Synthesis and Characterization of Tantalum Silyl and Disilyl Imido Complexes That Do Not Contain Anionic π-Ligands

Zhongzhi Wu and Ziling Xue*

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600

Received June 15, 2000

*Summary: Tantalum disilyl and silyl complexes [(Me$_3$Si)$_2$N](Me$_3$SiN═)Ta(SiPh$_2$Bu^t)$_2$ (**1**) and [(Me$_3$Si)$_2$N](Me$_2$N)(Me$_3$SiN═)Ta(SiPh$_2$Bu^t) (**2**) have been prepared and characterized. They are, to our knowledge, the first known cyclopentadienyl-free group 5 imido disilyl and silyl complexes.*

Early-transition-metal silyl chemistry has attracted increasing interest recently.[1] Silyl complexes of the d^0 metals have been studied in, for example, insertion reactions,[2] silane dehydropolymerizations,[1,3] and hydrosilylation.[4] Most d^0 metal silyl complexes contain cyclopentadienyl (Cp) or analogous anionic π-ligands;[1] relatively fewer Cp-free d^0 metal silyl complexes have been reported.[2e,5,6] Cp ligands are believed to lead to enhanced stability of silyl complexes. Tilley and coworkers have recently reported Cp-free group 6 imido silyl complexes (2,6-Pr$^i_2$C$_6$H$_3$N═)$_2$M(R)Si(SiMe$_3$)$_3$ (M = Mo, W; R = Cl, CH$_2$Bu^t, H).[5] We have prepared a series of Cp-free d^0 silyl alkyl, alkylidene, alkylidyne, amide, and related complexes and studied their chemistry.[6] The synthesis and characterization of a Cp-free Ta imido silyl and a Cp-free Ta imido disilyl complex are reported here. We have studied such complexes with a 2-fold interest. (1) To our knowledge, they are the first known Cp-free group 5 imido silyl and disilyl complexes. So far, only d^0 Cp-free amido disilyl complexes [(Me$_2$N)$_3$Zr(SiPh$_2$Bu^t)$_2$Li(THF)$_4$][6k] and (Me$_2$N)$_3$Ta[Si(SiMe$_3$)$_3$]$_2$,[6k] and a few Cp-containing d^0 disilyl complexes Cp$_2$M(SiR$_3$)$_2$ and Cp$_2$M(SiR$_2$)$_n$ have been reported.[7] (2) These Ta complexes with N- and Si-containing ligands are potential precursors to Ta−Si−N ternary materials that are of current interest in microelectronic applications.[8,9] There have been no reported attempts to use Ta complexes containing N and Si ligands as single-source Ta−Si−N precursors.[8a]

The yellow Ta imido silyl complex [(Me$_3$Si)$_2$N](Me$_2$N)(Me$_3$SiN═)Ta(SiPh$_2$Bu^t) (**2**) was prepared from the reaction of {Ta(μ-Cl)Cl(═NSiMe$_3$)[N(SiMe$_3$)$_2$]}$_2$ (**3**)[10] first with 2 equiv of LiNMe$_2$ and then with 2 equiv of Li(THF)$_3$SiPh$_2$Bu^t [11] (Scheme 1).[12] The ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra and elemental analysis of **2** are consistent with the structural assignment. The X-ray crystal structure of **2** (Figure 1) shows a pseudotetrahedral arrangement in the Ta moiety with bond angles around the Ta atom ranging from 100.1(2) to 118.3(3)°. The d^0 Ta−Si bond length of 2.704(2) Å is

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 245, 309. (c) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 3, p 2037. (d) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (e) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (f) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (g) Xue, Z. *Comments Inorg. Chem.* **1996**, *18*, 223.

(2) See, e.g.: (a) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (b) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 3087. (c) Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284. (d) Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. *J. Organomet. Chem.* **1988**, *358*, 169. (e) Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1768. (f) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 2011. (g) Radu, N. S.; Engeler, M. P.; Gerlach, C. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 3621. (h) Wu, Z.; McAlexander, L. H.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 4853. (i) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1999**, *18*, 1002.

(3) (a) Imori, T.; Tilley, T. D. *Polyhedron* **1994**, *13*, 2231. (b) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548; **1997**, *16*, 2798. (c) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Polyhedron* **1995**, *14*, 45. (d) Huhmann, J. L.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1997**, *533*, 61. (e) Hengge, E.; Gspaltl, P.; Pinter, E. *J. Organomet. Chem.* **1996**, *521*, 145. (f) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700. (g) Verdaguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. (h) Fu, P. F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747.

(4) (a) Corey, J. Y.; Zhu, X. H. *Organometallics* **1992**, *11*, 672. (b) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095.

(5) Casty, G. L.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4746.

(6) (a) Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169. (b) McAlexander, L. H.; Hung, M.; Li, L.; Diminnie, J. B.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 5231. (c) Diminnie, J. B.; Hall, H. D.; Xue, Z. *J. Chem. Soc., Chem. Commun.* **1996**, 2383. (d) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520. (e) Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1997,** *119*, 12657. (f) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 2917. (g) Chen, T.; Wu, Z.; Li, L.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.; Guzei, I. A.; Rheingold, A. L.; Xue, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13519. (h) Liu, X.; Li, L.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z. *Organometallics* **1998**, *17*, 4597. (i) Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 6366. (j) Choi, S.-H.; Lin, Z,; Xue, Z. *Organometallics* **1999**, *18*, 5488. (k) Wu, Z.; Diminnie, D. B.; Xue, Z. *J. Am. Chem. Soc.* **1999**, *121*, 4300. (l) Chen, T.; Xue, Z. *Chinese J. Inorg. Chem.* **1999**, *15*, 413.

(7) (a) Cp$_2$Zr(SiMe$_3$)[Si(SiMe$_3$)$_3$]: see ref 2a. (b) Cp$_2$Ti(SiPh$_3$)$_2$: Kingston, B. M.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 69. (c) Cp$_2$Ti(SiPh$_2$)$_5$: Igonin, V. A.; Ovchinnikov, Yu. E.; Dementev, V. V.; Shklover, V. E.; Timofeeva, T. V.; Frunze, T. M.; Struchkov, Yu. T. *J. Organomet. Chem.* **1989**, *371*, 187. (d) Cp$_2$Ti(SiPh$_2$)$_4$: Holtman, M. S.; Schram, E. P. *J. Organomet. Chem.* **1980**, *187*, 147. (e) Cp$_2$Ta(H)(SiMe$_2$H)$_2$: Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (f) [Cp$_2$Ln(SiMe$_3$)$_2$][Li(DME)$_2$] (Ln = Sm, Lu): Schumann, H.; Nickel, S.; Hahn, E.; Heeg, M. J. *Organometallics* **1985**, *4*, 800.

(8) (a) Winter, C. H. *Aldrichim. Acta* **2000**, *33*, 3. (b) Custer, J. S.; Smith, P. M.; Fleming, J. G.; Roherty-Osmun, E. *ACS Symp. Ser.* **1999**, *No. 727*, 86. (b) Reid, J. S.; Kolawa, E.; Garland, C. M.; Nicolet, M.-A.; Cardone, F.; Gupta, D.; Ruiz, R. P. *J. Appl. Phys.* **1996**, *79*, 1109.

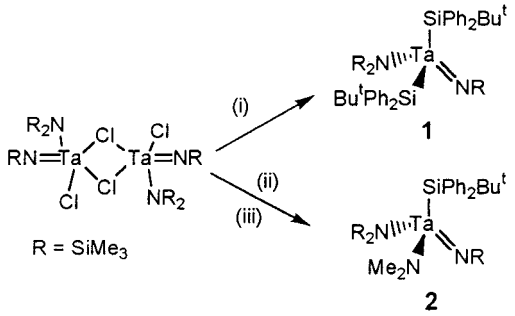
(9) Cabral, C., Jr.; Saenger, K. L.; Kotecki, D. E.; Harper, J. M. E. *J. Mater. Res.* **2000**, *15*, 194.

(10) Bradley, D. C.; Hursthouse, M. B.; Howes, A. J.; Jelfs, A. N. de M.; Runnacles, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 841.

(11) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1993**, *12*, 2584.

10.1021/om000503d CCC: $19.00
Publication on Web 09/21/2000

Scheme 1[a]



[a] Legend: (i) +2Li(THF)$_3$SiPh$_2$Bu^t; (ii) LiNMe$_2$; (iii) Li(THF)$_3$SiPh$_2$Bu^t.

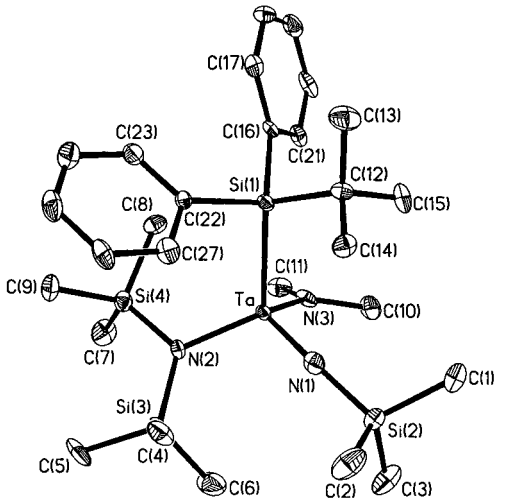


Figure 1. ORTEP diagram of **2**, showing 35% probability thermal ellipsoids.

longer than, e.g., 2.611(7) Å in $(Me_3SiCH_2)_2Ta(=CH\text{-}SiMe_3)Si(SiMe_3)_3$,[6d] 2.624(12)−2.633(2) Å in $Cp_2Ta(H)(SiMe_2H)_2$,[7e] 2.651(4) Å in $Cp_2Ta(H)_2SiPhMe_2$,[13] 2.669(4) Å in $(C_5Me_5)Ta(SiMe_3)Cl_3$,[14] and 2.689(1) Å in Cp*(2,6-Pr$^i_2$C$_6$H$_3$N=)Ta[Si(SiMe$_3$)$_3$]H.[15] The Ta−Si bond length in **2** is, however, shorter than 2.809(2) Å in Cp*(2,6-Pr$^i_2$C$_6$H$_3$N=)Ta(CO)[Si(SiMe$_3$)$_3$]H.[15] The Ta=N(1)−Si(2) bond angle (167.2(5)°) is close to being linear, indicating a significant degree of d−p π bonding between the electron-deficient Ta atom and the lone-pair electrons on the imido N atom.[16] The Ta−N bond length of 1.954(6) Å in Ta−NMe$_2$ is slightly shorter than that (1.993(7) Å) in the bulkier Ta−N(SiMe$_3$)$_2$.

The red Ta imido disilyl complex [(Me$_3$Si)$_2$N](Me$_3$SiN=)Ta(SiPh$_2$Bu^t)$_2$ (**1**) was prepared from the reaction of {Ta(μ-Cl)Cl(=NSiMe$_3$)[N(SiMe$_3$)$_2$]}$_2$ (**3**) with 4 equiv of Li(THF)$_3$SiPh$_2$Bu^t (Scheme 1).[17] The disilyl imido complex **1** was unstable in solution and photosensitive in the solid state. In comparison, such decomposition was not observed in the monosilyl imido complex **2**. Attempts to obtain the X-ray crystal structure of **1** were unsuccessful. The structure assignment of **1** is based on its ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra in comparison to its monosilyl analogue **2** and its elemental analysis. The ^{29}Si resonance of the silyl ligand in diamide **2** (64.9 ppm) is shifted upfield from that in monoamide **1** (95.0 ppm). The additional amido ligand in **2** and the d−p π bond between its lone-pair electrons and the Ta atom perhaps increases the electron density and magnetic shielding around the metal center. This enhanced shielding may also be reflected in the upfield shifts of the resonances of β-Si atoms in **2**. These ^{29}Si resonances are −1.9 ppm in −N(*Si*Me$_3$)$_2$ and −6.5 ppm in =N*Si*Me$_3$ in diamido **2**. In comparison, ^{29}Si resonances of −N(*Si*Me$_3$)$_2$ and =N*Si*Me$_3$ are 7.4 and −2.4 ppm, respectively, in monoamide **1**.

The diamido imido silyl complex [(Me$_3$Si)$_2$N](Me$_2$N)(Me$_3$SiN=)Ta(SiPh$_2$Bu^t) (**2**) is analogous to dialkyl alkylidene silyl complexes (RCH$_2$)$_2$(RCH=)TaSiR′$_3$ (R = Bu^t, Me$_3$Si; R′$_3$ = (SiMe$_3$)$_3$, Ph$_2$Bu^t) (Scheme 1).[6a,d] However, a key difference between the two structural types is that there are substantial d−p π bonds between the lone-pair electrons in the amido imido ligands and the metal atom in **2**, and the metal centers in these complexes are thus more electron rich.[16] [(Me$_3$Si)$_2$N](Me$_3$SiN=)Ta(SiPh$_2$Bu^t)$_2$ (**1**) is the first known Cp-free amido imido disilyl complex. Its alkyl alkylidene disilyl analogue "(RCH$_2$)(RCH=)Ta(SiR′$_3$)$_2$" is, to our knowledge, unknown. Studies are currently underway to probe the reactivities of **1** and **2** and to evaluate their potentials as precursors for the preparation of Ta−Si−N ternary materials.

Acknowledgment is made to the National Science Foundation (Grant No. CHE-9904338 and the NSF Young Investigator program Grant No. CHE-9457368), Camille Dreyfus Teacher-Scholar program, and DuPont Young Professor program for financial support of this research.

Supporting Information Available: Complete listings of the crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000503D

(12) [(Me$_3$Si)$_2$N](Me$_2$N)(Me$_3$SiN=)Ta(SiPh$_2$Bu^t) (**2**). To a pale yellow solution of {Ta(μ-Cl)Cl(=NSiMe$_3$)[N(SiMe$_3$)$_2$]}$_2$ (1.00 g, 1.00 mmol) in 20 mL of diethyl ether was added 2 equiv of LiNMe$_2$ (0.l0 g, 2.0 mmol). The solution was stirred at room temperature for 4 h. Two equivalents of Li(THF)$_3$SiPh$_2$Bu^t (0.92 g, 2.00 mmol) in 20 mL of diethyl ether was added dropwise with stirring to the reaction solution at room temperature. After the mixture was stirred at room temperature for 10 h, the volatiles were removed under vacuum to give a yellow solid. Extraction of the solid with hexanes, followed by filtration and crystallization at −20 °C, yielded yellow crystals of **2** (0.33 g, 23%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 7.93−7.15 (m, 10H, C$_6H_5$), 3.22 (s, 6H, N*Me*$_2$), 1.36 (s, 9H, C*Me*$_3$), 0.41 (b, 9H, =NSi*Me*$_3$), 0.18 [s, 18H, N(Si*Me*$_3$)$_2$]. ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C): 144.2, 143.8, 137.9, 137.6, 128.2, 128.1, 127.8, 127.7 (*C*$_6$H$_5$), 47.3 (N*Me*$_2$), 30.4 (C*Me*$_3$), 23.8 (*C*Me$_3$), 5.6 [N(Si*Me*$_3$)$_2$], 4.0 (=NSi*Me*$_3$). ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 64.9 (*Si*Ph$_2$Bu^t), −1.9 [N(*Si*Me$_3$)$_2$], −6.5 (=N*Si*Me$_3$). Anal. Calcd for $C_{27}H_{52}N_3Si_4Ta$: C, 45.55; H, 7.36. Found: C, 45.32; H, 7.28.

(13) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.

(14) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037.

(15) Burckhardt, U.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 6328.

(16) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988; pp 22−23, 154−155.

(17) [(Me$_3$Si)$_2$N](Me$_3$SiN=)Ta(SiPh$_2$Bu^t)$_2$ (**1**). To a pale yellow solution of {Ta(μ-Cl)Cl(=NSiMe$_3$)[N(SiMe$_3$)$_2$]}$_2$ (1.00 g, 1.00 mmol) in 20 mL of hexanes was added 4 equiv of Li(THF)$_3$SiPh$_2$Bu^t (1.85 g, 4.00 mmol) in 20 mL of hexanes with stirring at −50 °C. The reaction solution was slowly warmed to room temperature and stirred for about 30 min. The solvent was removed under vacuum to give a red-brown solid. Extraction of the solid with hexanes, followed by filtration and crystallization at −20 °C yielded deep red crystals of **1** (0.96 g, 53%). ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C): δ 7.81−7.08 (m, 20H, C$_6H_5$), 1.28 (s, 18H, C*Me*$_3$), 0.69 [s, 9H, N(Si*Me*$_3$)$_2$], 0.36 [s, 9H, N(Si*Me*$_3$)$_2$], 0.28 (b, 9H, =NSi*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C): δ 145.1, 143.2, 139.0, 137.9, 128.4, 128.2, 127.8, 127.7 (*C*$_6$H$_5$), 30.9 (C*Me*$_3$), 25.3 (*C*Me$_3$), 6.3 (=NSi*Me*$_3$), 5.0 [N(Si*Me*$_3$)$_2$]. ^{29}Si{^{1}H} NMR (DEPT, benzene-d_6, 79.5 MHz, 23 °C): δ 95.02 (*Si*Ph$_2$Bu^t), 7.38 [N(*Si*Me$_3$)$_2$], −2.40 (=N*Si*Me$_3$). Anal. Calcd for $C_{41}H_{65}N_2Si_5Ta$: C, 54.27; H, 7.22. Found: C, 54.56; H, 7.31.