underway in our laboratories.

**Acknowledgment.** This work was supported by grants from the National Science Foundation (CHE-9100048), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. W.E.H. gratefully acknowledges the Office of Naval Research for partial support.

**Supplementary Material Available:** Structural details for **1** including tables of positional and thermal parameters, selected bond distances, bond angles, and torsion angles, and Figure S1 (11 pages); listing of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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(11) IR (cm$^{-1}$; $C_6D_6$ vs $C_6D_6$): 2960 (ms), 2899 (w), 2840 (w) [$\nu$(CH)], 2520 (s), 2455 (s) [$\nu$(BH)], 2260 (s), 1455 (s) [$\delta(CH)_{asym}$], 1330 (s), 1245 (vs) [$\delta(CH)_{sym}$], 1180 (s), 1160 (s), 835 (vvs, br) [$\rho$(CH)], 750 (mw), 625 (w). Anal. Calcd for $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$: C, 42.37; H, 9.48; N, 4.12; Si, 16.51; Mn, 12.11. Found: C, 43.64; H, 9.36; N, 4.25; Si, 16.66; Mn, 11.77.

(12) $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$: fw, 1360.85. A data set was collected at 210 K on a dark brown platelike crystal of monoclinic space group *C*2/*c* with the following unit cell parameters: $a = 16.917$ (6) Å, $b = 23.925$ (10) Å, $c = 20.585$ (8) Å, $\beta = 97.05$ (3)°, $V = 8269$ (5) Å$^3$, $Z = 4$, and $D_{calcd} = 1.093$ g/cm$^3$, $\mu = 0.619$ mm$^{-1}$. Of 4801 data collected using a Nicolet R3m/V diffractometer (Mo K$\alpha$; 2$\theta$, 3.5-42.0°), 2763 reflections were considered as observed [$I > 3.0\sigma(I)$]. Compound **1** has a 2-fold symmetry in which the rotation axis, parallel to *b*, passes through the atoms Mn(1), Li(1), and O(40) and bisects the angle Mn(2)-Mn(1)-Mn(2a) (see Table I, supplementary material, for atomic coordinates). Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by the heavy-atom methods stored in the program package SHELXTL-PLUS (Sheldrick, G. M. *Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990). All non-H atoms were refined anisotropically. The exo-cage Si-C bond distances of the two disordered $SiMe_3$ groups [Si(1)-$Me_3$ and Si(2)-$Me_3$] were constrained during the refinements. Cage H atoms were located in difference Fourier maps, and methyl and methylene H atoms, except for those in the disordered methyl groups, were calculated. The final refinement converged at $R = 0.076$, $wR = 0.099$, and GOF = 2.08 for observed reflections. Maximum and minumum residual electron densities are 0.84 and -0.56 e/Å$^3$, respectively.

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# An Unprecedented Rapid and Direct $Br^+$ Transfer from the Bromonium Ion of Adamantylideneadamantane to Acceptor Olefins

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Adamantylideneadamantane (Ad=Ad) is unique among presently investigated olefins in that its structure absolutely impedes the progress of $Br_2$ addition beyond the stage of bromonium ion (I) formation.[1,2] In halogenated hydrocarbons, an equilibrium

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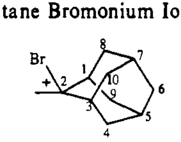
**Table I.** $^{13}C$ Nuclear Magnetic Resonance Chemical Shifts for the Adamantylideneadamantane Bromonium Ion (**I**-OTf$^-$) in $CD_2Cl_2$[a]



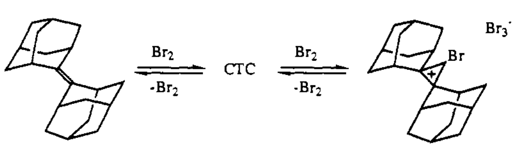
| carbon no. | δ (ppm) | lit.[b] | carbon no. | δ (ppm) | lit.[b] |
|---|---|---|---|---|---|
| 2,2′ | 156.24 | (158.6) | 7,7′ | 26.57 | (29.3)[c] |
| 1,1′,3,3′ | 36.99 | (39.8) | 5,5′ | 26.54 | (29.3)[c] |
| 8,8′,10,10′ | 42.69 | (45.0) | 6,6′ | 36.18 | (38.8) |
| 4,4′,9,9′ | 40.31 | (42.9) | | | |

[a] −45 °C; ppm using $CD_2Cl_2$ as internal reference; 100.6 MHz using a Bruker WH-400 spectrometer. [b] Reference 5, $T$ = 30–35 °C, neat $Br_2$ solvent. [c] $C_{7,7'}$–$C_{5,5'}$ resonances not resolvable.[5]

between **I**-Br$_3^-$, Ad═Ad, the Ad═Ad:Br$_2$ charge-transfer complex (CTC), and **I**-Br$_5^-$ is instantaneously established.[3] That equilibrium complicates the analysis of the solution properties of any of the partners in eq 1 and proves to be the source of an apparent 3-fold symmetry[4] of the carbon skeleton reported for the $^1H$ NMR spectrum of **I**.[2,5] It may also account for the observation that **I**-Br$_3^-$ transfers Br$_2$ to cyclohexene. Herein we report that the Br$_3^-$ can be successfully replaced by a nearly nonnucleophilic triflate counterion (OTf$^-$; $CF_3SO_3^-$) as outlined in eq 2. Also

$$\text{I-Br}_3^- + CF_3SO_3CH_3 \rightarrow \text{I-OTf}^- + CH_3Br + Br_2 \qquad (2)$$

we present dynamic NMR evidence for a completely unprecedented rapid transfer of Br$^+$ from bromonium ion **I** to acceptor olefins.



Ad═Ad I-Br$_3^-$

(1)

A $CH_2Cl_2$ suspension of 20–25 mg of **I**-Br$_3^-$ and excess $CH_3OTf$ in a 0.5-cm NMR tube with a Teflon liner was sonicated for 30–60 min until both dissolution and reaction were effected. Removal of the volatiles with a stream of Ar yielded a white residue that could be recrystallized from a 1:1 mixture of $CH_2Cl_2$/hexane to yield crystals suitable for X-ray diffraction,[6] which unambiguously showed the residue to be **I**-OTf$^-$.

The $^{13}C$ NMR spectrum of **I**-OTf$^-$ in $CD_2Cl_2$ at −80 °C consisted of a seven-line pattern indicative of a 2-fold symmetry: assignments given in Table I were made on the basis of APT experiments and are compared with those reported by Olah et al.[5] for **I** produced from Ad═Ad in neat Br$_2$. Addition of small amounts of Ad═Ad to the NMR tube caused broadening of the pairs of signals at δ 42.69, 40.31 and 26.57, 26.54. In the limit of addition, these pairs coalesce and the spectrum consists of five lines arising from species having an apparent 3-fold symmetry.[4] Line-shape analysis of the signals at δ 42.69, 40.31 as a function of seven added portions of Ad═Ad gave a second-order rate constant for the process of $1.0 \times 10^6$ $M^{-1}$ $s^{-1}$ (±5%, seven data) at −81 °C. That the process is first order in added [Ad═Ad] rules out the involvement of free BrOTf and any mechanism other than degenerate transfer of Br$^+$ from **I** to Ad═Ad. In a second set of experiments, the $^{13}C$ NMR spectrum of a $CD_2Cl_2$ solution of ~100 mM **I**-OTf$^-$ containing 2–3 mM [Ad═Ad] was monitored at six temperatures between −103 and −51 °C. Line-shape analysis of the two signals (δ 42.69, 40.31) gave the activation parameters $\Delta H^\ddagger = 1.8 \pm 0.2$ kcal mol$^{-1}$; $\Delta S^\ddagger = -21 \pm 1$ cal K$^{-1}$ mol$^{-1}$.[8]

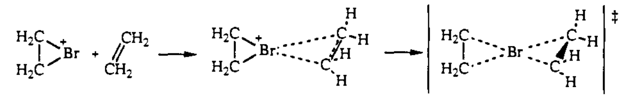
**Table II.** Selected Geometric Parameters for the Species in Eq 3

| fragment | parameter | isolated systems **II** | adduct **III** | transition structure **IV** |
|---|---|---|---|---|
| $C_2H_4Br^+$ | CC (Å) | 1.438 | 1.431 | 1.359 |
| | C–C(H$_2$)[a] (deg) | 14.75 | 14.35 | 4.90 |
| | CBr (Å) | 2.071 | 2.082 | 2.488 |
| $C_2H_4$ | CC (Å) | 1.318 | 1.323 | 1.359 |
| | C–C(H$_2$)[a] (deg) | 0.0 | 2.26 | 4.90 |
| | CBr (Å) | | 3.464 | 2.488 |

[a] C–C(H$_2$) denotes angle between CC bond and adjacent HCH plane.

**I**-OTf$^-$ also transfers Br$^+$ directly to cyclohexene. The $^2H$ NMR spectrum of a 500-μL solution of $CH_2Cl_2$, 6.4 mg of **I**-OTf$^-$ ($5 \times 10^{-6}$ mol), and 1 μL of cyclohexene-$d_{10}$[7] at −90 °C displayed only the $^2H$ resonances of $C_6D_{10}$ (δ (ppm) 5.75 (s, 2 D), 1.98 (s, 4 D), 1.60 (s, 4 D)). At −50 °C, the signals of $C_6D_{10}$ were slowly replaced by those of a $d_{10}$ product having no plane of symmetry (δ (ppm) 4.91 (s, 1 D), 4.06 (s, 1 D), 2.35 (s, 1 D), 2.30 (s, 1 D), 1.84 (s, 1 D), 1.76 (s, 1 D), 1.69 (br s, 2 D), 1.40 (s, 1 D), 1.30 (s, 1 D)). At ambient temperature, only the latter material was observed by $^2H$ NMR: no transient peaks or D-containing decomposition products were observed. The product proved to be *trans*-2-bromocyclohexyl trifluoromethanesulfonate-$d_{10}$[9] a material previously reported to be synthesized in 10–15% yield.[10]

Ab initio SCF calculations were carried out on the model system $C_2H_4Br^+$–$C_2H_4$ (eq 3) using effective-core potentials[11,12] in order to minimize the computational effort and the basis set superposition error (BSSE). The molecular basis set utilized triple ζ valence contraction for all atoms, augmented with two d type polarization functions[13] for heavy atoms, a diffuse p-type function ($\zeta_p = 0.044$) for bromine, and a polarization p-type function ($\zeta_p = 1.0$) added to Huzinaga's (5s/3s) basis for hydrogen.[14] The valence quality of this basis set was similar to the TZ2P basis used in a recent all-electron study on the ethylenebromonium ion.[15,16]



II III ($C_{2v}$) IV ($D_{2d}$)

(3)

The adduct of the ethylenebromonium ion and ethylene (**III**, eq 3) was stable in $C_{2v}$ symmetry (the C atoms in perpendicular planes) with an interaction energy of 4.27 kcal mol$^{-1}$ and a 3.464-Å distance between the Br and the carbon atoms of the ethylene. Both the geometric structure and the Mulliken atomic populations of the individual components remain essentially unchanged on formation of complex **III**.

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(9) (a) The $^1H$ NMR spectrum of *trans*-2-bromocyclohexyl brosylate exhibits peaks at δ 1.20–2.50 (m, 8 H), 4.00 (m, 1 H, C*H*Br), 4.60 (m, 1 H, C*H*OSO$_2$Ar): Brown, R. S.; Gedye, R.; Ślebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. The $^1H$ NMR spectrum of the addition product of 3,3,6,6-cyclohexene-$d_4$ and **I**-OTf$^-$ in $(CD_2Cl)_2$ shows two mutually coupled protons at δ 4.93 and 4.07; $J_{1,2}$ = 8.5 Hz.

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(16) The present valence-electron structure of the ion approximated the all-electron structure with satisfactory accuracy: $r_{CC}$ = 1.438 Å (1.434), $r_{CH}$ = 1.074 Å (1.073), $r_{CBr}$ = 2.071 Å (2.060), ∠HCBr = 107.14° (107.3), ∠HCH = 118.26° (118.2), where the all-electron values are given in parentheses.

The transfer of $Br^+$ between the two ethylenes requires a transition through the $D_{2d}$ structure (IV),[17] the energy of which was calculated to be 13.47 kcal $mol^{-1}$ above the energy of III (9.20 kcal $mol^{-1}$ above the energy of the isolated systems, II), reflecting sizable distortion of the molecular structure. The geometric parameters that vary most in the transfer are given in Table II.

From the experimental activation parameters, the second-order rate constant for the degenerate transfer of $Br^+$ from I to Ad=Ad at 25 °C is calculated to be $\sim 2 \times 10^7$ $M^{-1}$ $s^{-1}$. While it may be argued that I is atypical in that it cannot form normal addition products, we see no reason why a less encumbered bromonium ion would not be prone to transfer at comparable or even greater rates. These results indicate that intermolecular $Br^+$ transfer from ion to olefin must be considered as competitive with the various product-forming steps during the electrophilic bromination of olefins.

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[17] The energy of the $D_{2h}$ structure is $\sim$0.3 kcal $mol^{-1}$ above the energy of the $D_{2d}$ conformer.

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# Observation of the Heme–Globin Complex in Native Myoglobin by Electrospray-Ionization Mass Spectrometry

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In their native state, globular proteins are tightly folded, compact structures, certain of which may be characterized by the association of the globin with small, noncovalently bound cofactors and prosthetic groups. These proteins can be denatured and caused to unfold by subjecting them to high temperatures, extremes of pH, detergents, and solutions containing high concentrations of compounds like urea, guanidinium chloride, and organic solvents.[1] As the severity of the denaturing conditions is increased, the interaction between the globin and the cofactor can be weakened, with possible separation of the cofactor from the globin. For example, the oxygen-carrying protein myoglobin contains a noncovalently bound heme group in the hydrophobic pocket of the native globin chain that can be induced to unfold under acidic conditions, thus weakening the heme–globin interaction. Under these conditions, the heme moiety can be readily extracted into an organic phase, and this phenomenon forms the basis of widely used procedures for preparing apomyoglobin from the native proteins.[2,3]

A variety of techniques including acid–base titrations, spectrophotometry, viscometry, circular dichroism, fluorescence, and nuclear magnetic resonance have been applied to monitor these conformational changes in myoglobin.[4] Recently, we have demonstrated[5,6] that conformational changes in proteins can also be detected by electrospray-ionization mass spectrometry. Electrospray is a gentle method of ionization that produces intact, multiply protonated gas-phase ions directly from protein molecules in solution.[7-9] The multiply charged ions observed in the positive-ion spectra are produced by proton attachment to basic and deprotonated acidic sites in the protein and reflect, to some extent, the degree of protonation in solution. Because the availability and the effective p$K$'s of the acidic and basic side chains are determined by the precise conformation that the protein assumes under the conditions of study, the conformation can be probed by the extent to which the protein is observed to be protonated in electrospray ionization.[5,6,10]

The acid denaturation of myoglobins has been studied extensively under a variety of conditions.[11-14] In the case of horse[15] and sperm whale myoglobin,[4,14] the onset of denaturation occurs in the pH range 4.5–3.5 and depends strongly on the ionic strength of the solution. It has been shown that some of the histidines are

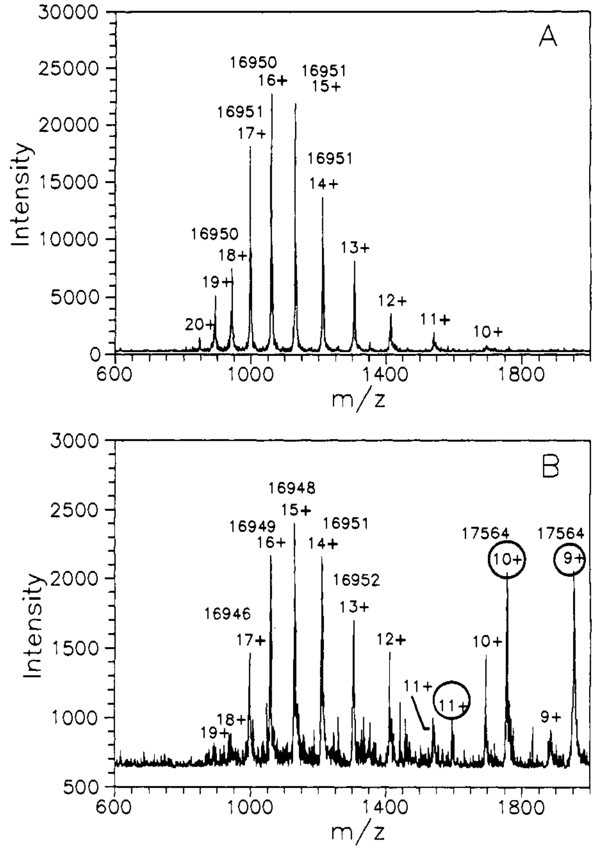

**Figure 1.** Electrospray-ionization mass spectra of equine skeletal muscle myoglobin obtained from aqueous solutions at different pH values: (A) 3.35; (B) 3.90. The protein concentration is 20–40 μM. The peaks are labeled with the protonation state, $n$+, and the number of protons, $n$, attached to the protein molecule. The circled protonation states designate the peaks corresponding to the intact heme–globin complex in myoglobin. The most intense peaks are also labeled with the molecular masses determinated from the measured $m/z$ values.

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