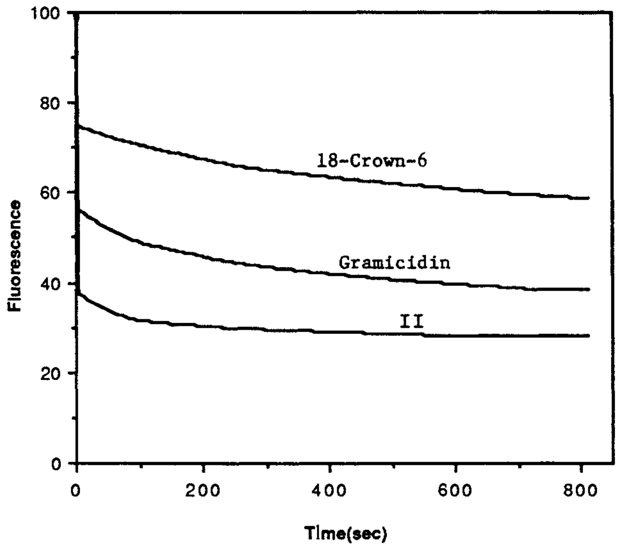

**Figure 2.** Comparison of 18-crown-6, gramicidin D, and II under conditions given in the caption of Figure 1. 18-Crown-6 is inactive, while the activity of II exceeds that of gramicidin D at 45 channel compounds/vesicle.

sufficed for total and immediate equilibration between external and internal ions. Greater than 1 molecule/vesicle is required for II because its ion-conducting segment (the polyether) is sufficiently long to traverse only a single leaflet. A *minimum* of two molecules (one in each leaflet) must, therefore, become aligned to permit passage across the entire membrane. This is also true of gramicidin.

Figure 1 compares the behavior of II (plot C) with that of related structures (plots A and B). Plot A, identical with the blank,[17] shows that all activity is lost if $n = 5$ and *both* R and R′ are dodecanoyl or *both* R and R′ are benzyl. Activity also disappears if R is II is shortened to a hexanoyl group. Plot B shows that activity is impaired if the polyether unit of II is shortened to $n = 3$. We conclude that spanning a polyether moiety across a leaflet to form a channel component requires (a) a benzyl group (presumably to associate with a DSCP quaternary nitrogen by an ion-dipole attraction)[18] and (b) a distal hydrocarbon tail that embeds itself in the apolar region of the membrane.

Figure 2 compares II with gramicidin D and 18-crown-6 at concentrations of 45 molecules/vesicle. Under these conditions, II actually exceeds gramicidin in activity! 18-Crown-6, on the other hand, manifests no enhancement above background. The latter is noteworthy because a U-tube system (a so-called "liquid membrane")[19] gives exactly the opposite behavior: $K^+$ was transported through $CHCl_3$ by 18-crown-6 at a concentration where II was totally inert. The simplest explanation is that the crown ether is a good ion carrier through $CHCl_3$,[20] whereas II (a poor $K^+$ ligand according to spectrophotometric studies)[21] is able to form channels in bilayers but not, obviously, in bulk $CHCl_3$.

Does II actually forge a channel, or does it merely create a defect? Although this is a difficult question to answer (especially since the distinction between a "channel" and "defect" is ill-defined), we prefer to view II as a channel element for the following reasons: (a) II is extremely active at nanomole levels. (b) Flux enhancement is structurally specific; several analogs of II that were both more and less hydrophobic lost all activity. (c) Leakage induced by II is not general; dye, for example, could not escape the channelized vesicles.[22]

**Acknowledgment.** This work was supported by the National Institutes of Health.

**Registry No.** II, 125109-54-8; $H_3C(CH_2)_{10}CO_2(CH_2CH_2O)_5CO(CH_2)_{10}CH_3$, 92411-21-7; $PhCH_2O(CH_2CH_2O)_5CH_2Ph$, 60389-48-2; $CH_3(CH_2)_4CO_2(CH_2CH_2O)_5CH_2Ph$, 125109-55-9; $CH_3(CH_2)_{10}CO_2(CH_2CH_2O)_3CH_2Ph$, 125109-56-0.

---

[17] The fluorescence decrease for DSPC without channels corresponds to an electrically uncompensated proton diffusion.[15]

[18] Stauffer, D. A.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 6039. Eriksson, J. C.; Gillberg, G. *Acta Chem. Scand.* **1966**, *20*, 2019.

[19] Cram, D. J. *J. Inclusion Phenom.* **1988**, *6*, 397. Lehn, J.-M. *J. Inclusion Phenom.* **1988**, *6*, 351.

[20] Stolwijk, T. B.; Sudhölter, E. J. R.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *J. Org. Chem.* **1989**, *54*, 1000.

[21] Flora, H. B., II; Gilkerson, W. R. *J. Phys. Chem.* **1976**, *80*, 679.

[22] A further account of work in the area will appear in an issue of the *Boletin de la Sociedad Chilena de Quimica* honoring the important Chilean chemist Professor Lucho Sepulveda.

---

## Production and Study in the Gas Phase of Multiply Charged Solvated or Coordinated Metal Ions

Palitha Jayaweera, Arthur T. Blades, Michael G. Ikonomou, and Paul Kebarle*

*Chemistry Department, University of Alberta*
*Edmonton, Alberta, Canada T6G 2G2*

*Received November 17, 1989*

Determinations of the gas-phase equilibria involving singly charged ions and solvent molecules such as $H_2O$ (see eq 1), or other ligands, providing the sequential bond enthalpies $\Delta H°_{n-1,n}$ and entropies $\Delta S°_{n,n-1}$ were initiated some 20 years ago.[1,2] Such

$$M^+(H_2O)_{n-1} + H_2O = M^+(H_2O)_n \qquad (n-1,n) \qquad (1)$$

studies have provided a wealth of data[3] on ion-solvent and ion-ligand interactions.[4] Extensive theoretical work[5,6] and experimental studies such as laser spectroscopy of ion clusters in molecular beams[7] were also stimulated.

The above studies were limited to singly charged ions $M^+$, yet doubly charged ions $M^{2+}$ are of paramount importance in chemistry and biochemistry. The general method used for ion clusters like $M^+(H_2O)_n$ is to generate $M^+$ in a gas phase in which ligand molecule vapor is present. The formation of $M^+(H_2O)_n$ then proceeds spontaneously by third body dependent association reactions like reaction 1. This method may not work[8] for $M^{2+}$ when the second ionization energy of M, IE($M^+$), is larger than the ionization energy of the ligand, e.g., IE($Mg^+$) = 15.0 and IE($H_2O$) = 12.6 eV.

Doubly and triply charged ions exist in solution, but preparation of gas-phase ions like $M^{2+}(H_2O)_n$ by ion transfer from solution to the gas phase would not have been considered possible until recently. However, new mass spectrometric research has shown[9-11]

---

[1] Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

[2] Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

[3] Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

[4] Kebarle, P. *Modern Aspects of Electrochemistry*; Conway, B. E., Bockris, J. O. M., Eds.; Plenum Press: New York, 1974; Vol. 9, p 1.

[5] (a) Kraemer, W. P.; Diercksen, G. H. F. *Chem. Phys. Lett.* **1970**, *5*, 463. (b) Diercksen, G. H. F.; Kraemer, W. P. *Theor. Chim. Acta* **1972**, 387. (c) Kishenmacher, H.; Popkie, H.; Clementi, E. *J. Chem. Phys.* **1973**, *59*, 5842.

[6] Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903.

[7] Okumura, M.; Yeh, L. I.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 79.

[8] Little information is available on the outcome of gas-phase reactions: $M^{2+} + L$ where IE($M^+$) > IE(L). Charge transfer to the ligand, leading to $M^+$ and $L^+$ and formation of $M^+OH + H_3O^+$ for cases where the ligand and the third body are $H_2O$, are reaction channels that could compete with formation of stabilized $M^{2+}\cdot L$.

[9] In electrospray, a solvent such as methanol containing low concentrations of an electrolyte ($10^{-6}$–$10^{-4}$ M) flows through a narrow metal capillary. When the capillary is placed at a high voltage relative to ground (~5–10 kV), a fine spray of charged droplets is emitted from the capillary tip. The evaporation of the droplets in the ambient air leads to formation of gaseous ions. Electrospray has been known since the 1940s, but ion detection with a mass spectrometer, first reported by Fenn,[10] led to a renewed interest in this phenomenon.

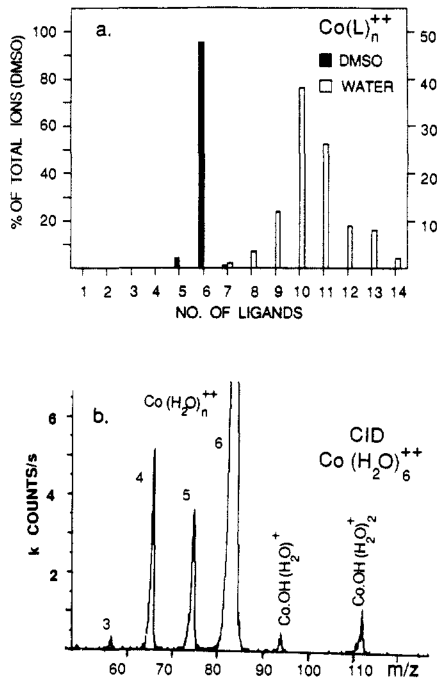

**Figure 1.** (a) Ions from separately electrosprayed solutions of $10^{-4}$ M $CoBr_2$ in methanol, with $10^{-2}$ M DMSO and 1 M $H_2O$. Observed $Co^{2+}(H_2O)_n$ had a total intensity of $2 \times 10^5$ ions $s^{-1}$. (b) CID of $Co^{2+}(H_2O)_6$.

that such ion transfer is feasible.

In the present work, we found that doubly charged gaseous ions are formed as major ions when solutions of doubly charged ions are electrosprayed.[12,13] Hydrates and other ligand complexes of $M^{2+}$ were observed as major ions for the alkaline earths ($Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) and the transition metals ($Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$.) A variety of $M^{2+}$ ion–ligand complexes with the above $M^{2+}$ and $Cr^{2+}$, $Cu^{2+}$, $Co^{3+}$ with the ligands dimethyl sulfoxide, dimethylformamide, ammonia, pyridine and the polydentate peptides, di- and polyketones, cyclic tetramines (cyclams), and the polycyclic hexaaminesepulchrate, could also be prepared and observed. This represents a very exciting variety of species and leads to the question: How can one study these ions?

So far electrospray has been operated only at atmospheric pressure.[10,11,14] Thermal ion–hydrate equilibria studies depend on mass spectrometric determination of ion–hydrate ratios at equilibrium,[2] and such determinations are difficult when the sampled gas is at atmospheric pressure.[16] In order to minimize the problem, the ions produced by electrospray in ambient air were transferred by means of an electric field into an "interface" or conditioning chamber,[13] which contains high-purity $N_2$ gas at atmospheric pressure and known, very low ligand gas pressure ($\sim 10^{-3}$ Torr). The ion residence time in the interface chamber is long enough ($\sim$200 $\mu$s)[17] for equilibria to become established,[18,19] and due to the high dilution of the ligand, no further growth of the ion–ligand complexes occurs during the sampling.[19]

The $Co^{2+}(H_2O)_n$ intensities, Figure 1a, can be used to obtain the $\Delta G°_{n,n-1}$ values: (10,9) 8.5, (11,10) 7.6, and (12,11) 7.2 (kcal/mol, 300 K, standard state 1 atm). Assuming[1,2] a "typical" $\Delta S°_{n,n-1}$ = 23 cal deg$^{-1}$ mol$^{-1}$, one obtains the corresponding $\Delta H_{n,n-1}$: 15.4, 14.5, and 14.1 kcal/mol. These can be compared with $\Delta H°_{3,2}(Na^+)$ = 15.8 kcal/mol.[1] The interface chamber can be heated, and results obtained at different temperatures will be reported.

The thermal ion equilibria method becomes difficult to apply for $\Delta H_{n,n-1} > 30$ kcal/mol, due to the required high temperatures. However, the triple quadrupole mass spectrometer used[13] allows measurements of higher energy processes by collision-induced decomposition (CID).[20]

The successive losses of $H_2O$ on CID of $Co^{2+}(H_2O)_6$ are shown in Figure 1b. These lead ultimately to $Co^{2+}(H_2O)_4$. At $n = 4$, the $H_2O$ loss reaction decreases greatly and a charge reduction reaction (2) becomes more probable. The $H_3O^+$ formation was

$$Co^{2+}(H_2O)_4 = CoOH^+(H_2O)_2 + H_3O^+ \qquad (2)$$

observed although this ion is not shown. A thermodynamic cycle based on the observed competitive loss of $H_2O$ and reduction 2 allows a rough estimate[21] of $\Delta H°_{3,0} \approx 180$ kcal/mol. The average ($n$,$n$-1) energy in the inner shell is $\sim$60 kcal/mol and thus very much larger than the $\Delta H°_{10,9} \approx 15$ kcal/mol for the outer-shell molecules, deduced above.

CID reactions analogous to reaction 2 at $n = 4$ were observed for $Mn^{2+}$, $Fe^{2+}$, and $Ni^{2+}$; however, the lower $IE(M^+)$ alkaline earths $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ could be dissociated down to $n = 1$ or $n = 0$ before a reduction reaction like 2 became competitive.

Binding energies $\Delta E_{n,n-1}$ can be obtained with the triple quadrupole CID technique, as shown by Magnera[22] and Squires[23] for single charged ions. Such measurements with $M^{2+}$ complexes are underway and will be reported.[24]

The $Co^{2+}(DMSO)_n$ results, Figure 1a, suggest special stability for $n \leq 6$. $Co^{2+}$ and $Ni^{2+}$ are known to form stable $M^{2+}(DMSO)_6$ complexes in the solid state.[25] The spectrum also illustrates how

---

(10) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4451, 4671. Whitehouse, C. M.; Dreyer, R. N.; Yamashita, M.; Fenn, J. B. *Anal. Chem.* **1985**, *57*, 675. Wong, S. F.; Menz, C. K.; Fenn, J. B. *J. Phys. Chem.* **1988**, *92*, 546.

(11) Ikonomou, M. G.; Blades, A. T.; Kebarle, P. *Anal. Chem.*, in press.

(12) Electrospray produces high yields, up to $5 \times 10^5$ ions/s, of $M^+$ ions, when salts of $M^+$ in $10^{-5}$–$10^{-4}$ M solutions in methanol and a few percent water are electrosprayed.[11] Similar conditions with $M^{2+}$ salts lead also to high $M^{2+}$ yields. The observation of $M^{2+}$ ions is not critically dependent on the electrospray capillary design. However, ions that are prone to charge reduction (see reaction 2), due to high $IE(M^+)$, should not be exposed to high electric fields at gas pressures that lead to CID. The mass spectrometer used in this work was an atmospheric pressure ionization triple quadrupole instrument[13] (TAGA 6000E, manufactured by SCIEX Ltd., Thornhill, Ontario, Canada).

(13) Reid, N. M.; Buckley, J. A.; French, J. B.; Poon, C. C. *Adv. Mass Spectrom.* **1979**, *8B*, 1843.

(14) Systematic investigations of ions produced by electrospray at lower pressures have not been reported; however, $M^{2+}$ ions at low pressures have been observed with a related technique, electrohydrodynamic ionization.[15] The $M^{2+}$ ions had to be complexed to polydentate ligands, and the yields relative to the reduced species $M^+$ were very low.[15]

(15) Callahan, J. H.; Hool, K.; Reynolds, J. D.; Cook, K. D. *Anal. Chem.* **1988**, *60*, 714.

(16) Searcy, Q. J.; Fenn, J. B. *J. Chem. Phys.* **1974**, *61*, 5282. Searcy, Q. J. *J. Chem. Phys.* **1975**, *63*, 4114.

(17) Sunner, J.; Nicol, G.; Kebarle, P. *Anal. Chem.* **1988**, *60*, 1300. (See Appendix I.)

(18) (a) In the $M^{2+}(H_2O)_n$ equilibria measurements, the ions were electrosprayed into ambient air which contained $\sim$3 Torr of $H_2O$ due to humidity. A similar pressure of methanol solvent is also present.[11] The $M^{2+}$ clusters in this regime have a very high $n$, but on entering the dry interface gas, they decluster thermally to much lower $n$. Simultaneous forward clustering reactions 1, which are believed to proceed at collision rates, lead to equilibrium. A voltage drop of 600 V across the 0.5-cm-thick interface chamber at 700 Torr leads to $E/N \approx 5$ Td (townsend), which is in the range used for thermal equilibria studies.[18b] Decrease of the potential to 300 V, which doubles the reaction time, had no effect on the relative ion $M^{2+}(H_2O)_n$ intensities, as expected for reaction equilibrium conditions. No electric fields were used in the vacuum region outside the 100-$\mu$m orifice of the interface chamber. This ensures no collisional breakup of the $M^{2+}(H_2O)_n$ ions. (b) Keesee, R. G.; Lee, N.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2599.

(19) (a) Determinations of equilibria 1 at 300 K with electrosprayed $Li^+$, $Na^+$, $K^+$, and $Rb^+$ led to $\Delta G°_{n-1,n}$ in good agreement with previous work.[1] Details of these results will be given elsewhere.[19b] (b) Blades, A. T.; Jayaweera, P.; Ikonomou, M. G.; Kebarle, P. *J. Chem. Phys.*, in press.

(20) Douglas, D. J. *J. Phys. Chem.* **1982**, *86*, 185. Dawson, P. H.; French, J. B.; Buckely, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 205, 212.

(21) $\Delta H_2 = \Delta H_{4,0}(Co^{2+}) - IE(CO^+) - D(Co^+OH) + \Delta H_{0,2}(CoOH^+) + IE(H_2O) + \Delta H_3 + CouE$; using $IE(Co^+) = 394$; $D(Co^+OH) = 71$ (Magnera[22]); $\Delta H_{0,2}(Co^+OH) \approx -60$ (arbitrary estimate); $IE(H_2O) = 290$; $\Delta H_3 = -26$, where $\Delta H_3$ corresponds to reaction $H_2O^+ + H_2O = H_3O^+ + OH$; and $CouE \approx 80$, where CouE corresponds to the kinetic energy released due to the coulombic repulsion of the two positive charges, estimated to be initially at 0.4 nm distance (all values in kcal/mol). Setting $\Delta H_2 \approx \Delta H_{4,3}(Co^{2+})$, since the two processes compete (see Figure 1b), one obtains $\Delta H_{3,0}(Co^{2+}) \approx 181$ kcal/mol.

(22) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Finkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100, 5036.

(23) Martinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

(24) Jayaweera, P.; Blades, A. T.; Kebarle, P., in preparation.

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.

---

(25) Cotton, F. A.; Francis, R. *Nucl. Chem.* **1961**, *17*, 62.

(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

R. Allen Williams and Timothy P. Hanusa*

*Department of Chemistry, Vanderbilt University*
*Nashville, Tennessee 37235*

John C. Huffman

*Molecular Structure Center*
*Department of Chemistry, Indiana University*
*Bloomington, Indiana 47405*

*Received November 27, 1989*

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 $\{Li(LiOEt_2)(^tBu{-}C{\equiv}C{-}C{-}C{\equiv}C{-}^tBu)\}_4$[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 $\pi$-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.

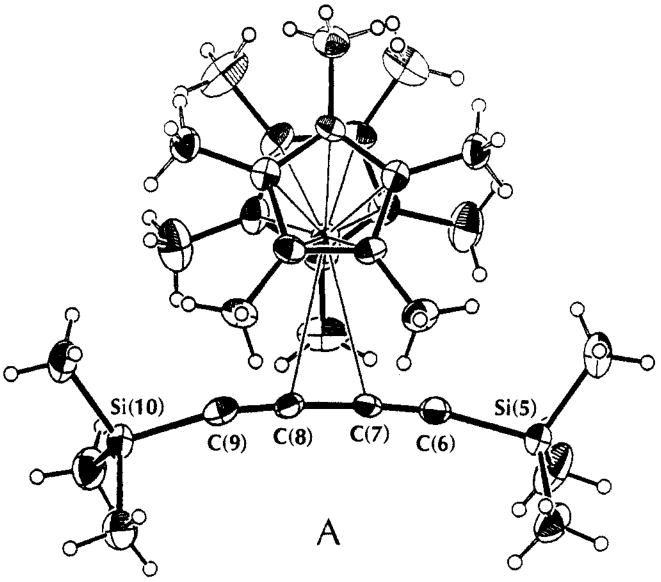

**Figure 1.** ORTEP view of adduct "A" of $(Me_5C_5)_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$, indicating the symmetrical attachment of the diyne to the calcium center. The lines from the Ca to the diyne depict the two shortest Ca–C(methyne) contacts.

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 $\delta$ 1.96 and 0.04; both values are only slightly shifted from the values in uncomplexed $Cp^*_2Ca$ ($\delta$ 1.91)[14] and BTMSBD ($\delta$ 0.06), respectively.[16] The $^{13}C$ NMR spectrum reveals the expected resonances for the Cp* rings ($\delta$ 114.1 ($Me_5\mathit{C}_5$), $\delta$ 10.5 ($\mathit{Me}_5C_5$)), which are close to the values of the parent metallocene ($\delta$ 114.3, 10.3 respectively). Chemical shift values for the methyne carbons in the free ligand ($\delta$ 89.2, 86.8) move only minimally on complexation ($\delta$ 89.5, 86.2). Addition of an extra 1.5 equiv of BTMSBD generates an averaged set of resonances for the methyne carbons at $\delta$ 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 $\delta$ 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 $\eta^5$-Cp* rings, with the BTMSBD unit wedged between them. The

---

(1) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217-295.

(2) Unpublished results cited in the following: Setzer, W. N.; von Ragué Schleyer, P. *Adv. Organomet. Chem.* **1985**, *24*, 354-451.

(3) Bell, N. A.; Nowell, J. W.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 147-148.

(4) Stucky, G. D.; McPherson, M. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941-1942.

(5) Almenningen, A.; Fernholt, L.; Haaland, A. *J. Organomet. Chem.* **1978**, *155*, 245-257.

(6) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235-271.

(7) Jeffrey, E. A.; Mole, T. *J. Organomet. Chem.* **1968**, *11*, 393-398.

(8) Fries, W.; Schwarz, W.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1978**, *159*, 373-384.

(9) Fjedberg, T.; Haaland, A.; Seip, R.; Weidlein, J. *Acta Chem. Scand.* **1981**, *A35*, 437-441.

(10) Nast, R.; Käb, K. *J. Organomet. Chem.* **1966**, *6*, 456-463.

(11) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401-1403.

(12) Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837-838.

(13) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 941-942.

(14) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31-37.

(15) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* In press.

(16) Williams, R. A.; Hanusa, T. P. Unpublished results.

(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 K$\alpha$ radiation ($\lambda = 0.71069$ Å). Continuous $\theta$–$2\theta$ 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.

0002-7863/90/1512-2454$02.50/0