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Preparations of Novel Cage Molecules: 2,3,5,6-Tetrachalcogena-1,4-disilabicyclo[2.1.1]hexanes

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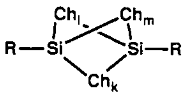
Summary: A new type of cage molecule that consists of two silyne units and three chalcogen bridges (containing four S or Se atoms) was prepared. Its notable stabilities are discussed.

Some trifunctional silanes react with chalcogens (or chalcogen-containing molecules) under appropriate conditions to give silsesquioxanes,[1] adamantane-type silthianes,[2] or silselenanes.[2a] These cage molecules consist of chalcogens and four or more silyne units. However, such a molecule consisting of only two silyne units and three chalcogen bridges (general form **1**) is not known, although interesting properties have been predicted.[3] Moreover, the carbon analogue **2** (Ch = a chalcogen atom; k, l, m = 1, 2, 3, ...) also is not known. In this paper, we report the first preparations of novel cage molecules **1a** and **1b** ($l = m = 1$, $k = 2$; Ch = S, Se).[4]



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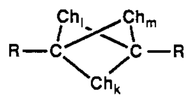
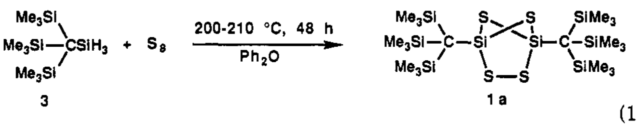


2

The trisyl group (trisyl = tris(trimethylsilyl)methyl) was introduced on the Si atom as a very bulky substituent in order to prevent polymerization or oligomerization of the silyne unit.[5]

A mixture of 1.50 g (5.71 mmol) of trisylsilane (**3**), 10 g (0.31 mol) of elemental sulfur, and 30 mL of diphenyl ether was heated at 200–210 °C for 48 h under a nitrogen atmosphere. 1,4-Bis[tris(trimethylsilyl)methyl]-2,3,5,6-tetrathia-1,4-disilabicyclo[2.1.1]hexane (**1a**) was isolated from the reaction mixture by silica gel column chromatography, TLC, and GPC in a 6.1% yield as odorless, pale yellow crystals (eq 1, Table I). An analytically pure sample was obtained by sublimation and repeated recrystallization from CCl_4/EtOH or n-hexane/EtOH mixed solvent.[6] The structure was determined on the basis of its elemental analysis and ^1H NMR, ^{13}C NMR, and MS spectra.[7] The ^1H and ^{13}C NMR spectra show the Me_3Si signal as one singlet, respectively, and no IR absorption due to Si–H or Si–SH was observed. These data were consistent with the structure of the cage molecule **1a**.[8]



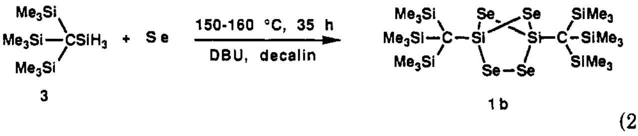
(1)

Table I. Spectral Data and Physical Properties of 1a,b

	1a	1b
color and habit	pale yellow needles	reddish orange plates
mp/°C[a]	330–334	342–345
sublimation point/°C	250	280
absorption spectra, λ_{max}/nm (ϵ)[b]	227 (s) (1600) 251 (s) (730) 319 (s) (130)	243 (s) (2400) 280 (s) (620) 450 (60) 500 (s) (30)
^1H NMR[c]/δ	0.418 (s)	0.441 (s)
^{13}C NMR[d]/δ	5.00 (q), 6.43 (s)	5.10 (q), 6.04 (s)
^{29}Si NMR[e]/δ	0.5 (SiMe)[f]	13.1 (Se–Si), 0.9 (SiMe)

[a] In sealed tubes. [b] In n-hexane. [c] In $CDCl_3$; 500 MHz. [d] In $CDCl_3$; 125 MHz. [e] In $CDCl_3$; 18 MHz. [f] The measurement of the ^{29}Si NMR signal for the bridgehead silicon was unsuccessful by routine methods.

The compound **3** did not react with elemental Se in decalin (or Ph_2O) under the same reaction conditions described above, so DBU (1,8-diazabicyclo[5.4.0]-7-undecene) was added to the reaction mixture as an activator of elemental Se (eq 2).[9] A mixture of 200 mg (0.761 mmol) of trisylsilane (**3**), 0.6 g (7.6 mol) of elemental Se, 0.1 mL of DBU, and 10 mL of decalin was heated at 150–160 °C for 35 h under a nitrogen atmosphere. 1,4-Bis[tris(trimethylsilyl)methyl]-2,3,5,6-tetraselena-1,4-disilabicyclo[2.1.1]hexane (**1b**) was isolated by silica gel column chromatography and GPC in 8.4% yield as reddish orange crystals. The structure of **1b** was determined on the basis



(2)

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(1) Silsesquioxanes, $(XSiO_{1.5})_n$ with $n = 2m$ ($m \geq 2$); i.e., n = 4, 6, 8, 10, 12: Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199. Agaskar, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 6858. Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288. Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *373*, 153.

(2) (a) Forstner, J. A.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 552. (b) Bart, J. C. J.; Daly, J. J. *J. Chem. Soc., Chem. Commun.* **1968**, 1207. Bart, J. C. J.; Daly, J. J. *J.* Chem. *Soc., Dalton Trans.* **1975**, 2063.

(3) The nonbonded Si–Si distance of 2,4,5-trioxa-1,3-disila[1.1.1]pentane is predicted to be comparable to the Si–Si triple-bond distance by: Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063.

(4) For conversion or lectures, we use the nonsystematic name "chaclane" as the general name of 1 and 2 for simplicity: Definitive Rules for Nomenclature of Organic Chemistry. *J. Am. Chem. Soc.* **1960**, *82*, 5545. Chaclane is associated with the systematic name "...*chalco*-genabicyclo[*k.l.m*]...*ane*".

(5) Eaborn, C. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, U.K., 1985; p 123, and references cited therein.

(6) The multistep isolation and purification processes were required to remove elemental sulfur and polymeric sulfur and to deal with the following problems. An NMR sample needs purifying above 99.9%, because a small amount of impurity makes the assignment of the signals very difficult in this system. For example, in ^{13}C NMR spectra the number of primary carbons is 9 times as many as that of quaternary carbons; actually, the intensity of quaternary carbons was about $^1/_{30}$ times as small as that of the primary carbons. It is hard to distinguish from a signal of an impurity if an impurity is present.

(7) **1a**: MS m/e 646 (M^+). Anal. Calcd for $C_{20}H_{54}Si_8S_4$: C, 37.10; H, 8.41. Found: C, 37.07; H, 8.51.

(8) The measurement of ^{29}Si NMR spectra of **1a** was unsuccessful by routine methods. The ^{29}Si NMR signal of the bridgehead silicon is hard to observe, probably because of the effect of the quadrupole moment of the sulfur atoms. In other thiachaclanes, the ^{29}Si NMR signal could be observed; details will be published in a forthcoming paper. The other spectral data are given in Table I. The X-ray crystal structure of **1a** could not be analyzed because of its internal twin structure.

(9) With the aid of DBU, Se was dissolved in the solution: Tokitoh, N.; Hayakawa, H.; Goto, M.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 1935. Chenard, B. L.; Miller, T. J. *J. Org. Chem.* **1988**, *49*, 1221.

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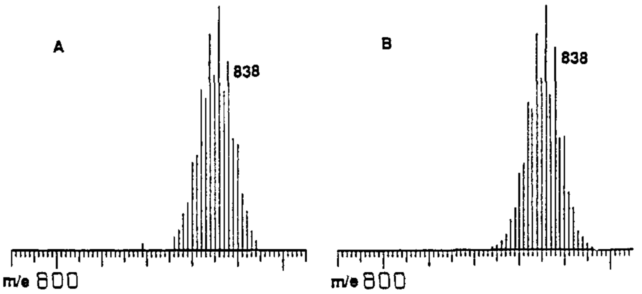


Figure 1. Mass spectra for **1b**: observed abundance of isotopomers of M^+ (A) and its computer simulation (B) for $C_{20}H_{54}Si_8Se_4$.

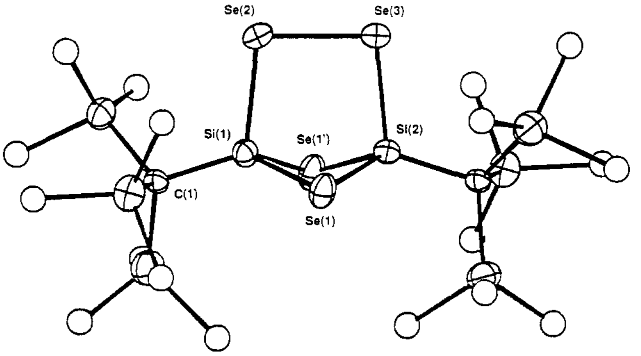


Figure 2. X-ray structure of **1b**. Selected bond lengths (Å) and angles (deg): Si(1)–Se(1), 2.252; Si(2)–Se(1), 2.234; Si(1)–Se(3), 2.325; Si(1)–Se(1′), 2.331; Si(2)–Se(1′), 2.312; Si(2)–Se(2), 2.294; Se(2)–Se(3), 2.353; Si(1)–C(1), 1.855; Si(1)–Si(2), 2.820; Si(1)–Se(1)–Si(2), 77.9; Si(1)–Se(1′)–Si(2), 74.8; Se(1)–Si(1)–Se(1′), 95.9; Se(1)–Si(1)–Se(3), 100.9; Si(1)–Se(3)–Se(2), 95.7; Si(2)–Se(2)–Se(3), 95.9; Se(1)–Si(2)–Se(2), 100.9.

of its spectral data (Table I).[10] An analytically pure sample was obtained by recrystallization from *n*-hexane/EtOH or chloroform. The electronic absorption spectrum of **1b** showed nearly the same absorption maximum (450 nm) as observed for five-membered cyclic diselenides (ca. 440 nm), which in the case of the latter depends on the dihedral angle between the lone-pair orbitals.[11] The observed abundance of isotopomers of M^+ in the EI 20-eV mass spectrum of **1b** was in good agreement with the computer-simulated abundance (Figure 1).[12]

Compounds **1a**,**b** had nearly the same physical properties and spectral features. They are extremely stable to solvolysis even in boiling MeOH or EtOH. The steric protection of the trisyl group must be effective, because normal silthianes and silselenanes (for example, $Me_3SiSSiMe_3$ and $Me_3SiSeSiMe_3$) easily react with alcohol or atmospheric moisture.[2,13] Silsesquioxanes are expected to be used for new materials displaying a very high heat resistance and thermooxidative resistance;[1] **1a**,**b** also showed high thermal stability (Table I).

The structure of **1b** was confirmed by an X-ray crystal analysis (Figures 2 and 3).[14] The tetraselenadisilabicyclo[2.1.1]hexane framework and the SiMe group exhibited inversional disorder with regard to the center of symmetry, which locates the middle Se atoms of Si–Se–Si bridges (Figure 3). One of the molecules is separately shown in Figure 2. Since the quaternary carbons, one SiMe of the trisyl group, and Se atoms of Si–Se–Si bridges are coincidental with regard to two disordered molecules, the site occupancy factors of the remaining atoms should be 0.5, not 1.0. An X-ray structure of a trisyl-substituted compound is often observed as a disordered structure.[15] The Si–Se–Si angle of **1b** is very sharp, compared with a normal Si–Se–Si angle (ca. 96°).[16] One of the anges 74.8°, has almost the same value as the Si–O–Si angle of 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane (74.7°).[3,17]

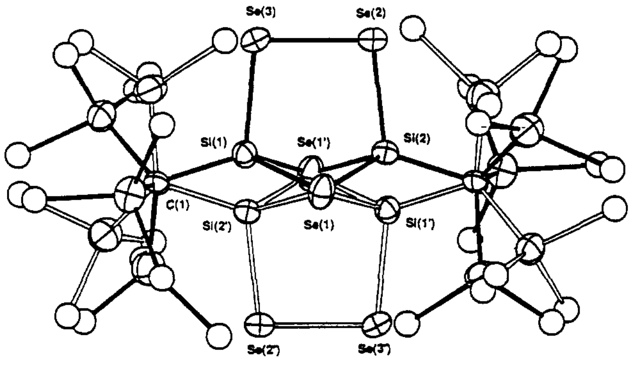
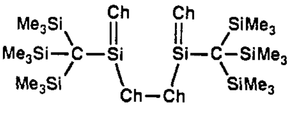


Figure 3. X-ray structure of **1b**, showing the original disordered structure. One of the molecules is described with solid lines.

The success of the isolation of **1a**,**b** is perhaps due to the relative instability of the isomeric form **4**, because such an unsaturated compound of silicon is generally thought to be energetically unfavorable.[18,19]



4; Ch = S or Se

Acknowledgment. We are grateful to Shin-etsu Chemical Co., Ltd., for a gift of chlorosilanes. This work

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[10] **1b**: MS *m/e* 838 (M^+). Anal. Calcd for $C_{20}H_{54}Si_8Se_4$: C, 28.76; H, 6.52. Found: C, 28.53; H, 6.20.

[11] Linderberg, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 2619. Bergson, G. *Ark. Kemi* **1958**, *13*, 11. Bergson, G. *Ark. Kemi* **1962**, *19*, 195.

[12] Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden*; Springer: Berlin, Heidelberg, New York, 1981.

[13] Eaborn, C. *J. Chem. Soc.* **1950**, 3077. Louis, E.; Urry, G. *Inorg. Chem.* **1968**, *7*, 1253. Harpp, D. N.; Steliou, K. *Synthesis* **1976**, 721. Laguerre, M.; Dunogues, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1980**, *193*, C17. Praefcke, K.; Weichsel, C. *Synthesis* **1980**, 216. Schmidt, M.; Kiewert, E.; Lux, H.; Sametschek, C. *Phosphorus Sulfur Relat. Elem.* **1986**, *26*, 163. Schmidt, M.; Ruf, H. *Z. Anorg. Allg. Chem.* **1963**, *321*, 270.

[14] Compound **1b**: $C_{20}H_{54}Se_4Si_8$, fw 835.18, orthorhombic, a = 23.321 (3) Å, b = 13.510 (4) Å, c = 11.488 (14) Å, V = 3619.5 Å^3, Z = 4, space group $Pbca$, ρ = 1.53 g/cm^3, μ = 42.9 cm^{-1}. The 1364 independent observed reflections ($2\theta \le 50°$; $|F_o^2| > 3\sigma|F_o^2|$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and ω–θ scans. No absorption correction was made. The structure was solved by direct methods, and only silicon and selenium atoms were refined anisotropically to R = 0.061 and R_w = 0.079.

[15] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23. Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800. Buttrus, N. H.; Eaborn, C.; El-Kheli, M. N. A.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C.; Tavakkoli, K. *J. Chem. Soc., Dalton Trans.* **1988**, 381 and references cited therein.

[16] Barrow, M. J.; Ebsworth, E. A. V. *J. Chem. Soc., Dalton Trans.* **1981**, 211.

[17] Masamune reported that some cyclic or cage molecules have structurally required NBD/BL values (NBD is the nonbonded distance; BL is the bond length).[20] The NBD/BL value for **1b** is 1.23, so that **1b** may belong to the same class as 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane.

[18] The Gibbs free energy changes ($\Delta G°$) for dimerization of $H_2Si{=}O$, $H_2Si{=}S$, and $H_2C{=}O$ are calculated to be −92.1, −55.8, and +17.1 kcal/mol, respectively: Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

[19] Gusel'nikov, L. E.; Volkova, V. V.; Avakyan, V. G.; Nametkin, N. S.; Voronkov, M. G.; Kirpichenko, S. V.; Suslova, E. N. *J. Organomet. Chem.* **1983**, *254*, 173. Thompson, D. P.; Boujouk, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1466.

[20] Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794.

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Supplementary Material Available: Detailed information on the X-ray crystal analysis of **1b** and a mass spectral data table (observed and calculated abundances of isotopomers of M^+) for **1b** (18 pages); a table of observed and calculated structure factors for **1b** (7 pages). Ordering information is given on any current masthead page.

Reduction of Coordinated Carbon Dioxide by Transition-Metal Hydrides

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Summary: The reactions of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (**1**) with the transition-metal hydrides $HCo(CO)_4$ and $H_2Fe(CO)_4$ have been examined. **1** reacts with excess $HCo(CO)_4$ rapidly at −78 °C to produce $[(\eta^5\text{-}C_5H_5)_2MoH(CO)]Co(CO)_4$ (**2**), $HCo_3(CO)_9$, and H_2O. $^{13}CO_2$-labeling experiments indicate that the original CO_2 in **1** is converted to coordinated CO in **2**. Complex **2** slowly converts to a novel unsymmetrically bridged hydrido complex $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ (**3**) whose structure has been established by X-ray diffraction. Complex **1** also reacts with excess $H_2Fe(CO)_4$ to produce $[(\eta^5\text{-}C_5H_5)_2MoH(CO)][HFe_3(CO)_{11}]$ (**4**).

The attractiveness of carbon dioxide as a potential feedstock for organic chemicals has stimulated increasing interest in the organometallic chemistry of this abundant, yet typically unreactive molecule.[1] Nonetheless, proven examples of reactions of *coordinated* CO_2 are surprisingly few. In this regard, we have shown recently that $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (1) undergoes novel photoinduced disproportionation[2] and reacts readily with a variety of polar reagents E–Nu, giving complexes of the type $[(\eta^5\text{-}C_5H_5)_2Mo(CO)Nu]Nu$ and E–O–E, the result of O-transfer from coordinated CO_2.[3] In an effort to assess the potential benefits of cooperative bimetallic activation[4,5] for facilitating *catalytic* carbon dioxide reduction, we have begun to examine the interaction of 1 with representative transition-metal hydride complexes producible from dihydrogen. We report herein our initial observations, which include (1) the discovery of facile reduction of coordinated CO_2 in 1 by $HCo(CO)_4$ and $H_2Fe(CO)_4$, resulting in the formation of heterobimetallic carbonyl complex salts, and (2) the production of a novel unsymmetrically bridged hydridocarbonyl dinuclear complex.

We first examined the reaction of 1[2,6] with strongly acidic $HCo(CO)_4$ (pK_a = <0 in H_2O, 8.4 in CH_3CN[7]). Treatment of a CD_2Cl_2 solution of 1 with an excess (ca. 5 equiv) of $HCo(CO)_4$ at −90 °C resulted in an immediate darkening of the solution; ^1H NMR monitoring indicated complete consumption of 1 and the appearance of new absorptions at δ 5.60 (Cp), −8.30 (MH), and 1.62 (H_2O, confirmed by spiking). A preparative-scale reaction in toluene followed by addition of pentane afforded greenish yellow crystals of 2 (82% yield) whose NMR spectrum,[8] prominent M–CO IR absorptions at 1880 and 2030 cm⁻¹, and mass spectral data[8] suggested the presence of $[Co(CO)_4^-]$[9] and $[Cp_2Mo(CO)X^+]$[3,10] units. On the basis of these spectroscopic data and comparison with literature values,[11] 2 is identified as $[Cp_2Mo(CO)H][Co(CO)_4]$. Evaporation of the above solution afforded $HCo_3(CO)_9$[12] as the other

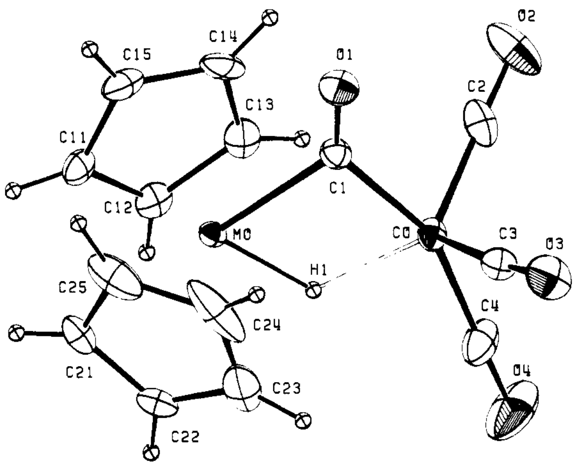

Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$ (**3**). Selected bond distances (Å): Mo–Co 2.8449 (4); Mo–C(1) 2.190 (2); Co–C(1) 1.905 (2); C(1)–O(1) 1.181 (3); Mo–H(1) 1.64 (3); Co–H(1) 1.88 (3); Mo–Cp(1) 1.969 (1); Mo–Cp(2) 1.965 (2); Co–C(2) 1.768 (3); Co–C(3) 1.772 (3); Co–C(4) 1.818 (3). Selected bond angles (deg): Cp(1)–Mo–Cp(2) 141.5 (1); C(1)–Mo–H(1) 81 (1); C(1)–Co–H(1) 83 (1); C(1)–Co–C(2) 92.0 (1); C(1)–Co–C(3) 89.7 (1); C(1)–Co–C(4) 158.0 (1); C(2)–Co–C(3) 113.0 (1); C(2)–Co–C(4) 103.7 (1); C(3)–Co–C(4) 97.9 (1).

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* Address correspondence (except for X-ray results) to this author.

† Address correspondence regarding X-ray diffraction results to this author.

[1] Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: W. Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[2] Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

[3] Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967.

[4] The reduction of a bimetallic μ-carboxylate complex by Cp_2ZrHCl has been reported: Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

[5] Several examples of bimetallic and trimetallic complexes of CO_2 exist, but little is known of their reactivity; see: Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Chem. Soc.* **1982**, *104*, 5082. Also see other examples cited in ref 4.

[6] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

[7] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, CA, 1987; p 91.

[8] ^1H NMR (acetone-d_6) 5.85 (s, 10 H), −8.2 (s, 1 H); MS for **2** (12 eV DIP) *m/e* 256 ($Cp_2{}^{98}MoCO$), 228 ($Cp_2{}^{98}Mo$), 172 ($HCo(CO)_4$), 144 ($HCo(CO)_3$), 116 ($HCo(CO)_2$), 88 ($HCo(CO)$).

[9] Edgell, W. F.; Hedge, S.; Barbetta, A. *J. Am. Chem. Soc.* **1987**, *100*, 1406.

[10] Bell, L. G.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *135*, 173.

[11] Mugnier, Y.; Moise, C. *J. Organomet. Chem.* **1963**, *248*, C33.

[12] Green-black solid: IR (KBr) 2060, 2030, 1850, 1830 cm⁻¹; MS (70 eV, DIP) *m/e* 430 (M^+), 429 ($Co_3(CO)_9$), 401 ($Co_3(CO)_8$). Literature data for $HCo_3(CO)_9$: Fachinetti, G.; Balocchi, L.; Secco, F.; Venturini, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 204. Fachinetti, G.; Pucci, S.; Zanuzzi, P.; Methong, U. *Ibid.* **1979**, *18*, 619.

0276-7333/91/2310-0029$02.50/0