plexes, but all with macrocyclic, crown-type ligands (so giving, usually, single K^+ units); any bonding $K^+\cdots NCS^-$ contacts are typically of length 2.8–3.0 Å. Perusal of a recent review of organometallic compounds containing heavier alkali metals (Na–Cs)[9] has also failed to find a structure comparable with that of **1**. Some comment can, though, be made concerning this structure; cf. that of $(LiNCS{\cdot}2HMPA)_2$.[4] The ionic radii of (six-coordinate) Li^+ and K^+ differ by about 0.62 Å, so that the M–N distances (2.007 Å in the Li complex, ~0.69 Å longer when M = K, in **1**) and the M-μ_2-O distances (of HMPA; 2.015 Å in the Li complex, ~0.74 Å longer in **1**) only roughly fall in line. Within the thiocyanate anions of the two complexes, there is better agreement (N–C and C–S distances in the Li complex being 1.156 and 1.629 Å, respectively, and in **1** being 1.142 (16) and 1.625 (12) Å, respectively), enabling their formulation as

$$[\mathrm{N}\overset{\cdots}{=}\mathrm{C}\overset{\cdots}{-}\mathrm{S}]^-$$

For the M^+-μ_3-O (of HMPA) coordinations, there are seemingly no precedents in alkali-metal chemistry. Even though each $(Me_2N)_3P{=}O$ ligand has just two lone pairs formally available for bonding to, one supposes, just two metal centers, the $\mathrm{O}\overset{\cdots}{-}\mathrm{P}$ distances within the μ_2 and μ_3 ligands of **1** show no significant difference [being 1.473 (9) and 1.491 (8) Å, respectively], which could be attributed to use of π-electron density in the latter case.

Clearly, **1** has a highly ionic structure. It can be viewed as a bicapped $(K_3O_3)^{3+}$ hexagon [see Figure 1, looking along O(1)–K(1)–O(1a); angles at K 156.6 (2)°] or as a $(K_3)^{3+}(\mu_3\text{-HMPA})_2$ trigonal bipyramid whose $K^+\cdots K^+$ edges are stitched (borane-like) by μ_2-HMPA ligands. Either way, the equatorial belt is pulled out, presumably to maximize $K^+\cdots K^+$ distances.

Acknowledgment. We thank the SERC (D.B., P.R.R., R.S., D.S.W.), the Associated Octel Co. Ltd. (R.S., D.S.W.), the ICI (M.J.D.), and St. John's College, Cambridge (S.R.D.), for financial support.

Supplementary Material Available: Details of the crystal structure determination, Tables S1–S4, listing final atomic coordinates, bond lengths, bond angles, and thermal parameters, and a view of the unit cell contents showing the two trimeric molecules of **1** (6 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

---

[9] Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169.

University Chemical Laboratory
Cambridge University
Lensfield Road
Cambridge CB2 1EW, U.K.

Donald Barr
Michael J. Doyle
Simon R. Drake
Paul R. Raithby
Ronald Snaith*
Dominic S. Wright

Received November 30, 1988

Tris(trimethylsilyl)silyl Derivatives of Tri-*tert*-butoxyzirconium and Tri-*tert*-butoxyhafnium. X-ray Crystal Structure of $(Me_3CO)_3ZrSi(SiMe_3)_3$

Recent investigations in our laboratory have focused on the formation and reactivity of early-transition-metal–silicon bonds.[1] Studies with d^0 zirconium and hafnium derivatives such as $Cp_2M(SiMe_3)Cl$ (Cp = η^5-C_5H_5),[2] $Cp_2M[Si(SiMe_3)_3]Cl$,[2c] $Cp^*{}_2Zr(SiHMes_2)Cl$ (Cp* = η^5-C_5Me_5; Mes = 2,4,6-$Me_3C_6H_2$),[3] $Cp^*Cl_2MSi(SiMe_3)_3$,[4] and $CpCp^*M[Si(SiMe_3)_3]Cl$[1c,5] have shown that these metal–silicon bonds are unusually reactive toward a variety of substrates. A common feature of these silyl compounds is the presence of cyclopentadienyl (C_5H_5 or C_5Me_5) ancillary ligands. Because the reactivity of early-transition-metal–silicon bonds is dramatically influenced by substituent effects at both the transition metal and silicon,[1c,2c,3,5] we have sought syntheses of early-transition-metal–silyl complexes with different ligand environments. We now report the synthesis of complexes $(Me_3CO)_3MSi(SiMe_3)_3$ (**1**, M = Zr; **2**, M = Hf), which to our knowledge are the first group 4 silyl derivatives that do not contain cyclopentadienyl ligands.

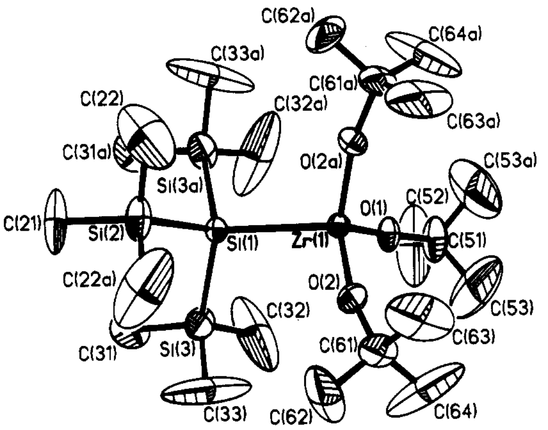

Figure 1. ORTEP view of $(Me_3CO)_3ZrSi(SiMe_3)_3$ (**1**) with thermal ellipsoids drawn at the 20% probability level. Important bond lengths (Å) and angles (deg) are as follows: Zr(1)–Si(1) = 2.753 (4), Zr(1)–O(1) = 1.90 (1), Zr(1)–O(2) = 1.884 (7); Si(1)–Zr(1)–O(1) = 107.5 (3), Si(1)–Zr(1)–O(2) = 107.7 (2), O(1)–Zr(1)–O(2) = 110.9 (3), Si(2)–Si(1)–Zr(1) = 110.7 (2), Si(3)–Si(1)–Zr(1) = 110.2 (1), Zr(1)–O(1)–C(51) = 165 (1), Zr(1)–O(2)–C(61) = 167.2 (8).

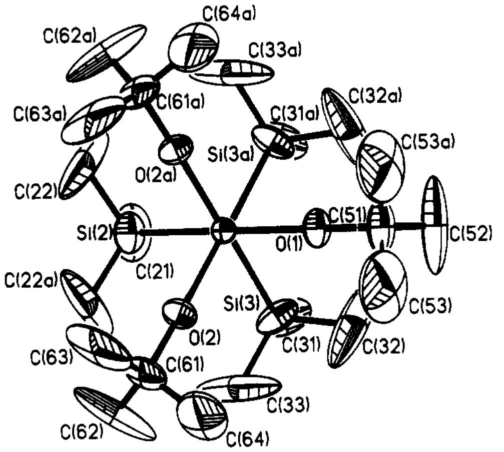

Figure 2. View of **1** down the Zr(1)–Si(1) bond.

By a modification of the literature procedure for $(CH_3CH_2CH_2CH_2O)_3MCl$,[6] the alkoxides $(Me_3CO)_3MCl$ were generated in solution by reaction of MCl_4 with 3 equiv of $M(OCMe_3)_4$[7] in diethyl ether for 12 h at 0 °C. After the solution was warmed to room temperature addition of $(THF)_3LiSi(SiMe_3)_3$[8] to this solution resulted in formation of silyl complexes **1** and **2** (reaction time 3 h), isolated in 60–70% yield by crys-

---

[1] (a) Tilley, T. D. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149. (c) Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Organomet. Chem.* **1988**, *358*, 169 and references therein.

[2] (a) Tilley, T. D. *Organometallics* **1985**, *4*, 1452. (b) Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084. (c) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

[3] Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324.

[4] (a) Arnold, J.; Woo, H.-G.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 2045. (b) Arnold, J.; Roddick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1988**, *27*, 3510. (c) Arnold, J.; Elsner, F. H.; Engeler, M. P.; Heyn, R. H.; Tilley, T. D. Submitted for publication.

[5] (a) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.*, in press.

[6] Weidmann, B.; Maycock, C. D.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 1552.

[7] Thomas, I. M. *Can. J. Chem.* **1961**, *39*, 1386.

[8] Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

0020-1669/89/1328-1768$01.50/0

tallization from pentane (eq 1). Spectroscopic properties[9] for

$$(\mathrm{Me_3CO})_3\mathrm{MCl} + (\mathrm{THF})_3\mathrm{LiSi}(\mathrm{SiMe_3})_3 \xrightarrow{-3\mathrm{THF},\ -\mathrm{LiCl}} (\mathrm{Me_3CO})_3\mathrm{MSi}(\mathrm{SiMe_3})_3 \quad (1)$$

$$\mathbf{1},\ \mathrm{M} = \mathrm{Zr}$$
$$\mathbf{2},\ \mathrm{M} = \mathrm{Hf}$$

these air- and water-sensitive complexes resemble those observed for other group 4 $-\mathrm{Si(SiMe_3)_3}$ derivatives. However, in contrast to other d^0 silyl compounds which are highly colored, **1** and **2** are colorless.

The molecular structure of **1** is shown in Figure 1.[10] A crystallographically imposed mirror plane at $y = 0.2500$ bisects the molecule and contains C(21), Si(2), Si(1), Zr(1), O(1), C(51), and C(52). Additionally, two noncrystallographic mirror planes give the molecule nearly C_{3v} symmetry, with the 3-fold rotation axis containing the Zr(1)–Si(1) bond. This symmetry is reflected in the Si–Si–Zr–O dihedral angles of 179.3, 179.3, and 180.0°. A view down the Zr–Si bond (Figure 2) illustrates the staggered conformation about these two tetravalent atoms. The geometry about Si(1) is nearly tetrahedral, with average Si–Si–Si angles of 108.5 (3)°, and Zr–Si–Si angles averaging 110.4 (2)°. In other complexes containing the $\mathrm{Si(SiMe_3)_3}$ ligand, distortions of these angles about the metal-bound silicon atom, apparently due to steric interactions, are observed.[4b,11] The Zr(1) center also exhibits an approximate tetrahedral coordination geometry, with a mean Si–Zr–O angle of 107.6 (3)° and a mean O–Zr–O angle of 111.4 (4)°. The average Zr–O bond distance (1.89 (1) Å) and Zr–O–C angle (166 (1)°) compare favorably with other zirconium alkoxide structures in which some degree of O(pπ)–Zr(dπ) bonding is presumed.[12] The Zr–Si bond distance of 2.753 (4) Å is shorter than either of the two previously reported Zr–Si distances, 2.813 (2) Å in $\mathrm{Cp_2Zr(SiPh_3)Cl}$[13] and 2.815 (1) Å in $\mathrm{Cp_2Zr(SiMe_3)S_2CNEt_2}$.[2a] This is consistent with the formally lower coordination number in **1**. According to Shannon, the effective ionic radius of four-coordinate Zr(IV) is 0.25 Å smaller than that of eight-coordinate Zr(IV).[14] Since the Zr–Si distance in **1** is only 0.06 Å less than other reported Zr–Si distances, the Zr–Si bond in **1** is longer than expected. Apparently there are no crystal structures of $\mathrm{(RO)_3Zr(alkyl)}$ complexes available for comparison.

Preliminary experiments show that these compounds are surprisingly inert. **1** and **2** are unreactive toward carbon monoxide (24 h, 70 psi, pentane), ethylene (24 h, 70 psi, pentane), and $\mathrm{PhSiH_3}$ (1 equiv, 3 days, benzene-d_6). However, both compounds react with $2,6\text{-}\mathrm{Me_2C_6H_3NC}$ to afford the insertion products $(\mathrm{Me_3CO})_3\mathrm{M}[\eta^2\text{-}\mathrm{C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3}]$ (**3**, M = Zr; **4**, M = Hf).[15] Heating **1** and **2** to 90 °C in benzene-d_6 results in only slow thermal decomposition, to $\mathrm{HSi(SiMe_3)_3}$ and as yet uncharacterized metal-containing species. Studies are under way to examine further aspects of the synthesis, structure and reactivity of mixed alkoxy/silyl complexes of the early transition metals.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-88-0273, and to the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–90).

Supplementary Material Available: Tables of crystal and data collection parameters, atomic coordinates (Table 1), bond distances and angles (Tables 2 and 3), anisotropic thermal parameters (Table 4), and hydrogen atom coordinates and their isotropic thermal parameters (Table 5) (6 pages); a listing of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

---

(9) Data for **1**: mp 225–228 °C dec. Anal. Calcd for $\mathrm{C_{21}H_{54}O_3Si_4Zr}$: C, 45.2; H, 9.75. Found: C, 45.1; H, 9.72. IR (Nujol, CsI, $\mathrm{cm^{-1}}$): 1361 s, 1254 m, 1240 s, 1206 s, 1182 s, 1042 s, 998 vs, 862 s, 832 vs, 791 m, 746 w, 735 w, 681 m, 621 m, 548 w, 480 w, 439 w, 388 w, 350 w. UV (pentane, $\lambda_{\max}$/nm ($\epsilon/\mathrm{M^{-1}\,cm^{-1}}$): 228 (21 500). ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.48 (Si*Me*$_3$), 1.28 (OC*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 3.61 (Si*Me*$_3$), 32.29 (OC*Me*$_3$), 77.46 (O*C*Me$_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ −115.82 (*Si*SiMe$_3$), −7.20 (Si*Si*Me$_3$). Data for **2**: mp 144–147 °C dec. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.47 (Si*Me*$_3$), 1.31 (OC*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 4.75 (Si*Me*$_3$), 33.53 (OC*Me*$_3$), 78.40 (O*C*Me$_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ −103.47 (*Si*SiMe$_3$), −5.04 (Si*Si*Me$_3$).

(10) Crystal data for **1**: $\mathrm{C_{21}H_{54}O_3Si_4Zr}$, orthorhombic, *Pnma*, $a = 21.48$ (1) Å, $b = 16.850$ (8) Å, $c = 10.033$ (5) Å, $V = 3631$ (3) Å^3, $Z = 4$, $D_c = 1.021$ g cm^{-3}, $F(000) = 1200$, $\mu = 4.41$ cm^{-1}, Mo Kα radiation (λ = 0.710 73 Å). An irregularly shaped colorless crystal of approximate dimensions 0.4 mm × 0.4 mm × 0.4 mm was mounted under $\mathrm{N_2}$ in a glass-walled capillary and flame-sealed. Data was collected at ca. 23 °C on a Nicolet R3m/V automated diffractometer with a highly ordered graphite monochromator, using $\theta/2\theta$ scans (variable scan speed, 1.5–15° min^{-1}) and was corrected for slight crystal decay (3.3%). No absorption correction was applied. Of the 4793 reflections collected (3° $\le 2\theta \le$ 45°), 2480 were considered independent ($R_{\mathrm{int}} = 2.62\%$). Systematic absences indicated the space group to be either of the nonstandard settings $Pc2_1n$ or *Pcmn*. After conversion to the standard space group, only the centrosymmetric group *Pnma* gave a solution that could be refined. The Zr atom was located by Patterson methods, and all remaining non-hydrogen atoms were located and refined anisotropically by difference Fourier and full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). The refinement was based on 1190 observed reflections ($F_o > 6\sigma(F)$). Hydrogen atoms were fixed in calculated, idealized positions (d(C–H) = 0.96 Å, with fixed isotropic thermal parameters 1.2 times the isotropic thermal parameter for the carbon to which the hydrogen is attached). $R_F = 6.00\%$, $R_{wF} = 6.77\%$, GOF = 1.82, data/parameter = 8.4, mean $\Delta/\sigma = 0.001$, and $\Delta(\rho) = 0.53$ e Å^{-3} (1.24 Å from Si(2), 1.47 Å from C(22)).

(11) (a) Nicholson, B. K.; Simpson, J.; Robinson, W. T. *J. Organomet. Chem.* **1973**, *47*, 403. (b) Couldwell, M. C.; Simpson, J.; Robinson, W. T. *J. Organomet. Chem.* **1976**, *107*, 323. (c) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1987**, *26*, 2106. (d) Chisholm, M. H.; Chiu, H.-T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097.

(12) (a) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. (b) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977. (c) Karia, R.; Willey, G. R.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2493. (d) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204. (e) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.

(13) Muir, K. *J. Chem. Soc. A* **1971**, 2663.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(15) Data for **3**: mp 64–67 °C dec. Anal. Calcd for $\mathrm{C_{30}H_{63}NO_3Si_4Zr}$: C, 52.3; H, 9.21; N, 2.03. Found: C, 51.7; H, 9.17; N, 2.13. IR (Nujol, CsI, cm^{-1}): $\nu_{\mathrm{C=N}}$ 1509 w. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.26 (s, Si*Me*$_3$), 1.34 (s, OC*Me*$_3$), 2.06 (s, *o-Me*), 6.90 (m, *m,p-CH*). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 2.24 (Si*Me*$_3$), 19.04 (*o-Me*), 33.20 (OC*Me*$_3$), 75.27 (O*C*Me$_3$), 125.55 (*p-C*), 127.41 (*o-C*), 128.62 (*m-C*), 155.35 (ipso *C*), 299.01 (Zr*C*N). Data for **4**: IR (benzene-d_6 solution, CsF, cm^{-1}): $\nu_{\mathrm{C=N}}$ 1503 w. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.26 (s, Si*Me*$_3$), 1.35 (s, OC*Me*$_3$), 2.08 (s, *o-Me*), 6.89 (m, *m,p-CH*). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 2.26 (Si*Me*$_3$), 19.01 (*o-Me*), 33.34 (OC*Me*$_3$), 75.36 (O*C*Me$_3$), 125.68 (*p-C*), 128.62 (*m-C*), 155.21 (ipso *C*), 310.21 (Zr*C*N).

Chemistry Department, D-006
University of California at San Diego
La Jolla, California 92093-0506

Richard H. Heyn
T. Don Tilley*

Received December 21, 1988

Synthesis and Redox and Structural Chemistry of Monomeric Rhenium(IV) Phenoxide Complexes

Next to molybdenum and tungsten, rhenium catalysts are the most widely used for olefin metathesis[1] and remain the catalysts of choice for metathesizing certain functionalized olefins.[2] Two important principles have emerged from studies of homogeneous

---

(1) (a) Drăgutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, 2nd revised ed.; Wiley-Interscience: Chichester, England, 1985. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

(2) (a) Mol, J. C.; Woerlee, E. F. G. *J. Chem. Soc., Chem. Commun.* **1979**, 330. (b) Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35. (c) Bosma, R. H. A.; van der Aardweg, G. C. N.; Mol, J. C. *J. Organomet. Chem.* **1983**, *255*, 159. (d) Bosma, R. H. A.; van der Aardweg, G. C. N.; Mol, J. C. *Ibid.* **1985**, *280*, 115.

0020-1669/89/1328-1769$01.50/0