Early-Transition-Metal Silyl Complexes Free from Anionic π-Ligands. A New Family of Alkyl, Alkylidene, and Alkylidyne Compounds

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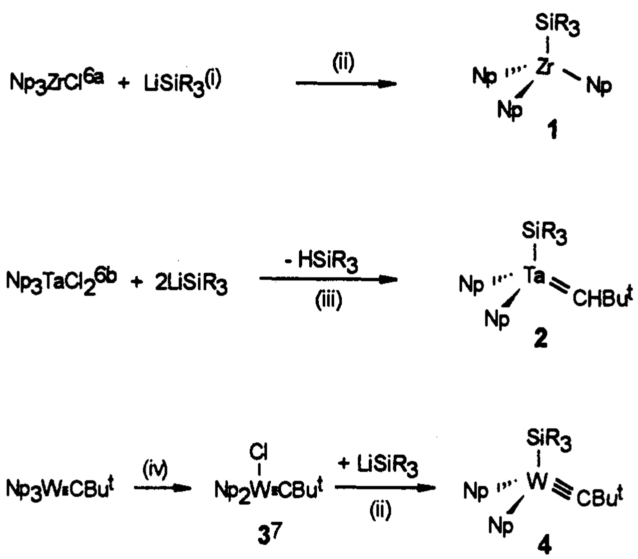
Early-transition-metal silyl chemistry is of great current interest. Such chemistry has been concentrated mostly on silyl complexes containing cyclopentadienyl (Cp) or analogous anionic π-ligands as stabilizing groups.[2] Berry and co-workers observed a thermally labile silyl alkylidene complex $Cp_2Ta({=}CH_2)(SiHBu^t_2)$ *in situ* at −70 °C through photolysis of $Cp_2Ta(PMe_3)(SiHBu^t_2)$ in the presence of $Me_3P{=}CH_2$.[2c] Early-transition-metal silyl chemistry free from anionic π-bondings, however, is a relatively young area.[3] We report here the synthesis of a new family of silyl complexes $Np_3ZrSi(SiMe_3)_3$ (**1**), $Np_2Ta({=}CHBu^t)[Si(SiMe_3)_3]$ (**2**), and $Np_2W({\equiv}CBu^t)[Si(SiMe_3)_3]$ (**4**; Np = neopentyl, Bu^tCH_2). These three complexes represent, to our knowledge, the first silyl alkyl, stable alkylidene, and alkylidyne compounds of early transition metals.

The syntheses of these complexes in either hexanes or toluene are summarized in Scheme 1.[4] Workup (i.e., filtration, removal of solvents, extraction with hexanes, and crystallization) yielded crystals of **1**, **2**, and **4**. In the formation of **2** monitored by ^1H NMR, 1 equiv of $HSi(SiMe_3)_3$ was produced. Neither $ClSi(SiMe_3)_3$ nor CMe_4 was observed in the reaction mixture. To our knowledge, such alkylidene bond formation by preferential elimination of a silane through α-hydrogen abstraction is unprecedented.[5]

Scheme 1[a]



[a] R = $SiMe_3$. (i) $LiSiR_3$ exists as $Li(THF)_3SiR_3$;[6c] (ii) −3THF, −LiCl, (iii) −6THF, −2LiCl; (iv) +HCl/Et_2O.

Spectroscopic properties [^1H, $^{13}C\{^1H\}$, ^1H-gated-decoupled ^{13}C, and $^{29}Si\{^1H\}$ NMR] of **1**, **2**, and **4** are consistent with the structure assignments. In $(Bu^tCH_2)_2Ta({=}CHBu^t)[Si(SiMe_3)_3]$ (**2**) and $(Bu^tCH_2)_2W({\equiv}CBu^t)[Si(SiMe_3)_3]$ (**4**), there are large chemical shift differences between diastereotopic H_a and H_b atoms of the $Bu^tCH_aH_b$ groups (1.96 ppm for **2** and 4.56 ppm for **4**). The α-carbon resonance of the neopentyl ligands of **2** in the ^1H-gated-decoupled ^{13}C NMR at 23 °C and −70 °C appears as a triplet. The presence of an agostic CH_a–Ta interaction is essentially ruled out by the equality of $^1J_{CH_a}$ and $^1J_{CH_b}$ coupling constants. The chemical shift differences in **2** and **4** are probably the result of diamagnetic anisotropy of the metal–carbon multiple bonds.

The molecular structure of **2** is shown in Figure 1.[8] A crystallographically imposed 3-fold rotation axis containing the Si(1)—Ta(1) bond results in a disorder between the $Bu^tCH{=}$ and the two Bu^tCH_2 ligands. The average Ta—C bond length is 1.97(3) Å. In comparison, the Ta—C and Ta=C bond lengths in $[Ta({=}CHBu^t)(CH_2Bu^t)(PMe_3)_2]_2(\mu\text{-}N_2)$ are 2.285(10) and

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[2] See, for example: (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. J. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (b) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (c) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952. (d) Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031. (e) Corey, J. Y.; Zhu, X.-H. *J. Organomet. Chem.* **1992**, *439*, 1. (f) Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 69. (g) Schubert, U.; Schenkel, A. *Chem. Ber.* **1988**, *121*, 939. (h) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (i) Hengge, E.; Weinberger, M. *J. Organomet. Chem.* **1992**, *433*, 21. (j) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (k) For a more complete list, see reviews: Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 245, 309. Schubert, U. *Transition Met. Chem.* **1991**, *16*, 136. Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151 and references therein.

[3] Early-transition-metal silyl complexes free from anionic π-ligands usually contain carbonyls, alkoxides, or phosphines. For example, (a) $V(CO)_6SiH_3$: Allinson, J. S.; Aylett, B. J.; Colquhoun, H. M. *J. Organomet. Chem.* **1976**, *112*, C7. (b) $[R_3SiM(CO)_5]^-$ (M = Cr, Mo, W): Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 467. Darensbourg, D. J.; Bauch, C. G.; Reibenspies, J. H.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4203. (c) $C_6R_6(CO)_2Cr(H)SiX_3$ (R = H, SiX_3 = $SiCl_3$): Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4. (R = Me, SiX_3 = $SiHPh_2$): Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469. (d) $W_2(CO)_{10}(SiR_2)_2$ and $W_2(CO)_8H_2(SiR_2)_2$: Hoyano, J. K., Ph.D. Thesis, University of Alberta, Canada, 1971. Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156. (e) $(dppe)(CO)_3M(H)SiR_3$ (M = Cr, Mo, W): Schubert, U.; Kirchgässner, U.; Grönen, J.; Piana, H. *Polyhedron* **1989**, *8*, 1589. (f) $(Bu^tO)_2Si{=}Cr(CO)_5{\cdot}HMPT$: Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (g) $(Bu^tO)_3MSi(SiMe_3)_3$ (M = Zr, Hf): Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1768. (h) $(PMe_3)_3W(H)_2I(SiMe_3)$: Barron, A. R.; Wilkinson, G.; Montevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 837. (i) In the reaction of $Me_2Ti(dmpe)_2$ with $PhSiH_3$, $PhMeSiH_2$ and CH_4 are observed. Spencer, M.; Girolami, G. S., private communication.

[4] (a) Data for **1**: ^1H NMR (benzene-d_6, 250.1 MHz) δ 1.59 (6H, $Me_3CC\mathit{H}_2$-), 1.19 (27H, Me_3CCH_2-), 0.40 (27H, $Si\mathit{Me}_3$, $^2J_{Si-H}$ = 4.1 Hz); ^{13}C (benzene-d_6, 62.9 MHz) δ 127.4 ($Me_3C\mathit{C}H_2$-, $^1J_{C-H}$ = 102.2 Hz), 37.9 ($Me_3\mathit{C}CH_2$-), 34.7 (Me_3CCH_2-), 4.2 ($Si\mathit{Me}_3$, $^1J_{Si-C}$ = 40.6 Hz); $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz) δ −7.64 ($\mathit{Si}Me_3$), −85.77 ($\mathit{Si}SiMe_3$). (b) Data for **2**: ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 1.65 (1H, ${=}C\mathit{H}$), 1.52 (2H, $CH_a\mathit{H}_b$, $^2J_{H-H}$ = 12.2 Hz), 1.50 (9H, ${=}CHC\mathit{Me}_3$), 1.16 (18H, $CH_2C\mathit{Me}_3$), 0.41 (27H, $Si\mathit{Me}_3$), −0.44 (2H, $C\mathit{H}_aH_b$); ^{13}C NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 263.1 (${=}\mathit{C}H$, $^1J_{C-H}$ = 80.5 Hz), 144.8 ($\mathit{C}H_2$, $^1J_{C-H}$ = 101.9 Hz), 48.6 (${=}CH\mathit{C}Me_3$), 38.1 ($CH_2\mathit{C}Me_3$), 35.1 ($CH_2C\mathit{Me}_3$), 34.7 (${=}CHC\mathit{Me}_3$), 4.0 ($Si\mathit{Me}_3$); $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz, 23 °C) δ −5.30 ($\mathit{Si}Me_3$), −53.47 ($\mathit{Si}SiMe_3$); MW (cryoscopic in cyclohexane) 637 (calcd 641.0). (c) Data for **4**: ^1H NMR (benzene-d_6, 250.1 MHz) δ 2.70 (2H, $CH_a\mathit{H}_b$, $^2J_{H-H}$ = 11.1 Hz; $^2J_{W-H}$ = 11.4 Hz), 1.66 (9H, ${\equiv}CC\mathit{Me}_3$), 1.16 (18H, $CH_aH_bC\mathit{Me}_3$), 0.39 (27H, $Si\mathit{Me}_3$, $^2J_{Si-H}$ = 6.3 Hz), −1.86 (2H, $C\mathit{H}_aH_b$); ^{13}C NMR (benzene-d_6, 62.9 MHz) δ 321.3 (${\equiv}\mathit{C}CMe_3$, $^1J_{W-C}$ = 216.7 Hz), 134.9 ($\mathit{C}H_2$, $^1J_{C-H}$ = 104.7 Hz, $^1J_{W-C}$ = 84.0 Hz), 53.7 (${\equiv}C\mathit{C}Me_3$, $^2J_{W-C}$ = 45.6 Hz), 38.5 ($CH_2\mathit{C}Me_3$), 34.4 ($CH_2C\mathit{Me}_3$), 33.1 (${\equiv}CC\mathit{Me}_3$), 3.7 ($Si\mathit{Me}_3$); $^{29}Si\{^1H\}$ (benzene-d_6, 79.5 MHz) δ −5.75 ($\mathit{Si}Me_3$), −46.05 ($\mathit{Si}SiMe_3$). Anal. Calcd for $C_{24}H_{58}Si_4W_1$: C, 44.84; H, 9.09. Found: C, 44.66; H, 9.09.

[5] (a) Elimination of $HSiMe_3$ has been reported in the decomposition of $(C_5Me_5)Ta(SiMe_3)Me_3$: Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (b) Syntheses of carbene M=C bonds were reported[3e] by cleavage of M—Si bonds in anionic silyl complexes through 1,2-elimination of halosilanes.

[6] (a) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319. (b) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (c) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

[7] **3** was used *in situ* for the next step synthesis. Data for **3**: ^1H NMR (benzene-d_6, 250.1 MHz) δ 1.75 (2H, $CH_a\mathit{H}_bCMe_3$, $^2J_{H-H}$ = 13.3 Hz), 1.42 (9H, ${\equiv}CC\mathit{Me}_3$), 1.11 (18H, $CH_2C\mathit{Me}_3$), 0.98 (2H, $C\mathit{H}_aH_bCMe_3$).

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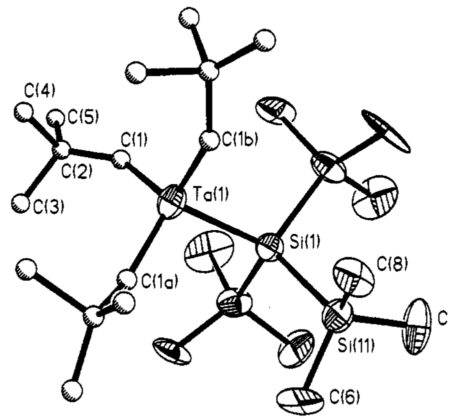
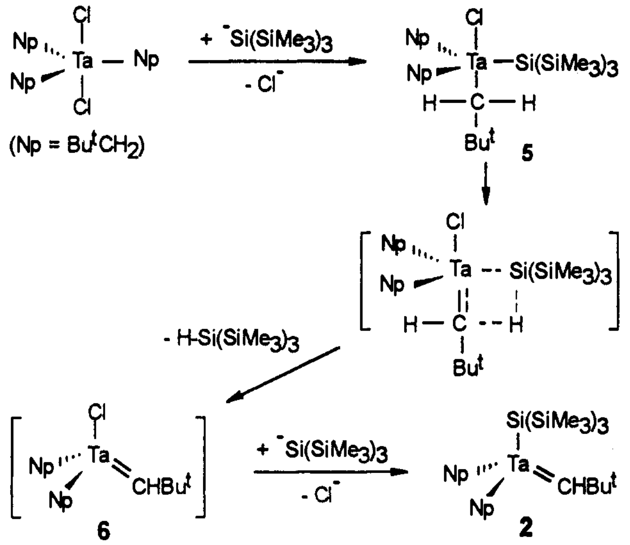


Figure 1. Molecular structure and labeling scheme for **2**. Selective bond lengths (Å) and angles (deg): Ta(1)–Si(1) = 2.680(15), Ta(1)–C(1) = 1.97(5), Si(1)–Ta(1)–C(1) = 105.4(12), Ta(1)–Si(1)–Si(11) = 111.0(4), C(1)–Ta–C(1A) = 113.2(12), Ta–C(1)–C(2) = 149(3).

1.932(9) Å, respectively.[9a] The -Si(SiMe$_3$)$_3$ and Np$_2$(Bu^{t}CH=)-Ta- moieties are arranged in a staggered conformation, which has similarly been observed in (Bu^{t}O)$_3$Zr–Si(SiMe$_3$)$_3$.[3g] Both moieties present pseudotetrahedral geometries with bond angles ranging from 105.4(12) to 113.2(14)°. The Ta(1)–Si(1) distance of 2.680(15) Å is comparable to 2.624(2)–2.633(2) Å found in Cp$_2$Ta(H)(SiMe$_2$H)$_2$,[9b] 2.669(4) Å in (C$_5$Me$_5$)Ta(SiMe$_3$)Cl$_3$,[5a] and 2.651(4) Å in Cp$_2$Ta(H)$_2$SiPhMe$_2$.[9c] Molecular weight determination by cryoscopy in cyclohexane indicates that **2** exists as a monomer in solution.[4b]

Complex **2** was found to react with 1 equiv of HCl in ethyl ether at –78 °C to form an unstable purple complex with an NMR spectrum consistent with the formula Np$_3$Ta(Cl)[Si(SiMe$_3$)$_3$] (**5**).[10] This complex decomposed slowly at –90 °C to HSi(SiMe$_3$)$_3$ and yet unknown species. Neither ClSi(SiMe$_3$)$_3$ nor CMe$_4$ was found in the decomposition process as analyzed by ^{1}H NMR (toluene-d_8). In comparison, Schrock and Fellmann reported that Np$_4$TaCl began to decompose above about –10 °C to give CMe$_4$, Np$_3$TaCl$_2$, Np$_3$Ta=CHBu^t, and other unidentified products.[6b]

Scheme 2



In the synthesis of **2** (Scheme 1), the bulkiness of LiSi(SiMe$_3$)$_3$(THF)$_3$ seems to rule out its direct attack on an α-hydrogen atom in Np$_3$TaCl$_2$ to form a Ta=CHBu^t moiety. The preferential elimination of HSi(SiMe$_3$)$_3$ in the decomposition of **5** at –90 °C and the rapid formation of **2** at 23 °C suggest that there is a low-energy route for HSi(SiMe$_3$)$_3$ elimination from **5**. The elimination is perhaps driven by steric repulsion in the pentacoordinated **5** since tetracoordinated Np$_3$ZrSi(SiMe$_3$)$_3$ (**1**), Np$_2$Ta(=CHBu^t)[Si(SiMe$_3$)$_3$] (**2**), and Np$_2$W(≡CBu^t)[Si(SiMe$_3$)$_3$] (**4**) are stable at 23 °C. A mechanism involving an intermediate "Np$_2$Ta(=CHBu^t)Cl" (**6**) is proposed for the formation of **2** (Scheme 2).

Acknowledgment is made to Professor Clifton Woods III for assistance with the crystal structure analysis, Professor Gregory S. Girolami and a referee for interpretation of the H$_a$ and H$_b$ chemical shift differences in the ^{1}H NMR, the UTK Science Alliance and National Science Foundation for a summer fellowship (J.B.D.), and the University of Tennessee for financial support. The X-ray diffractometer and the Bruker 400 AMX NMR spectrometer were purchased with funds from the U.S. Department of Energy (DE-FG05-87ER75378 and DE-FG05-89ER75501, respectively).

Supplementary Material Available: Lists of complete crystallographic data and NMR spectra of **1**, **2**, and **4** (10 pages); table of observed and calculated structure factors (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(8) Crystal data for **2**: trigonal, *P*3 (No. 143), a = 16.292(2) Å, c = 11.373(2) Å, V = 2614.4(7) Å^3, Z = 3, R (R_w) = 6.31 (7.90)% with 1822 unique reflections with $F > 4.0\sigma(F)$, GOF = 1.37, number of parameters refined = 182, data-to-parameter ratio = 10.0:1. The tantalum, silicon, and eight of the nine carbon atoms in the three -SiMe$_3$ groups were anisotropically refined. No attempt was made to locate or calculate the hydrogen atoms.

(9) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899. Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809. (b) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (c) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.

(10) ^{1}H NMR (toluene-d_8, 400 MHz, –90 °C) of **5**: δ 2.32 (CH_2), 1.22 (CMe_3), 0.41 (SiMe_3). In comparison, the ^{1}H NMR (toluene-d_8, –10 °C) for the unstable Np$_4$TaCl:[6b] δ 2.1 (CH_2), 1.25 (CMe_3).