this process to the presence of a planar Me_3Sn arrangement provided by the trigonal bipyramidal tin coordination in chain polymers like **2–6**. That such a generalization is incorrect is clearly shown by the results for compound **1** where tetrahedral tin is involved in such a 3-site jump process. Just considering the polymeric species **2–6**, one might also be tempted to consider this process as a peculiarity of the Sn–O bond in the solid state. Again, compound **1** proves this statement wrong. Also, qualitative results concerning the internal rotation of Me_3Sn groups in a solid N–Sn–N environment have been reported recently.[37]

Based on our (admittedly still limited) data set, we can nevertheless predict that similar reorientational processes will also be observed for (i) further solid Me_3Sn-containing compounds and (ii) other solid Me_3M compounds with, for example, M = Si, Pb if the respective solid-state structure can accommodate such a process. For simple reasons of space requirements, contradicting the close packing principle, similar processes are most unlikely for solid triorganyltin compounds R_3SnX with ligands R bulkier than R = Me. It should be mentioned, however, that we have also observed nonrigidity for several triphenyltin and triphenyllead compounds[38]—for such compounds no mutual interchange of the phenyl groups has been observed, but smaller-scale motion such as ring wobbles/libration or flips are feasible.

So far, we have shown only that our NMR results do not contradict results from single crystal X-ray diffraction studies. We still need to explore whether, and how well, the kinetic data from NMR spectroscopy will correlate with the picture obtained from X-ray diffraction. In the case of compound **2**, the fairly high activation barrier can be rationalized on the basis of the strongly distorted trigonal bipyramidal Me_3SnO_2 coordination. The deviation of the Me_3Sn plane from perpendicular to the O–Sn–O axis leads to substantial intramolecular (or better, intrachain) van der Waals interactions and thus correlates with a fairly high activation energy for the reorientation of the Me_3Sn group. Compound **5**, $Me_3Sn(O_2CMe)$, also displays a fairly high activation barrier. In contrast to compound **2**, the trigonal bipyramidal environment in **5** is not distorted, and there are no intrachain interactions obstructing the $2\pi/3$ jump. Closer examination of the X-ray crystal structure of **5** reveals that in this case substantial intermolecular, i.e., interchain, van der Waals interactions are responsible for a high activation energy. A rather low activation energy in our series of compounds is determined for compound **3**, and also in this case the single crystal X-ray structure yields direct evidence for (in this case) the ease of Me_3Sn reorientation: the two H_2O molecules act as spacers, leaving room to accommodate this motional process without severe obstruction by van der Waals interactions of the intra- or interchain type. At first glance the low-temperature (178 K) X-ray crystal structure of **4** seems to contradict the low activation energy for Me_3Sn reorientation. The Sn–(OH)–Sn bond angle of 136.9 (1)° causes considerable van der Waals obstruction for the two neighboring Me_3Sn propellers in **4**. At room temperature, however, we observe fairly large—and different—jump rates for the two different Me_3Sn groups. Given the substantial temperature dependence of the ^{119}Sn chemical shift of one of the two tin sites in **4**, we suggest that the Sn–(OH)–Sn bond angle in **4** should increase with increasing temperature, thus lowering the mutual van der Waals interactions between the two Me_3Sn groups and allowing for their independent reorientation. We would also predict then that at sufficiently low temperatures, finally independent reorientation will become impossible and then much slower, correlated reorientation of the two Me_3Sn groups in **4** might occur. Further work along these lines is in progress in our laboratory and will be reported elsewhere.[39]

Acknowledgment. Support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank H. Reuter, Universität Bonn, and A. Blaschette and I. Hippel, Technische Universität Braunschweig, for their generous loan of samples **6** and **2–4**, respectively, as well as for making unpublished X-ray diffraction results available to us. We thank S. Gerstmann, Universität Bayreuth, for the preparation of compound **5**. We are most grateful to F. Seifert, Bayerisches Geoinstitut, Bayreuth, for his generous support of our work.

---

[37] Apperley, D. C.; Davies, N. A.; Harris, R. K.; Eller, S.; Schwarz, P.; Fischer, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 740–741.

[38] Challoner, R.; Kümmerlen, J.; Sebald, A., to be published.

[39] Blaschette, A.; Hippel, I.; Kümmerlen, J.; Sebald, A., to be published.

Communications to the Editor

A New Family of Icosahedral Cages with Transition Metal and Main Group IV (14) Atoms: Synthesis and Structural-Bonding Analysis of the $[Ni_{11}(SnR)_2(CO)_{18}]^{2-}$ Dianions (R = *n*-Bu, Me) Containing Ni-Centered Icosahedral $Ni_{10}Sn_2$ Cages and of Their Unusual $[Ni(SnRCl_2)_4(CO)]^{2-}$ Precursors Containing a Trigonal-Bipyramidal d^8 Nickel(II) Configuration

Jeffrey P. Zebrowski,[1] Randy K. Hayashi, and
Lawrence F. Dahl*

Department of Chemistry
University of Wisconsin—Madison
Madison, Wisconsin 53706

Received September 10, 1991

Reactions in our laboratory of $[Ni_6(CO)_{12}]^{2-}$ (**1**)[2] with organo(main group V (15)) dihalides have given rise to a variety of clusters, including ones with discrete noncentered metal(main group) icosahedral cages.[3] Such 12-atom clusters, which are electronically equivalent (i.e., 13 skeletal electron pairs) with the classic $[B_{12}H_{12}]^{2-}$ dianion[4] and $[Al_{12}R_{12}]^{2-}$ (R = *i*-Bu),[5] include members of the $[Ni_{12-x}(PMe)_x(CO)_{24-3x}]^{2-}$ (x = 2–4)[6] and $[Ni_{12-x}(AsR)_x(CO)_{24-3x}]^{2-}$ (x = 2, R = Me; x = 3, R = Ph)[7] series

---

[1] Current address: Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439.

[2] (a) Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616–2618. (b) Longoni, G.; Chini, P.; Cavalieri, A. *Inorg. Chem.* **1976**, *15*, 3025–3029.

[3] (a) DesEnfants, II, R. E.; Gavney, J. A., Jr.; Hayashi, R. K.; Rae, A. D.; Dahl, L. F.; Bjarnason, A. *J. Organomet. Chem.* **1990**, *383*, 543–572 and references therein. (b) Mlynek, P. D.; Dahl, L. F. Unpublished research.

[4] (a) Lipscomb, W. N.; Wunderlich, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 4427–4428. (b) Pitochelli, A. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 3228–3229. (c) Meutterties, E. L.; Merrifield, R. E.; Miller, H. C.; Knoth, Jr., W. H.; Downing, J. R. *J. Am. Chem. Soc.* **1962**, *84*, 2506–2508.

[5] Hiller, W.; Klinkhammer, K.-W.; Uhl, W.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179–180.

[6] (a) Rieck, D. F.; Rae, A. D.; Dahl, L. F. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL, Sept. 1985; American Chemical Society: Washington, D.C., 1985; INOR 157. (b) Rieck, D. F.; Gavney, J. A., Jr.; Norman, R. L.; Hayashi, R. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1992**, *114*, 10369–10379.

0002-7863/93/1515-1142$04.00/0

as well as $[Ni_{10}(SbR)_2(CO)_{18}]^{2-}$ (R = Ph, Me).[3] These noncentered icosahedral clusters are also electronically equivalent with the $[Rh_{12}Sb(CO)_{27}]^{3-}$ trianion[8] and the $[Ni_{12}E(CO)_{22}]^{2-}$ dianions (E = Ge, Sn),[9] whose icosahedral metal cages possess an encapsulated main group atom.[10-12] Recently, Longoni and coworkers[13] reported the synthesis and characterization of the $[Ni_{11}(SbNi(CO)_3)_2(CO)_{18}]^{n-}$ anions (n = 2–4) with Ni-centered $Ni_{10}Sb_2$ icosahedral cages. A salient feature is the unexpected higher electron counts with 8–10 additional cluster valence electrons (CVEs) than the number predicted by the electron-counting cluster model.[14] Their explanation was subsequently supported by EHMO computations[13b] of hypothetical icosahedral systems.

Our objective to obtain a new family of icosahedral cages composed of main group IV (14) and transition metal atoms has been realized. Herein we report the synthesis and characterization of the $[Ni_{11}(SnR)_2(CO)_{18}]^{2-}$ dianions (R = *n*-Bu (**2**), Me (**3**)) and their $[Ni(SnRCl_2)_4(CO)]^{2-}$ precursors (R = *n*-Bu (**4**), Me (**5**)). Both **2** and **3**, which contain Ni-centered $Ni_{10}Sn_2$ icosahedral cages, are the first examples of transition metal clusters with μ_5-SnR fragments. Their existence raises provocative bonding questions because they also have 8 more CVEs than the predicted number (150).[14] Because of the virtually identical covalent radii of Sn (1.41 Å) and Sb (1.40 Å),[15] a geometrical comparison of the 158-electron Ni-centered $Ni_{10}Sn_2$ cages of **2** and **3** with the 158-electron Ni-centered $Ni_{10}Sb_2$ cage of the $[Ni_{11}(SbNi(CO)_3)_2(CO)_{18}]^{2-}$ dianion (**6**)[13] and the 150-electron noncentered $Ni_{10}Sb_2$ cage of $[Ni_{10}(SbPh)_2(CO)_{18}]^{2-}$ (**7**)[3a] provides an integrated picture of the net bonding interactions of the interstitial d^{10} Ni atom with the 1,12-$Ni_{10}E_2$ frameworks. This "experimental quantum mechanical" analysis has important implications regarding the validity of the general electron-counting rules for high-nuclearity clusters containing late-first-row transition metals as interstitial atoms.

Addition of *n*-$BuSnCl_3$ (4 equiv) to an acetonitrile solution of the $[NMe_4]^+$ salt of **1** under N_2 caused the red solution to turn yellow-brown with concurrent gas evolution. After solvent removal, the residue was washed with 1:1 THF/hexane and then dissolved in THF. Addition of diisopropyl ether precipitated **4** (58% yield, Sn). **5** was similarly obtained by reaction of $MeSnCl_3$ with **1** (85% yield).[16] Further reaction of **4** or **5** with **1** in acetonitrile at 55 °C produced brown **2** or **3**, which was extracted from the residue with 4:1 THF/hexane (30% yield).[17]

X-ray structural determinations[18] of salts of **4** and **5** revealed analogous five-coordinate d^8 Ni(II) complexes possessing idealized C_{2v} trigonal-bipyramidal (TBP) geometries with the carbonyl ligand at an equatorial site; an EHMO treatment[19] of TBP d^8 metal complexes indicated that good π-acceptor ligands would prefer equatorial positions. To our knowledge, the only other structurally determined TBP Ni(II) carbonyl complex containing main group IV (14) ligands is the highly reactive $Ni(CO)_3(SiCl_3)_2$.[20]

Structural determinations[21] of $[PPh_3Me]^+$ salts of **2** and **3** revealed a Ni-centered $Ni_{10}Sn_2$ icosahedral cage of pseudo-D_{5d} symmetry (Figure 1) surrounded by a polyhedral array of 18 carbonyl and two Sn-attached R substituents. Whereas **3** has 10 terminal, four doubly, and four triply bridging carbonyl ligands, **2** has 10 terminal, six doubly, and two triply bridging carbonyl ligands. Despite the different bridging carbonyl arrangements, the corresponding mean interatomic distances (under D_{5d} symmetry) in the Ni-centered $Ni_{10}Sn_2$ cages of **2** and **3** are within 0.01 Å of each other.

A geometrical comparison of the Ni-centered $Ni_{10}Sn_2$ cage in **2** and **3** with the Ni-centered and noncentered $Ni_{10}Sb_2$ cages in **6** and **7**, respectively, disclosed that the formal insertion of an interstitial nickel, Ni(i), into the centrosymmetric site of the empty E,E′-bicapped pentagonal-antiprismatic cage of 10 surface Ni(s) in **7** causes a substantial enlargement of the highly compressed icosahedral cavity only along the principal 5-fold E···E′ axis; no major bond-length changes occur other than those directly involving capping E atoms, viz., (1) a 0.40–0.45-Å increase in distance between the inversion center and independent E atom from 1.95 in **7** to 2.35 Å in both **2** and **3** and to 2.40 Å in **6** due to formation of unusually short Ni(i)–E bonds in **2**, **3**, and **6**, and (2) an elongation of the mean Ni(s)–E distances from 2.55 in **7** to 2.72 Å in both **2** and **3** and to 2.73 Å in **6**. The mean radial inversion center–Ni(s), intrapentagonal Ni(s)–Ni(s′), and interpentagonal Ni(s)–Ni(s′) distances are within 0.02 Å in **2**, **3**, **6**, and **7**.

The CVO model[14] assumes that the interstitial d^{10} Ni(i) in **2**, **3**, or **6** contributes 10 CVEs (five bonding skeletal electron pairs) without any alteration in the total number of CVOs because the radial interactions between the 4s, 4p, and 3d AOs of the Ni(i) and the cage orbitals of the same symmetry are sufficiently strong

---

(7) Rieck, D. F.; Montag, R. A.; McKechnie, T. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 1330–1331.

(8) Vidal, J. L.; Troup, J. M. *J. Organomet. Chem.* **1981**, *213*, 351–363. (b) Heaton, B. T.; Strona, L.; Pergola, R. D.; Vidal, J. L.; Schoening, R. C. *J. Chem. Soc., Dalton Trans.* **1983**, 1941–1947.

(9) Ceriotti, A.; Demartin, F.; Heaton, B. T.; Ingallina, P.; Longoni, G.; Manassero, M.; Marchionna, M.; Masciocchi, N. *J. Chem. Soc., Chem. Commun.* **1989**, 786–787.

(10) The dissimilar electronic requirements of the 162-electron $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ trication[11] containing a Au-centered Au_{12} icosahedral cage have been explained from different bonding models.[12]

(11) Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 201–202.

(12) (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1163–1169. (b) Briant, C. E.; Hall, K. P.; Wheeler, A. C.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1984**, 248–250. (c) King, R. B. *Inorg. Chim. Acta* **1986**, *116*, 109–117.

(13) (a) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Longoni, G.; Sironi, A.; Zanotti, V. *J. Chem. Soc., Chem. Commun.* **1990**, 547–548. (b) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Laschi, F.; Longoni, G.; Sironi, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1991**, 739–748.

(14) (a) Mingos, D. M. P.; Zhenyang, L. *J. Chem. Soc., Dalton Trans.* **1988**, 1657–1664 and references therein. (b) Mingos, D. M. P.; May, A. P. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kalsz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 2, pp 11–119. (c) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Old Tappan, NJ, 1990.

(15) (a) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; pp 258–259. (b) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*; Addison-Wesley: Reading, MA, 1984; p 168.

(16) Red crystals of the $[NMe_4]^+$ salt of **4**: IR (THF) 2000 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.84 (m, C1), 1.72 (m, C2), 1.37 (sextet, C3), 0.89 (p, C4), 3.42 (s, $[NMe_4]^+$); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 56.3 ($[NMe_4]^+$), 39.7 (C1), 28.3 (C2), 27.3 (C3), 14.0 (C4); $^{119}Sn\{^1H\}$ NMR (acetone-d_6) δ 225 (s), $^2J(^{119}Sn{-}H)$ 34.9 Hz; elemental analysis 40.92% Sn (calcd 38.86%), Desert Analytics, Tucson, AZ. Red crystals of the $[NMe_4]^+$ salt of **5**: IR (THF) 2000 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.12 (s, C1), 3.42 (s, $[NMe_4]^+$).

(17) Brown crystals of the $[NMe_4]^+$ salt of **2**: IR (THF) 1982 (s), 1845 (m), 1800 (sh) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.68 (m, C1), 2.56 (m, C2), 1.72 (sextet, C3), 1.09 (p, C4), 3.42 (s, $[NMe_4]^+$); $^{119}Sn\{^1H\}$ NMR (acetone-d_6) δ 438 (s); CV (THF) one reversible oxidation, $E_{1/2} = -0.25$ V, one reversible reduction, $E_{1/2} = -1.18$ V (vs SCE); elemental analysis 40.92% Ni (calcd 39.14%), Desert Analytics, Tucson, AZ. IR (THF) of **3** was indistinguishable from that of **2**.

(18) X-ray data were collected on Siemens diffractometers with Mo Kα radiation. All crystal structures were determined by use of SHELXTL PLUS. $[NMe_4]^+{}_2[Ni(SnBuCl_2)_4(CO)]^{2-}$ (fw 1221.8): orthorhombic, *Pbca*; a = 20.878 (7), b = 27.102 (9), c = 32.275 (12) Å; Z = 16; $R_1(F)$ = 6.13%, $R_2(F)$ = 7.32% for 11 655 reflections (−60 °C). $[NMe_4]^+[Ni_2Cl_3(THF)_6]^+[Ni(SnMeCl_2)_4(CO)]^{2-}$ (fw 1635.8): monoclinic, $P2_1/n$; a = 12.088 (8), b = 13.720 (6), c = 35.582 (17) Å, β = 97.96 (5)°; Z = 4; $R_1(F)$ = 6.57%, $R_2(F)$ = 7.42% for 6725 reflections (−60 °C).

(19) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374 and references therein.

(20) Janikowski, S. K.; Radonovich, L. J.; Groshens, T. J.; Klabunde, K. J. *Organometallics* **1985**, *4*, 396–398.

(21) The $[NMe_4]^+$ salts of **2** and **3** were metathesized to $[PPh_3Me]^+$ salts via addition of excess $[PPh_3Me]^+[Br]^-$ to a methanol solution followed by precipitation with water. $[PPh_3Me]^+{}_2[Ni_{11}(SnBu)_2(CO)_{18}]^{2-}$ (fw 2056.0): monoclinic, $P2_1/c$; a = 14.202 (6), b = 18.925 (6), c = 14.452 (5) Å, β = 115.18 (3)°; Z = 2; $R_1(F)$ = 7.86%, $R_2(F)$ = 8.79% for 4060 reflections (−60 °C). $[PPh_3Me]^+{}_2[Ni_{11}(SnMe)_2(CO)_{18}]^{2-}\cdot(C_4H_8O)$ (fw 2044.0): monoclinic, $C2/c$; a = 26.603 (4), b = 12.054 (2), c = 22.562 (3) Å, β = 102.17 (1)°; Z = 4; $R_1(F)$ = 4.77%, $R_2(F)$ = 5.39% for 4197 reflections (21 °C).

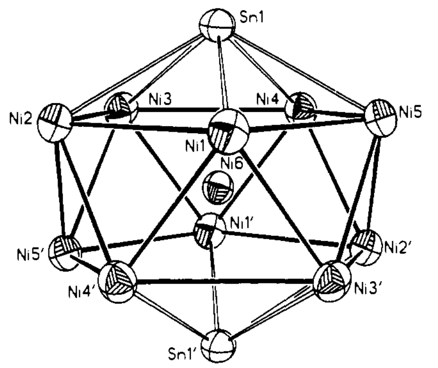

Figure 1. Ni-centered 1,12-Ni$_{10}$Sn$_2$ icosahedral cage in [Ni$_{11}$(SnMe)$_2$(CO)$_{18}$]$^{2-}$ (3) of crystallographic C_i-$\bar{1}$ site symmetry. This pentagonal antiprism of 10 surface Ni(s) with an interstitial Ni(i) and two capping Sn atoms has the following mean distances under assumed D_{5d}-$\overline{10}2m$ symmetry: Ni(i)–Sn, 2.351 (1) Å; Ni(i)–Ni(s), 2.58 Å; Ni(s)–Sn, 2.72 Å; intrapentagonal Ni(s)–Ni(s'), 2.79 Å; interpentagonal Ni(s)–Ni(s'), 2.51 Å. Atomic thermal ellipsoids are drawn at the 35% probability level.

that the bonding CVOs are occupied but the corresponding antibonding CVOs are empty. In the case of **2**, **3**, or **6**, the "extra" 8 electrons would then necessarily populate *antibonding tangential* cage LUMOs.[22,23] However, the structural parameters provide evidence that the antibonding tangential cage LUMOs in **7** remain empty in **2**, **3**, or **6** when the Ni(i) is added to the icosahedral cavity.

The only reasonable electronic scheme involves a breakdown of the CVO model[14] with the 10 valence d electrons of Ni(i) in **2**, **3**, or **6** occupying the five *antibonding radial* Ni(i)–cage CVOs. One major consequence is that the "net" bonding effects due to the 3d Ni(i) AOs are essentially nullified; the unusually short Ni(i)–E bonds in **2**, **3**, or **6** must then be attributed to strong interactions involving the 4s,4p Ni(i) AOs. This experimentally deduced proposal is consistent with the view that the d^{10} Ni(i) contributes its empty 4s,4p AOs but no "net" bonding skeletal electron pairs in stabilizing the Ni$_{10}$E$_2$ cage. Weak radial interactions between the filled 3d Ni(i) AOs and appropriate cage orbitals in **2**, **3**, or **6** (producing *occupied* bonding and antibonding MOs) are readily rationalized for late-first-row transition metals because their high effective nuclear charges give rise to relatively small, low-energy d AOs. This structural-bonding analysis is in harmony with that reported[13] for **6**.

Electrochemical measurements indicate that **2** and **3**, which do not conform to the PSEP model,[24] can be reversibly oxidized and reduced. Work in progress includes attempts to isolate these redoxed species for further structural-bonding studies.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (Grant CHE-9013059).

Supplementary Material Available: Tables listing the atomic parameters, interatomic distances, and bond angles for **2–5** (32 pages). Ordering information is given on any current masthead page.

---

(22) The 13 skeletal electron pairs in a regular icosahedral I_h cage (e.g., [B$_{12}$H$_{12}$]$^{2-}$) were shown[23] to occupy bonding a$_g$, t$_{1u}$, h$_g$, and g$_u$ MOs; the quadruply degenerate g$_g$ LUMOs, which are composed of symmetry-adapted antibonding combinations of tangential surface orbitals, transform as e$_{1g}$ + e$_{2g}$ under the lower pseudo-D_{5d} symmetry of the 1,12-Ni$_{10}$E$_2$ cage.

(23) (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179–2189. (b) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 1627–1638. (c) Johnston, R. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 647–656. (d) Mingos, D. M. P.; Zhenyang, L. *J. Organomet. Chem.* **1988**, *341*, 523–534.

(24) (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792–793. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66. (c) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435–447. (d) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311–319. (e) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1352–1354. (f) Johnston, R. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 1445–1456.

Lithium Pentakis(dimethylsilyl)cyclopentadienide and Formation of Isolable Coordination Complexes with Ketones: [(R$_2$C=O)Li·{C$_5$(SiMe$_2$H)$_5$}][1]

Akira Sekiguchi,* Yoshiya Sugai, Keisuke Ebata,
Chizuko Kabuto, and Hideki Sakurai*

Department of Chemistry and Organosilicon Research
Laboratory, Faculty of Science, Tohoku University
Aoba-ku, Sendai 980, Japan

Received July 27, 1992

Although polysilylated cyclopentadienide anions have been of interest for a long time,[2] persilylated cyclopentadienide has been elusive.[3] As a part of the study on persilylated π-electron systems,[4] we report herein the preparation and interesting properties of lithium pentakis(dimethylsilyl)cyclopentadienide as the first example of persilylated cyclopentadienide anions.

Treatment of hexakis(dimethylsilyl)cyclopentadiene (**1**, 200 mg, 0.48 mmol), prepared by the reaction of hexabromocyclopentadiene and dimethylchlorosilane in the presence of magnesium,[5] with *n*-BuLi (0.63 mmol) in dry oxygen-free hexane/THF at room temperature led to the formation of [pentakis(dimethylsilyl)cyclopentadienyl]lithium by cleavage of an Si–C bond. Removal of the solvent afforded a THF complex of the anion, [(THF)Li·{C$_5$(SiMe$_2$H)$_5$}] (**2**), as colorless solids.[6]

Quite expectedly, the reaction of **2** with benzaldehyde and formaldehyde gave the corresponding fulvene derivatives **3a** and **3b**, respectively (Scheme I).[7] With acetone and acetophenone, **2** gave complex mixtures. However, the reaction of **2** with benzophenone gave interesting results. Thus, addition of an equivalent amount of benzophenone (90 mg, 0.49 mmol) to a solution of **2** produced a benzophenone adduct **4a** as air- and moisture-sensitive yellow crystals. Pure **4a** appears to be thermally quite stable, with no change observed on heating at 90 °C for 2 h. The adduct **4a** also reacted with benzaldehyde to give **3a**.

NMR data of the adduct of **4a** are fully consistent with the proposed structure: ^{1}H NMR (C$_7$D$_8$, δ) 0.57 (d, J = 3.9 Hz, 30 H, SiMe$_2$), 5.09 (sept, J = 3.9 Hz, 5 H, SiH), 7.05 (t, J = 7.2 Hz, 4 H, *m*-H), 7.15 (t, J = 7.2 Hz, 2 H, *p*-H), 7.44 (d, J = 7.2 Hz, 4 H, *o*-H); ^{13}C NMR (C$_7$D$_8$, δ) 0.66, 128.8, 130.7, 133.9, 135.8 (CpC), 136.9, 200.9 (C=O), ^{29}Si NMR (C$_7$D$_8$, δ) −26.5. Of particular interest is the chemical shift of ^{7}Li appearing at −7.51 ppm. A large high-field shift of the ^{7}Li NMR resonance indicates a structure in which the Li$^+$ ion is located at the center of the cyclopentadienyl ring.[8] The low-field shift of the carbonyl carbon

---

(1) Chemistry of Organosilicon Compounds. 297.

(2) For a review, see: Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

(3) Miftakhov, M. S.; Tolstikov, G. A.; Lomakina, S. I. *Zh. Obshch. Khim.* **1976**, *46*, 2754; *Chem. Abstr.* **1977**, *86*, 121430z. Miftakhov et al. reported the synthesis of C$_5$(SiMe$_3$)$_6$ by the reaction of hexachlorocyclopentadiene and trimethylchlorosilane with lithium in THF, but unfortunately we could not reproduce the results under various conditions ourselves.

(4) Reviews: (a) Sakurai, H. *J. Synth. Org. Chem. Jpn.* **1982**, *40*, 472. (b) Sakurai, H. *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn., Chem. Ind.*) **1990**, 439. (c) Sekiguchi, A. *J. Synth. Org. Chem. Jpn.* **1992**, *50*, 225.

(5) Compound **1**: colorless crystals, mp 138 °C; ^{1}H NMR (C$_7$D$_8$, 263 K, δ) 0.01 (d, J = 3.8 Hz, 12 H), 0.41 (d, J = 3.8 Hz, 12 H), 0.49 (d, J = 3.8 Hz, 12 H), 4.74 (sept, J = 3.8 Hz, 2 H), 4.80–4.92 (m, 4 H); ^{13}C NMR (C$_7$D$_8$, 263 K, δ) −3.85, −1.01, −0.66, 75.2, 159.8, 163.9; ^{29}Si NMR (C$_7$D$_8$, 263 K, δ) −25.5, −25.1, −20.1; high-resolution MS calcd for C$_{17}$H$_{42}$Si$_6$ 414.1902, found 414.1896.

(6) Compound **2**: ^{1}H NMR (C$_7$D$_8$, δ) 0.56 (d, J = 3.7 Hz, 30 H, SiMe$_2$), 1.14–1.22 (m, 4 H, THF), 3.16–3.24 (m, 4 H, THF), 5.04 (sept, J = 3.7 Hz, 5 H, SiH); ^{13}C NMR (C$_7$D$_8$, δ) 0.61, 25.4 (THF), 69.0 (THF), 135.7; ^{29}Si NMR (C$_7$D$_8$, δ) −26.5; ^{7}Li NMR (C$_7$D$_8$, δ) −8.49.

(7) **3a** (94% yield, red-orange crystals) and **3b** (93% yield, yellow-orange crystals) were characterized by NMR and mass spectroscopic analyses. Details will be reported elsewhere.

0002-7863/93/1515-1144$04.00/0