through proper choice of conditions it is possible to produce "cold" ion clusters which should be specially suitable for quantitative CID measurements.[26]

We believe that the described results indicate the dawning of a new era of gas-phase metal ion M^{2+} studies.

Acknowledgment. The present work was supported by grants from the Canadian Natural Sciences Research Council.

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[26] The $Co^{2+}(H_2O)_6$ used for the data in Figure 1b was "hot", i.e., it was produced by applying electric fields in the high-gas-density region outside the sampling orifice. This led to CID of the higher *n* clusters (see Figure 1a) and production of abundant but vibrationally excited $Co^{2+}(H_2O)_6$.

Synthesis and Crystallographic Characterization of $(Me_5C_5)_2Ca(Me_3SiC\equiv C-C\equiv CSiMe_3)$: The First Monomeric Diyne Complex of a Main-Group Element

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Although alkyne complexes are thought to be intermediates in a variety of transformations involving main-group metal and metalloid compounds (e.g., carbolithiation, carboalumination, and hydrostannation reactions), few well-documented examples of alkyne–main-group metal interaction exist.[1] Structurally characterized cases are limited to the complex lithium clusters $[Li({}^tBu-C\equiv C-C(SiMe_3)-C\equiv C-{}^tBu)]_2$ and $\{Li(LiOEt_2)({}^tBu-C\equiv C-C\equiv C-{}^tBu)\}_4$[2] and to Be,[3] Al,[4-6] Ga,[7,8] and In[8,9] complexes of the form $[RM-C\equiv CR']_2$ or $[R_2M-C\equiv CR']_2$ containing bridging alkynyl ligands. Alkynyl Tl(III) complexes of the form $Me_2TlC\equiv CR$ ($R = C_6H_5, CH_3$), $Me_2Tl-C\equiv C-TlMe_2$, and $M[Tl(C\equiv CR)_4]$ [$R = C_6H_5, CH_3$; $M = Na, K, (C_6H_5)_4P$] are also known and appear to remain monomeric in solution.[10] No structurally characterized monomeric main-group compound containing a neutral alkyne has yet been reported, and the inability of s- and p-block metals to engage in π-backbonding to the extent usually found in d-block metals might make the isolaton of a stable alkyne complex difficult. Nevertheless, alkynes have served as donors to relatively electron-poor metal centers, such as those of the lanthanides.[11-13] The calcium metallocene Cp^*_2Ca ($Cp^* = C_5Me_5$)[14,15] has been observed to bind to neutral donors such as ethers, nitrogen bases, and PEt_3, and we believed it would serve as a suitable substrate for studying alkyne–main-group metal interactions.

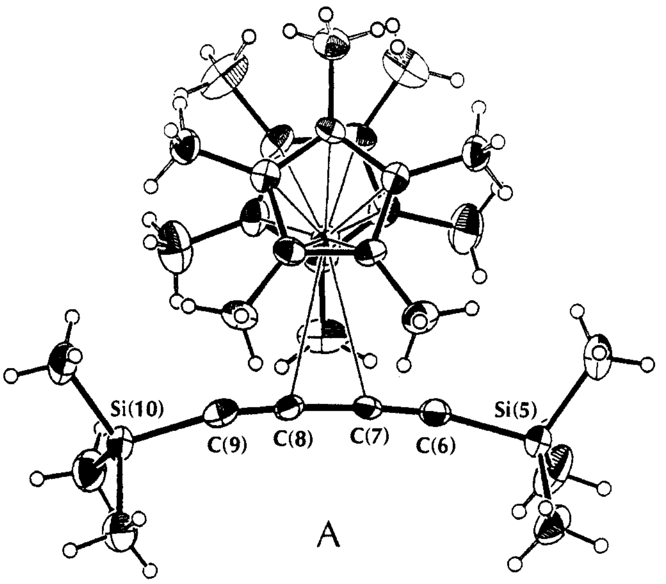

Figure 1. ORTEP view of adduct "A" of $(Me_5C_5)_2Ca(Me_3SiC\equiv C-C\equiv CSiMe_3)$, indicating the symmetrical attachment of the diyne to the calcium center. The lines from the Ca to the diyne depict the two shortest Ca–C(methyne) contacts.

Mixing colorless toluene solutions of Cp^*_2Ca and 1,4-bis(trimethylsilyl)-1,3-butadiyne (BTMSBD) under nitrogen results in the immediate formation of a deep orange color. Cooling a saturated hexane solution to −18 °C produces highly air-sensitive orange-yellow crystals. The proton NMR spectrum of the complex (300 MHz, C_6D_6, 20 °C) contains two peaks at δ 1.96 and 0.04; both values are only slightly shifted from the values in uncomplexed Cp^*_2Ca (δ 1.91)[14] and BTMSBD (δ 0.06), respectively.[16] The ^{13}C NMR spectrum reveals the expected resonances for the Cp* rings (δ 114.1 (Me_5C_5), δ 10.5 (Me_5C_5)), which are close to the values of the parent metallocene (δ 114.3, 10.3 respectively). Chemical shift values for the methyne carbons in the free ligand (δ 89.2, 86.8) move only minimally on complexation (δ 89.5, 86.2). Addition of an extra 1.5 equiv of BTMSBD generates an averaged set of resonances for the methyne carbons at δ 89.3 and 86.6, indicating that the free and complexed diyne are in fast exchange. At −80 °C, a toluene-d_8 solution of the complex containing an extra equivalent of BTMSBD reveals only two slightly broadened resonances at δ 88.1 and 87.7. In solution, the diyne is readily displaced by oxygen and nitrogen donors, such as ethers and amines. In the solid-state IR spectrum of the complex, $\nu(C\equiv C)$ appears at 2068 and 2053 cm^{-1}, a change from the uncomplexed value of 2067 cm^{-1} and an indication that the symmetry around the triple bonds has been reduced.

Details of the alkyne coordination were revealed in a single-crystal X-ray structure determination at −155 °C.[17] Two crystallographically independent molecules are present in the asymmetric unit; both contain a calcium atom flanked by two η^5-Cp* rings, with the BTMSBD unit wedged between them. The

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[17] Crystals of $Cp^*_2Ca(Me_3SiC\equiv C-C\equiv CSiMe_3)$ grown from hexane are monoclinic, space group $P2_1$, with $a = 10.325$ (2) Å, $b = 18.784$ (3) Å, $c = 16.390$ (3) Å, $\beta = 95.77$ (1)°, and $D_c = 1.06$ g cm^{-3} for $Z = 4$. Data were collected on a Picker four-circle goniostat at −155 °C using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Continuous θ–2θ scans with fixed backgrounds were used to collect a total of 6148 intensities (4277 unique) in the range $6° < 2\theta < 45°$, of which 4030 had $F > 2.33\sigma(F)$. No decay was observed during the collection. Data were reduced to a unique set of intensities and associated errors in the usual manner. The structure was solved with a combination of direct methods (MULTAN78) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. As not all of the hydrogens were evident on a difference Fourier map, their positions were calculated by using packing considerations and $d(C-H) = 0.95$ Å and were fixed for the final cycles of refinement. The final $R(F)$ value was 0.045 ($R_w(F) = 0.048$); GOF = 1.16.

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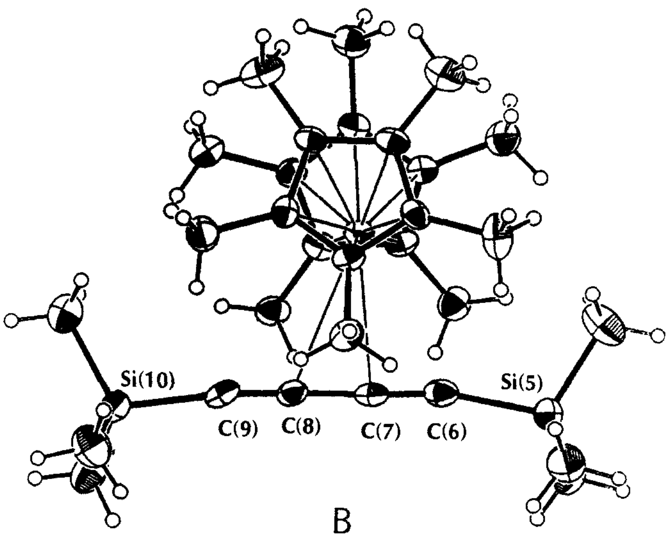

Figure 2. ORTEP view of adduct "B" of $(Me_5C_5)_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$. The two shortest Ca–C(methyne) contacts are represented by lines from the Ca to the diyne. Relative to adduct "A", the diyne has moved 0.81 Å to the side of the ring centroid–Ca–ring centroid plane.

average Ca–C distances are 2.64 (2) Å in one molecule ("A") and 2.66 (2) Å in the other ("B"); ring centroid–Ca–ring centroid angles are 143.4° and 145.4°, respectively (Figures 1 and 2). Although the average Ca–C distances are the same as those observed in Cp^*_2Ca (2.64 (2) Å),[15] the ring centroid–metal–ring centroid angles are slightly less than in the free metallocene (147.0°).

The distances within the butadiynes are typical for an uncomplexed alkyne, with C≡C, C–C, and C(methyne)–SiMe$_3$ distances averaging 1.21 (1), 1.38 (1), and 1.87 (1) Å, respectively. The terminal SiMe$_3$ groups are nearly eclipsed, with a torsion angle of 3.1° in "A" and 4.3° in "B". The SiMe$_3$ groups are bent away from the metal centers, the maximum deviation being 167.5 (4)° in "A" (C(8)–C(9)–Si(10)) and 167.4 (5)° in "B" (C(7)–C(6)–Si(5)).

The major difference between the conformers is the manner in which the butadiyne is associated with the metal center. In the "A" adduct (Figure 1), the diyne is symmetrically disposed around the ring centroid–Ca–ring centroid plane, with the two center methyne carbons at distances of 3.024 (5) Å (Ca–C(7)) and 2.991 (5) Å (Ca–C(8)), whereas the outer methyne carbons are substantially farther away (3.60 Å (Ca–C(6)) and 3.53 Å (Ca–C(9)). In the "B" adduct (Figure 2), the diyne has slipped ca. 0.81 Å to one side of the plane, so that the distances from the calcium to the center methyne carbons now differ by 0.23 Å (Ca–C(7), 2.878 (5); Ca–C(8), 3.104 (5) Å), and C(6) is brought to within 3.173 (5) Å of the metal center.

The significance of these Ca–diyne contacts is difficult to assess. The Ca–center methyne distances are considerably longer (by 0.24–0.46 Å) than the average Ca–Cp* distances, but the shorter ones are not far from the values observed for the f-element alkyne complex $Cp^*_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$ (2.829 (5), 2.871 (5) Å)[13] (the radius of Yb^{2+} differs by 0.02 Å from Ca^{2+}).[18] The Ca–C(8) distance of 3.104 Å is paralleled by a long Ca–(η^1-Cp) interaction at 3.100 (2) Å in the structure of Cp_2Ca.[19] Whether the 3.17 Å Ca–C(6) distance in "B" represents a significant bonding interaction, however, is not readily apparent.

The full extent of the interaction of group II organometallics with unsaturated hydrocarbons is under investigation.

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Supplementary Material Available: Tables of crystal data, fractional coordinates, bond distances and angles, and anisotropic thermal parameters (15 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

New μ_2-S^{2-}-Coupled, Singly Bridged Double Cubane with the $[(Fe_4S_4Cl_3)_2S]^{4-}$ Core. The Stepwise Synthesis and Structural Characterization of $(n\text{-}Bu_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$

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Synthetic analogues for the Fe/S sites in certain non-heme iron proteins, which contain cores such as $[Fe_2S_2]^{2+}$ and $[Fe_4S_4]^{2+}$, can be prepared conveniently by "spontaneous self-assembly", SSA, reactions from mixtures of appropriate reagents.[1] A drawback inherent in SSA reactions is the lack of predictability in situations where the target clusters are not necessarily the most thermodynamically stable species. An example of such a case has been encountered in attempts[2] to obtain Fe/Mo/S clusters, as analogues for the active site in nitrogenase.[2] The employment of SSA procedures thus far has not yielded clusters with the desired[2] Fe:Mo:S ratio of 7 ± 1:1:9 ± 1. Instead, single or double cubanes are obtained[3] with a Fe:Mo:S ratio of 3:1:4.

The Fe/M proteins in Mo nitrogenase[2] and in the recently discovered V[4] and Fe[5] variants (M = V, Fe) appear to contain structurally and stoichiometrically similar Fe/M/S centers. Recently we suggested[6] a general structural model for the Fe/M/S centers in the nitrogenases, with a site (M) capable of accommodating Mo, V, or Fe. This model (Figure 1) is a composite octanuclear cluster that contains the well-known Fe_4S_4[7] and MFe_3S_4 structural subunits (M = Mo,[3] V[8]) coupled by a single Fe–μ_2-S–Fe bridge. This cluster cannot be obtained by SSA reactions and must be synthesized by carefully controlled coupling reactions.

While this work was in progress, the solution NMR spectrum and electrochemical properties of a sulfide-bridged Fe_4S_4 double-cubane cluster were reported.[9] This compound was obtained by the sulfide coupling of a "site-differentiated" cubane.[10] In this communication, we demonstrate the feasibility of coupling

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