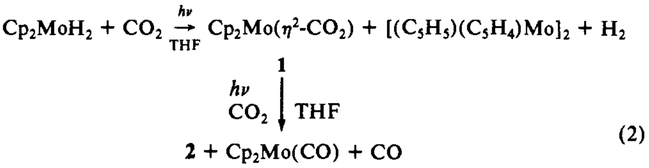
cm^{-1}, 4.48 ppm), free CO,[18] and a new complex **2** as a dark red precipitate with IR bands at 1670 and 1635 cm^{-1} (1620, 1590 cm^{-1} $^{13}CO_2$) and a single Cp resonance at 5.46 ppm.



$$Cp_2MoH_2 + CO_2 \xrightarrow[THF]{h\nu} \underset{\mathbf{1}}{Cp_2Mo(\eta^2\text{-}CO_2)} + [(C_5H_5)(C_5H_4)Mo]_2 + H_2$$
$$\downarrow h\nu,\ CO_2,\ THF$$
$$\mathbf{2} + Cp_2Mo(CO) + CO \qquad (2)$$

The fact that isolated complex **2** released CO_2 when treated with aqueous HCl and that **2** was also produced from the reactions of $NaHCO_3$ or Na_2CO_3 with Cp_2MoCl_2 ($EtOH/H_2O$/20 °C) led us to suspect **2** to be a carbonate complex. Ultimately, single crystals of **2** were obtained from THF/ethanol, and its structure was established by X-ray diffraction.[19] Figure 1 shows **2** to be $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_3)$. The structure of **2** features a planar molybdenum–carbonate fragment which approximately bisects the angle defined by the two Cp–Mo vectors (133.9 (2)°). Symmetrical bidentate coordination of the carbonate ligand is reflected in the equal Mo–O lengths. Within the carbonate unit essentially localized bonding is indicated by the long C(1)–O(1) and C(1)–O(2) bonds (1.337 (6), 1.322 (6) Å) and short C(1)–O(3) (1.216 (6) Å).[20-22]

The formation of carbonate complex **2** during photolysis naturally raises the question of whether the **1** → **2** transformation is itself photoinduced. Indeed, the following results clearly provide an affirmative response on this point: (1) the rate of carbonate (**2**) formation from Cp_2MoH_2 during irradiation is roughly the same at both −10 and +40 °C (determined by isolation), and (2) at −10 °C *transformation of CO_2 complex **1** to **2** occurs appreciably only during irradiation.* Figure 2 shows the dramatically accelerated disappearance of CO_2 complex **1**[23] (and appearance of carbonate **2**[18]) when irradiated compared to a dark control, monitored by IR. The quantum yield for the **1** → **2** conversion at 366 nm was found to be 0.04 (±0.02),[24] almost as efficient as the photoexpulsion of H_2 from Cp_2MoH_2 (ca. 0.1).[14a]

Although elucidation of the **1** → **2** mechanism must await the results of experiments in progress, free Cp_2MoO (Scheme I) apparently *is not* an intermediate since its reaction with CO_2 (Δ or $h\nu$) to give **2** was found to be much slower ($t_{1/2} > 100$ h) than the **1** → **2** photoconversion.[25]

These results provide the first solution phase example of photochemical activation of a metal–carbon dioxide complex.[26] Studies to further characterize the photoreactivity of **1** and to expand the scope of transition-metal-medated photochemical oxidations with carbon dioxide are underway.

Acknowledgment. We are grateful for financial support provided by the Energy Resources Institute of the University of Oklahoma and the U.S. Department of Energy (FG01-87FE61146). We also thank Dr. Eric Enwall for technical assistance and Dr. Harmon Abrahamson for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles and a structure of **2** showing numbering of Cp ring carbon atoms (5 pages). Ordering information is given on any current masthead page.

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[18] $Cp_2Mo(CO)$ photodissociates CO under these conditions[14] so that ^1H NMR monitoring initially shows parallel growth of **2** and $Cp_2Mo(CO)$ followed by gradual decline of the latter.

[19] Crystal data: Crystals of **2** were unstable at room temperature but stable at low temperature. Anal. Calcd for $C_{11}H_{10}MoO_3$: C, 46.2; H, 3.4; Mo, 33.5. Found: C, 45.5; H, 3.8; Mo, 32.7. $M_r = 286.14$, monoclinic space group $P2_1/n$ (nonstandard setting of $P2_1/c$), $a = 6.019$ (1) Å, $b = 12.752$ (2) Å, $c = 12.129$ (2) Å, $\beta = 94.60$ (3)°; $V = 927.9$ Å^3, $Z = 4$, $D_c = 2.048$ g cm^{-3}, $F(000) = 568$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 12.5 cm^{-1}. Cell dimensions and intensities of 1627 reflections were measured at −135 (2) °C ($2\theta_{max} = 50°$, $\pm h,k,l$) on an Enraf-Nonius CAD-4 diffractometer fitted with a low-temperature device. The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least-squares (hydrogen atoms were refined isotropically). All calculations were carried out by using the SHELX-76 program. For 1529 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.029$, $R_w = 0.034$, GOF = 1.6. $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

[20] In contrast, the only other second row metal–isobidentate complex, $(bipy)_2Ru(\eta^2\text{-}CO_3)$, has more nearly equal (1.297 (7) and 1.261 (13) Å) C–O lengths. Kimura, K.; Sakurai, T.; Shima, M.; Nagal, T.; Mizumachi, K.; Ishimori, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 112.

[21] Ionic carbonate, as in $CaCO_3$, has D_{3h} symmetry with C–O lengths of 1.294 (4) Å. Sass, R. L.; Vidale, R.; Donohue, J. *Acta Crystallogr.* **1957**, *10*, 567.

[22] For a review of metal–carbonate structures, see: Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

[23] The $Cp_2Mo(CO_2)$ employed in these experiments was isolated in ca. 33% yield by irradiation of Cp_2MoH_2 for 4 h followed by THF removal in vacuo and trituration with CO_2-saturated toluene (to remove unreacted Cp_2MoH_2 and $Cp_2Mo(CO)$).

[24] Lamp intensity was determined by using ferrioxalate actinometry at the 366-nm Hg line (band pass filter). Disappearance of **1** was monitored in the IR at 1745 cm^{-1}. The modest quantum yield may reflect the incursion of competing nonproductive processes, e.g., photoexpulsion/recombination of CO_2 and/or radiative decay to ground state.

[25] Furthermore, no Cp_2MoO was detected by IR or ^1H NMR during the photolysis of **1**.

[26] The studies listed in ref 4 involve photochemical production of a reduced metal complex which reacts thermally with CO_2 to give CO. Photooxidation of $M(CO)_6$ (M = Cr, W) by CO_2 in an argon matrix (20 K) has been observed, apparently via photoactivation of a transient CO_2 complex (ref 27).

[27] Almond, M. J.; Downs, A. J.; Perutz, R. N. *Inorg. Chem.* **1985**, *24*, 275.

The Gas-Phase Chemistry of the Silaacetylide Anion, $HCSi^-$

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Received December 14, 1987

The tandem flowing afterglow selected ion flow tube (FA-SIFT) is a versatile instrument which is especially suited to the investigation of the gas-phase chemistry of unusual ions.[1] We have used this instrument to generate the silaacetylide anion, $HC{\equiv}Si^-$,[11] and wish to report some chemistry of this interesting ion, particularly reactions which support the structure given over that of its tautomer. Ions of this type are of interest because of recent studies on the preparation of the neutral silicon–nitrogen triple bond[2] and the silicon–silicon triple bond synthon.[3] Our work represents the first report on the parent compound, $H_2C{=}Si{:}$.[4,11] A host of other unsaturated silicon anions can also be studied by this technique, and we report preliminary results on the chemistry of an ion of mass 43 to which we tentatively assign the structure $H_2Si{=}CH^-$.

In the FA-SIFT a mixture of anions of different masses can be produced by direct electron impact at 1 Torr helium pressure on silicon-containing neutrals in the first flow tube. Under these conditions, secondary reactions of ions with neutral precursors give rise to a rich array of ionic products. For example, electron impact on methylsilane produces over 20 anions corresponding in mass to Si^-, SiC^-, Si_2^-, and Si_2C^-, together with many of their hydrogenated analogues. At the end of this flow tube the ions

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[†] Denver.

[‡] Boulder.

[1] (a) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1987**, *109*, 4412. (b) DePuy, C. H.; Barlow, S. E.; Van Doren, J. M.; Roberts, C. R.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1987**, *109*, 4414. (c) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.*, in press.

[2] Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 111.

[3] Sekiguchi, A.; Zigler, S. S.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4241.

[4] For a review of the gas-phase chemistry of silicon compounds and their ions, see: DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Shelton, J. C. *Acc Chem. Res.* **1987**, *20*, 127.

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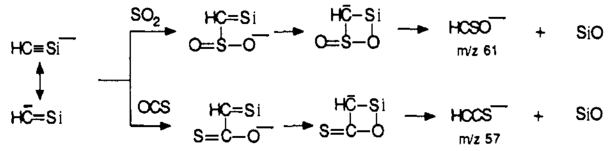
Scheme I



are sampled into a vacuum chamber, the neutral precursor and the helium are removed by pumping, and the ions whose chemistry is to be studied are separated in a quadrupole mass filter from ions of other masses and injected into the second flow tube. There they are allowed to react with neutral reagents, and the resulting anionic products are sampled, separated in a second quadrupole, and detected with an electron multiplier. The results reported in this communication for the silaacetylide ion (*m*/*z* 41) were obtained from ions produced from both methylsilane and tetramethylsilane; those for the silene anion (*m*/*z* 43) came from methylsilane.

We first measured the basicity of $HCSi^-$. It reacts readily with CH_3SH ($\Delta H^\circ_{(acid)} = 357 \pm 3$ kcal/mol)[5] to form CH_3S^- but not with HF (371 ± 2), acetone (369 ± 3), or acetophenone (362 ± 2). These results suggest that $\Delta H^\circ_{(acid)}$ ($H_2C{=}Si{:}$) = 360 ± 3 kcal/mol.[6] For comparison, $\Delta H^\circ_{(acid)}$ (acetylene) = 378 ± 2. The silaacetylide ion can have the structure with hydrogen either on silicon or on carbon. Preliminary ab initio computations by Professor M. S. Gordon[7] strongly favor a structure with hydrogen bound to carbon. This same structure also best fits the chemistry of the ion. Its most revealing reactions are cleavages with SO_2 and COS, leading to ions of *m*/*z* 61 and 57, respectively. We picture these ions as arising by initial attack by carbon followed by silicon-oxygen bond formation and fragmentation (Scheme I). An analogous cleavage reaction of the allenyl anion has been observed earlier.[8]

The silaacetylide ion does not appear to react with CO_2. However a cleavage reaction like that in Scheme I would lead to the ketene anion, also of *m*/*z* 41, so that reaction would be undetectable. Indeed, $^{13}CO_2$ converts the *m*/*z* 41 ion to *m*/*z* 42 (eq 1).

$$\mathrm{HC{\equiv}Si^- + {}^{13}CO_2 \longrightarrow \overline{C}H{=}{}^{13}C{=}O + SiO} \qquad (1)$$

We have looked briefly at the chemistry of the *m*/*z* 43 ion, which corresponds in mass to CH_3Si^- and is formed by electron impact on methylsilane. There are four possible tautomeric structures for an ion of planned. a mass, with $CH_2{=}SiH^-$ being favored on the basis of preliminary calculations by Gordon.[9] We find that upon reaction with SO_2 (eq 2), the same *m*/*z* 61 ion is formed from silaacetylide, a result which seems to favor the alternative tautomeric structure with a single hydrogen on carbon.

$$\mathrm{H\overline{C}{=}SiH_2 + SO_2 \longrightarrow HCSO^- + H_2SiO} \qquad (2)$$

However, COS and CS_2 react by sulfur atom transfer,[10] while CO_2 fails to react at all so that we do not consider this single reaction a definitive proof of structure. Additional studies on these and other unsaturated silicon anions are planned.

Acknowledgment. R.D. and C.H.D. thank the National Science Foundation for support of this work (CHE-8615808 and CHE-8503505, respectively).

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[5] Bartmess, J. E., personal communication. All acidity values used come from an unpublished compilation supplied by Professor Bartmess. This is an updated version of the tables published by Bartmess and McIver (Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2).

[6] This value assumes that proton abstraction from acetone and acetophenone by the silaacetylide ion is fast enough to be observed if it were exothermic. However, proton transfers to and from carbon and silicon can be slow.[7] Exothermic proton transfers from HF are unlikely to be slow, so that a more conservative value for $\Delta H_{(acid)}$ is 364 ± 7 kcal/mol.

[7] Gordon, M. S., personal communication to R.D. Professor Gordon has initiated a comprehensive computational study of the anions reported in this paper as well as a variety of others for which we have experimental work in progress.

[8] DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556.

[9] Preliminary computations on the silene anions suggest that $CH_2{=}SiH^-$ is more stable than $SiH_2{=}CH^-$ by some 35 kcal/mol. Though is it unlikely that the energy ordering of these two anions will change with additional computational refinements, computations on related isomeric structures have yet to be carried out and might reveal other stable isomers.

[10] DePuy, C. H.; Bierbaum, V. M *Tetrahedron Lett.* **1981**, *22*, 5129.

[11] We have called this the silaacetylide anion recognizing that the parent is undoubtedly $H_2C{=}Si{:}$ as has been demonstrated by a number of computational studies (see: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1986**, *108*, 270 and references therein). Both the acidity and reactivity studies in this communication are consistent with the formation of an anion, $[HCSi]^-$, which reacts at a relatively negative carbon to which hydrogen is bound.

Isolation and Structure of the Powerful Cell Growth Inhibitor Cephalostatin 1[1]

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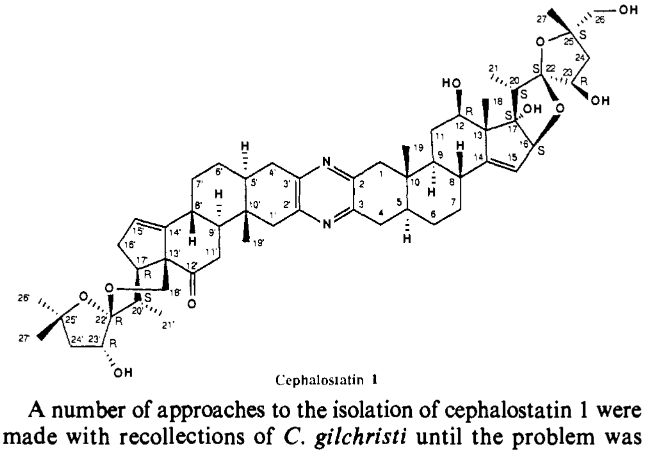
Received July 22, 1987

The invertebrate chordates have some vertebrate characteristics such as a dorsal tubular nervous system and notochord. Among such phyla lacking a vertebral column occurs the Hemichordata. The class Pterobranchia of this phylum has not heretofore been explored in respect to biologically active or other chemical constituents. In late 1972, we collected by SCUBA (ca. -20 m) in the Indian Ocean off Southeast Africa, in areas patrolled by the great white shark *Carcharodon carcharias*, specimens from this class of the marine worm (~5-mm long in tube colonies) *Cephalodiscus gilchristi* (order Cephalodiscida).[2] Two years later, methanol and water extracts of *C. gilchristi* reached the confirmed active level against the U.S. National Cancer Institute's murine P388 lymphocytic leukemia (PS system) with 32-41% life extension at 25-37.5 mg/kg. We now are pleased to report that 15 years of relentless research directed at discovering the active constituent(s) has culminated in the isolation and structural elucidation of a powerful cell growth inhibitory substance designated cephalostatin 1 (**1**) with PS cell line ED_{50} 10^{-7}–10^{-9} μg/mL.



Cephalostatin 1

A number of approaches to the isolation of cephalostatin 1 were made with recollections of *C. gilchristi* until the problem was eventually solved by using a 1981 acquisition (166 kg wet wt, including Coenecium). A methylene chloride–methanol extract was successively partitioned by using the system 9:1 → 4:1 → 3:2 methanol–water against hexane → carbon tetrachloride → methylene chloride, respectively. The active methylene chloride

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[1] Contribution 147 of "Antineoplastic Agents". For the prior part, see: Pettit, G. R.; Singh, S. B.; Hamel, E.; Lin, C. M.; Schmidt, J. M.; Alberts, D. S.; Kendall, D. G. *Experientia*, submitted for publication.

[2] Barrington, E. J. W. *The Biology of Hemichordata and Protochordata*; W. H. Freeman and Co.: San Francisco, CA, 1965; pp 1-176, and references therein.

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