

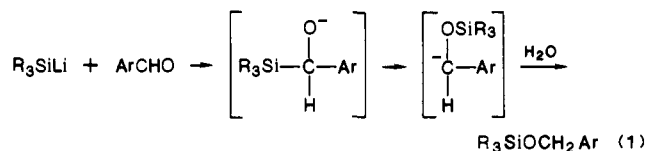
Insertion of Organic Carbonyls into the Tantalum-Silicon Bond of $(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3\text{TaSiMe}_3$. Preparation and Characterization of the α -Silylalkoxides $(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3\text{TaOCRR}'\text{SiMe}_3$

John Arnold and T. Don Tilley*

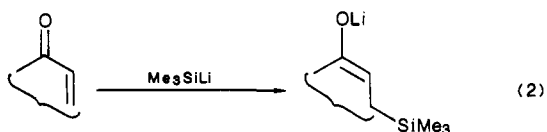
Contribution from the Chemistry Department D-006, University of California at San Diego, La Jolla, California 92093. Received November 5, 1987

Abstract: Organic carbonyl compounds $\text{O}=\text{CRR}'$ ($\text{R}, \text{R}' = \text{H}, \text{H}; \text{Me}, \text{H}; \text{Me}, \text{Me}; \text{Ph}, \text{H}; \text{Ph}, \text{Me}; -(\text{CH}_2)_5-$; $\text{CH}=\text{CH}_2$, $\text{H}; \text{CH}=\text{CH}_2$, Me) react with $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$ (**1**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) to give the α -silylalkoxide insertion products $\text{Cp}^*\text{Cl}_3\text{TaOCRR}'\text{SiMe}_3$ (**2a-h**). In contrast, reaction of **1** with benzophenone yields Me_3SiCl presumably via a reductive elimination pathway. Kinetic data for the insertion reactions are consistent with a second-order rate law, $\text{rate} = k[\text{1}][\text{carbonyl}]$. From reactions of **1** with acetone, the activation parameters are $\Delta H^\ddagger = 10.5$ (8) kcal mol^{-1} and $\Delta S^\ddagger = -35$ (3) eu. Hydrolyses of **2a**, **2b**, and **2h** produce the corresponding α -silyl alcohols $\text{HOCRR}'\text{SiMe}_3$. The insertion of diphenyldiazomethane into the Ta-Si bond of **1** leads to the orange complex $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-N}(\text{SiMe}_3)\text{NCPH}_2]$ (**3**).

The importance of organosilanes as intermediates in organic synthesis has increased interest in the development of methods that direct the placement of silyl groups in organic molecules.¹ Though many procedures are available for the electrophilic transfer of silyl groups,^{1,2} few exist for carrying out nucleophilic silylations. Alkali-metal silyl derivatives serve as silyl anion sources in the reduction of aldehydes or ketones to α -silyl alcohols.³ With aromatic aldehydes and ketones however, the initial adduct rapidly rearranges, and silyl ethers are isolated (eq 1).⁴ (Trimethyl-

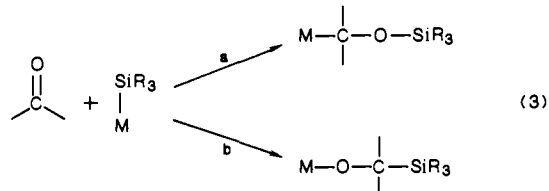


silyl)lithium⁵ and silylcuprate⁶ reagents add to α,β -unsaturated ketones to give 1,4-addition products (eq 2). (Trimethylsilyl)aluminum compounds can be used for the nucleophilic silylation of carbonyl compounds and add in a 1,2 sense to α,β -unsaturated aldehydes and ketones.⁷



Transition-metal silyl derivatives would seem to offer useful systems for selective silylations, but until now only electrophilic

transfer of silicon from a transition metal to a carbonyl group has been observed. A number of transition-metal complexes catalyze the hydrosilylation of carbonyl functionalities, and in some cases a high degree of regio- and enantioselectivity can be obtained.⁸ In these reactions, it has been postulated that a silyl group is transferred to the carbonyl oxygen by an insertion step that forms an α -siloxyalkyl complex (eq 3, path a).⁸ Stoichiometric insertion reactions of this kind involving manganese and iron silyls have been studied in detail by Gladysz and co-workers.⁹



In the reactions that are known to follow path a, the transition metal is electron-rich or low-valent. Our investigations of the chemistry of d^0 transition-metal silyl complexes¹⁰ have shown that the M-Si bonds in these compounds react as though polarized in the sense $\text{M}^{\delta+}-\text{Si}^{\delta-}$.^{10a,d} These observations, and the reactive nature of early-transition-metal silyl derivatives toward insertion of carbon monoxide^{10b,c,g} suggested that organic carbonyl compounds might be readily silylated by insertions into d^0 M-Si bonds, and that the insertion products might be α -silylalkoxide derivatives (eq 3, path b). Here we report the reactions of aldehydes and ketones with the tantalum silyl $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$ ^{10d} (**1**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), and the first examples of nucleophilic transfer of a silyl group from a transition metal to a carbonyl functionality.

(1) (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth and Co.: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

(2) Klebe, J. *Adv. Org. Chem.* **1972**, *8*, 97.

(3) (a) Gilman, H.; Wu, T. C. *J. Am. Chem. Soc.* **1954**, *76*, 2502. (b) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 2680.

(4) (a) Brook, A. G.; LeGrow, G. E.; MacRae, D. M. *Can. J. Chem.* **1967**, *45*, 239. (b) Wittenberg, D.; Wu, T. C.; Gilman, H. *J. Org. Chem.* **1959**, *24*, 1349. (c) Gilman, H.; Wu, T. C. *J. Am. Chem. Soc.* **1953**, *75*, 2935. (d) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (e) Brook, A. G.; Warner, C. M.; McGriskin, M. E. *J. Am. Chem. Soc.* **1959**, *81*, 981.

(5) (a) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. (b) Still, W. C.; Mitra, A. *Tetrahedron Lett.* **1978**, 2659.

(6) (a) Ager, D. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1978**, 177. (b) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. (c) Fleming, I.; Kilburn, J. D. *J. Chem. Soc., Chem. Commun.* **1986**, 305. (d) Fleming, I.; Marchi, D., Jr. *Synthesis* **1981**, 560.

(7) (a) Rösch, L.; Altnau, G.; Otto, W. H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 581. (b) Altnau, G.; Rösch, L. *Tetrahedron Lett.* **1983**, *24*, 45.

(8) (a) James, B. R. *Adv. Organomet. Chem.* **1978**, *17*, 319. (b) Ojima, I.; Nihonyanagi, M.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *94*, 449. (c) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. (d) Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (e) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1982**, *3*, 1354. (f) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *112*, 253. (g) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. (h) Peyronel, J. F.; Kagan, H. B. *Now. J. Chem.* **1978**, *2*, 211.

(9) (a) Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. (b) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433. (c) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508.

(10) (a) Tilley, T. D. *Organometallics* **1985**, *4*, 1452. (b) Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084. (c) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409. (d) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (e) Arnold, J.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5355. (f) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473. (g) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.*, in press.

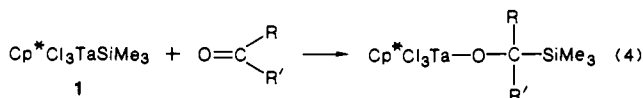
Table I. Data for the Alkoxides $Cp^*Cl_3TaOCRR'SiMe_3$ (**2**), Prepared from **1** and the Carbonyl Compound Listed

entry	CO compd	isolated yield, %	1H NMR, δ	^{13}C NMR, δ
2a	$(CH_2O)_n$	66	0.11 (s, 9 H, $SiMe_3$), ^a 2.40 (s, 15 H, C_5Me_5), 4.72 (s, 2 H, OCH_2Si)	-2.57 ($SiMe_3$), ^a 12.70 (C_5Me_5), 78.52 (OCH_2Si), $^1J_{CH} = 133$ Hz), 127.9 (C_5Me_5)
2b		60	0.11 (s, 9 H, $SiMe_3$), ^b 1.31 (d, 3 H, $J = 7.3$ Hz, $OCHMeSi$), 2.12 (s, 15 H, C_5Me_5), 5.05 (q, 1 H, $J = 7.3$ Hz, $OCHMeSi$)	-2.92 ($SiMe_3$), ^b 12.97 (C_5Me_5), 19.00 ($OCHMeSi$), 88.09 ($OCHMeSi$), $^1J_{CH} = 137$ Hz), 128.3 (C_5Me_5)
2c		75	0.16 (s, 9 H, $SiMe_3$), ^b 1.42 (s, 6 H, $OCMe_2Si$), 2.13 (s, 15 H, C_5Me_5)	-2.64 ($SiMe_3$), ^a 13.28 (C_5Me_5), 25.64 ($OCMe_2Si$), 94.95 ($OCMe_2Si$), 128.1 (C_5Me_5)
2d		78	0.19 (s, 9 H, $SiMe_3$), ^b 2.06 (s, 15 H, C_5Me_5), 5.91 (s, 1 H, $OCHPhSi$), 7.00-7.20 (m, 5 H, $OCHPhSi$)	-2.89 ($SiMe_3$), ^a 12.89 (C_5Me_5), 96.04 ($OCHPhSi$), $^1J_{CH} = 136$ Hz), 126.6, 126.9, 128.2, 141.4 (Ph), 128.7 (C_5Me_5)
2e		50	0.06 (s, 9 H, $SiMe_3$), ^a 1.93 (s, 3 H, $OCMePhSi$), 2.30 (s, 15 H, C_5Me_5), 7.25-7.40 (m, 5 H, $OCMePhSi$)	-2.93 ($SiMe_3$), ^a 13.17 (C_5Me_5), 20.86 ($OCMePhSi$), 98.37 ($OCMePhSi$), 125.4, 126.6, 127.9, 145.5 (Ph), 128.5 (C_5Me_5)
2f		70	0.23 (s, 9 H, $SiMe_3$), ^a 1.3-2.2 (m, 10 H, C_6H_{10}), 2.44 (C_5Me_5)	-0.46 ($SiMe_3$), ^a 13.30 (C_5Me_5), 22.90, 25.13, 35.05, 99.52 (C_6H_{10}), 128.2 (C_5Me_5)
2g		71	0.17 (s, 9 H, $SiMe_3$), ^b 2.12 (s, 15 H, C_5Me_5), 4.86 (m, 2 H, $OCH(CHCH_2)Si$), 5.40 (d, 1 H, $J = 9$ Hz, $OCH(CHCH_2)Si$), 5.91 (m, 1 H, $OCH(CHCH_2)Si$)	-3.06 ($SiMe_3$), ^b 12.97 (C_5Me_5), 94.94 ($OCH(CHCH_2)Si$), $^1J_{CH} = 135$ Hz), 113.5 ($OCH(CHCH_2)Si$), $^1J_{CH} = 162$ Hz), 128.2 (C_5Me_5), 137.9 ($OCH(CHCH_2)Si$), $^1J_{CH} = 156$ Hz)
2h		62	0.19 (s, 9 H, $SiMe_3$), ^b 1.51 (s, 3 H, $OCMe(CHCH_2)Si$), 2.13 (s, 15 H, C_5Me_5), 4.83 (m, 2 H, $OCMe(CHCH_2)Si$), 6.26 (m, 1 H, $OCMe(CHCH_2)Si$)	-2.82 ($SiMe_3$), ^b 13.15 (C_5Me_5), 96.80 ($OCMe(CHCH_2)Si$), 110.9 ($OCMe(CHCH_2)Si$), $^1J_{CH} = 157$ Hz), 128.2 (C_5Me_5), 142.0 ($OCMe(CHCH_2)Si$), $^1J_{CH} = 156$ Hz)

^aSpectrum recorded in chloroform-*d* at 300 (1H) or 75.5 MHz (^{13}C). ^bSpectrum recorded in benzene-*d*₆ at 300 (1H) or 75.5 MHz (^{13}C).

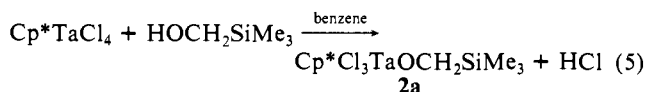
Results and Discussion

Green, benzene solutions of the tantalum silyl **1** react with organic carbonyl compounds at room temperature to give yellow solutions of the tantalum α -silylalkoxides **2a-h** (eq 4). The yellow,

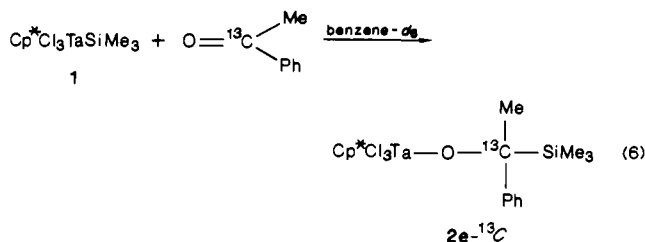


- 2a.** R = R' = H
2b. R = Me, R' = H
2c. R = R' = Me
2d. R = Ph, R' = H
2e. R = Ph, R' = Me
2f. R, R' = (-CH₂)₅
2g. R = CH=CH₂, R' = H
2h. R = CH=CH₂, R' = Me

crystalline insertion products were isolated in moderate to high yields following removal of volatiles and crystallization from diethyl ether (see Table I). Elemental analyses, 1H NMR, ^{13}C NMR, and IR spectroscopy confirm that insertion of the carbonyl compounds into the Ta-Si bond of **1** has occurred. The Ta-O-C-Si connectivity was established by three experiments (eq 5-7). First, compound **2a** was prepared independently from Cp^*TaCl_4 and $HOCH_2SiMe_3$ (eq 5). Yellow crystals of the compound obtained

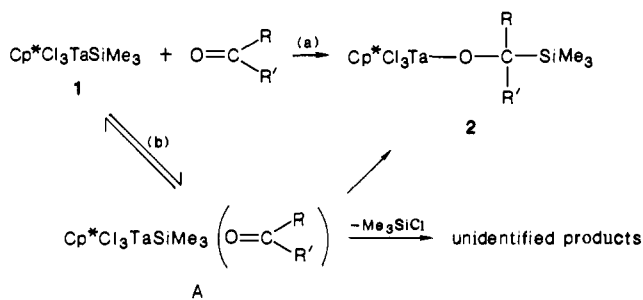


from this reaction were identical (by 1H NMR and melting point) with those from the reaction of formaldehyde with **1**. Second, ^{13}C -labeled **2e** (**2e**- ^{13}C) was prepared by using acetophenone- ^{13}C (eq 6). The 1H NMR spectrum of **2e**- ^{13}C shows



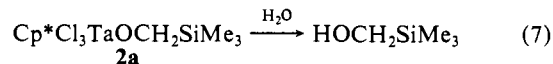
that the $SiMe_3$ protons are split into a doublet ($^3J_{CH} = 1.3$ Hz).

Scheme I



This result is also consistent with the indicated bonding arrangement, since we have observed similar three-bond coupling constants in related systems, e.g., $Cp^*Cl_3TaO^{13}CH(SiMe_3)^{13}C(O)OEt$ ($^3J_{CH} = 1.9$ Hz),^{10c} $Cp^*Cl_3Ta(\eta^2-^{13}COSiMe_3)$ ($^3J_{CH} = 1.5$ Hz),^{10c} and $Cp_2Zr(\eta^2-^{13}COSiMe_3)Cl$ ($^3J_{CH} = 1.8$ Hz).^{10g}

Finally, the α -silyl alcohol products are readily released from tantalum via hydrolysis. Reaction of **2a** with excess water in chloroform-*d* results in quantitative formation of (trimethylsilyl)methanol (eq 7), identified by 1H NMR and GC analysis.



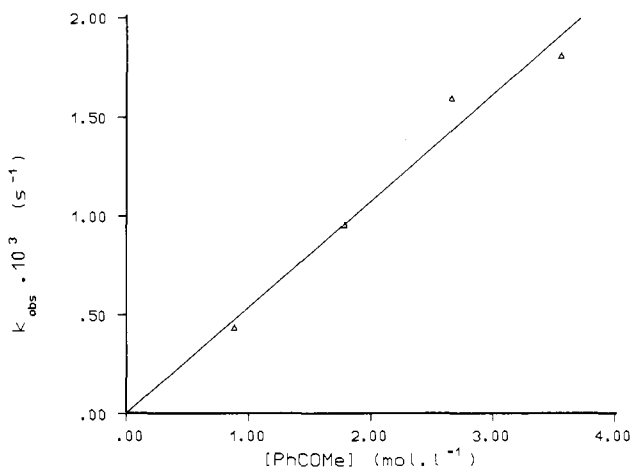
In a similar manner, **2b** and **2h** were hydrolyzed in benzene-*d*₆ to generate 1-(trimethylsilyl)ethanol and 1-vinyl-1-(trimethylsilyl)ethanol, respectively. The yellow, insoluble tantalum-containing products from these reactions were not identified.

The yields of the insertion reactions in eq 4 are quantitative by 1H NMR (benzene-*d*₆). The reaction involving acetophenone (1 equiv) also gave small amounts (ca. 15%) of Me_3SiCl after complete reaction (1 day), possibly due to some decomposition of **1**.^{10d} With excess acetophenone (>3 equiv), however, insertion occurs rapidly (<1 h at 34 °C) and quantitatively. In the reaction between **1** and benzophenone (benzene, room temperature, 3 days) elimination of Me_3SiCl was quantitative, and no insertion products were observed. None of the tantalum-containing products from these reductive elimination reactions could be characterized. We have previously shown that donor molecules (CO ,^{10c} PMe_3 ^{10d} and alkynes^{10d}) induce reductive elimination of Me_3SiCl from **1**. It

Table II. Rate Data for Reaction of **1** with Carbonyl Compounds^a

CO compd	half-life, min	CO compd	half-life, min
MeCHO	<0.5	CH ₂ (CH ₂) ₄ CO	3.6 ^b
Me ₂ CO	4.1 ^b	(CH ₂ CH)CHO	<1
PhCHO	<1	(CH ₂ CH)MeCO	<1
PhMeCO	26 ^b		

^aReactions carried out in benzene-*d*₆ with 1 equiv of carbonyl compound at 22 °C, unless otherwise stated. ^bReactions carried out in benzene-*d*₆ with a tenfold excess of carbonyl compound at 34 °C.

**Figure 1.** Plot of k_{obsd} vs. [acetophenone] (measured by ¹H NMR at 34 °C, with [1]_{initial} = 0.089 M, benzene-*d*₆).

therefore seems likely that similar processes occur in the reactions of **1** with carbonyl compounds and that insertion and reductive elimination from an intermediate adduct such as A (Scheme I) are competing reactions.

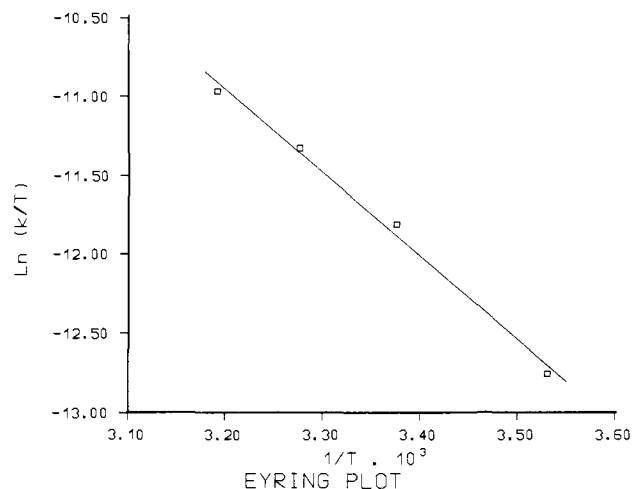
Rates of the insertion reactions in eq 4 are highly dependent upon the nature of the carbonyl substituents. **1** reacts with aldehydes (1 equiv) within seconds at room temperature,¹¹ whereas ketones insert much more slowly (see Table II). These results follow well-established trends for nucleophilic attack at carbonyl groups; i.e., bulky substituents and/or groups that serve to diminish the electrophilicity of the carbonyl carbon tend to lower the rate.^{12,13} Analogous chemoselectivity is observed in additions of titanium alkyls to carbonyl groups.¹⁴

The α,β -unsaturated carbonyl compounds acrolein and methyl vinyl ketone (R = CH=CH₂) react faster with **1** than the analogous derivatives with R = Me. No evidence was found for 1,4-addition products in these reactions. This contrasts the behavior of lithium and copper silyls, which add in a 1,4 manner to α,β -unsaturated carbonyl compounds,^{5,6} yet is analogous to the reactivity of aluminum silyls.⁷

Reaction rates were monitored by ¹H NMR in benzene-*d*₆ under pseudo-first-order conditions with excess carbonyl compound. The linearity of plots of ln[1] vs. time (in reactions with acetophenone or acetone) established first-order dependence in **1**. As shown in Figure 1, a plot of k_{obsd} vs. [acetophenone] is linear and intercepts the origin. The above results are consistent with a second-order rate law of the form:

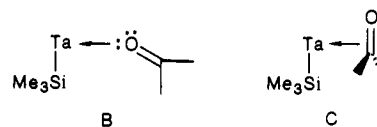
$$\text{rate} = k[1][\text{carbonyl}]$$

Further evidence for a bimolecular process was obtained from activation parameters for the reaction giving **2c** (Figure 2). Least-squares analysis gave the values $\Delta H^\ddagger = 10.5$ (8) kcal mol⁻¹

**Figure 2.** Eyring plot for reaction of **1** plus acetone in benzene-*d*₆.

and $\Delta S^\ddagger = -35$ (3) eu. These values are comparable to those obtained by Brown et al.^{13a} in studies of the sodium borohydride reduction of ketones. The latter reactions were also found to obey a second-order rate law with the same general ordering of reaction rates with respect to carbonyl substituents.

The kinetic data are consistent with two indistinguishable reaction mechanisms¹⁵ (Scheme I). One is a direct insertion process resulting from bimolecular collision between **1** and the carbonyl species (path a). The results are also explained by a mechanism involving a steady-state intermediate complex A (path b). In such an adduct, both η^1 - and η^2 -ligation of the carbonyl compound may be considered.^{16,17} The hard, d⁰ tantalum center in **1** would seem to prefer donation from a lone pair of a carbonyl oxygen to give an η^1 -geometry (B) analogous to that of *anti*-PhCHO-BF₃,¹⁸



although in such a structure the carbonyl compound and the metal are coplanar, and an intramolecular rearrangement involving Si-C bond formation may be geometrically unfavorable. In related additions of organometallic reagents to ketones, intermediate adducts analogous to A have been observed.¹⁹ Analysis of rate data for the addition of trimethylaluminum to benzophenone has led to formulation of a mechanism involving dissociation of the initially formed Ph₂C=O-AlMe₃ adduct within a solvent cage,

(15) Espensen, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 78.

(16) See, for example: (a) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (b) Wood, C. D.; Schrook, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421. (c) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173. (d) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056. (e) Brown, K. L.; Clark, G. R.; Headford, E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (f) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311. (g) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. (h) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (i) Boudjouk, P.; Woell, J. B.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 582. (j) Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 140.

(17) (a) Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430. (b) Brun, L. *Acta Crystallogr.* **1966**, *20*, 739.

(18) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

(19) (a) Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975**, *75*, 521. (b) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *Acc. Chem. Res.* **1974**, *7*, 272. (c) Ashby, E. C.; Laemmle, J. T. *J. Org. Chem.* **1968**, *33*, 3398. (d) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1968**, *90*, 5179. (e) Laemmle, J.; Ashby, E. C.; Neumann, H. M. *J. Am. Chem. Soc.* **1971**, *93*, 5120. (f) Smith, S. G.; Billet, J. J. *J. Am. Chem. Soc.* **1967**, *89*, 6948.

(11) Paraformaldehyde reacts slowly due to its insolubility.

(12) (a) Gutsche, D. C. *The Chemistry of Carbonyl Compounds*; Prentice-Hall: Englewood Cliffs, NJ, 1967; pp 24-44. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 782.

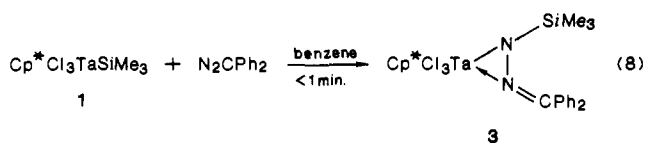
(13) (a) Brown, H. C.; Wheeler, O. H.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 214. (b) Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 221. (c) Brown, H. C.; Mead, E. J.; Rao, B. C. S. *J. Am. Chem. Soc.* **1955**, *77*, 6209.

(14) (a) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. (b) Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1.

followed by addition of an aluminum-carbon bond across the carbonyl group via a four-center transition state.²⁰ This mechanism avoids unfavorable rotation about the C-O double bond that would accompany a direct intramolecular rearrangement of the $Ph_2C=O \cdot AlMe_3$ complex to product. Presently definitive evidence for adduct **1** is lacking. The low-temperature ($-70^\circ C$) 1H NMR spectrum of **1** (toluene- d_6) was unaffected by addition of acetone (4 equiv). We have similarly been unable to directly observe intermediate complexes in reactions of **1** with donor ligands such as phosphines, alkynes, and carbon monoxide, although such adducts appear to play an important role in the reaction chemistry of **1**.^{10c,d}

We have briefly surveyed the reactivity of **1** toward other unsaturated substrates. Diphenylketene does not react with **1** at room temperature (1 day), but at $90^\circ C$ (benzene- d_6) Me_3SiCl is produced as the sole Me_3Si -containing product. Compound **1** is unreactive toward ethyl acetate (benzene- d_6 , room temperature, 2 days), phenyl isocyanate (benzene- d_6 , room temperature, 2 days), carbon dioxide (100 psi, pentane, room temperature, 2 days), and propylene oxide (neat, room temperature, 1 h).

Diphenyldiazomethane reacts with **1** to produce orange crystals of **3** in good yield (eq 8). The reaction is quantitative by 1H NMR (benzene- d_6). Complex **3** has been characterized by NMR, IR,



and mass spectroscopy and by elemental analysis. The proposed structure of **3** is analogous to that of $Cp_2Zr[\eta^2-N(Me)NCPH_2]Me$, characterized by X-ray crystallography.²¹ The $\nu(C=N)$ infrared absorption for **3** at 1537 cm^{-1} is similar to that observed for the zirconium compound (1515 cm^{-1}). In the $^{13}C\{^1H\}$ spectrum of **3**, the chemical shift of the diazo carbon atom ($\delta\ 156.3$) is in the range typically observed for free diazo compounds.²² As expected, the phenyl rings in **3** are inequivalent by ^{13}C NMR.

Summary and Conclusions

We have demonstrated that a variety of organic carbonyl compounds readily insert into the Ta-Si bond of **1**. Steric factors appear to be important, and with bulky carbonyl group substituents the insertion is sluggish and may not occur at all. In contrast to late transition-metal silyls, where carbonyl insertions yield α -siloxyalkyl derivatives via silyl migration to oxygen, **1** transfers the silyl group to carbon, producing α -silylalkoxides **2a-h**. Formation of a strong Ta-O bond and the nucleophilic character of the silyl group in **1** are presumably major factors in determining the course of the additions. The reactions obey clean second-order kinetics and may proceed through an intermediate donor-acceptor adduct. These results illustrate the potential for using transition-metal silyl complexes to achieve chemoselective nucleophilic transfer of silyl groups to unsaturated substrates. It seems likely that this synthetic method can be refined to provide a range of stereoselective silyl additions. Further studies of carbonyl insertion reactions in other early-transition-metal silyl complexes are in progress.

Experimental Section

Manipulations were performed under an atmosphere of nitrogen or argon by using Schlenk techniques or in a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Galbraith or Schwarzkopf laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer. Mass spectra were obtained at the UC Riverside Mass Spectroscopy facility. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (1H) and 75.5 MHz (^{13}C) or at 90 MHz with a Varian EM 390

spectrometer (1H). GC analyses were conducted on a Varian 3400 coupled to a Varian 4290 integrator, using a $3\text{ m} \times 1/8$ in. stainless steel column with 25% 1,2,3-tris(2-cyanoethoxy)propane as stationary phase. Paraformaldehyde (Aldrich) was heated at $60^\circ C$ under vacuum (10^{-3} mmHg) for 8 h before use. Methyl vinyl ketone, acrolein, acetone, acetaldehyde, ethylacetate, propylene oxide, acetophenone, benzaldehyde, and cyclohexanone were dried with 5A molecular sieves, and distilled before use. Benzophenone was recrystallized from ethanol and dried under vacuum overnight. Carbon dioxide (Matheson) was used as received. Phenyl isocyanate was dried over 5A molecular sieves and deoxygenated with a stream of nitrogen gas. Trimethylsilylmethanol (Petrarch) was distilled under nitrogen. Acetophenone- $carbonyl-^{13}C$ (99 atom % ^{13}C , Aldrich) was freeze-pump-thaw degassed (three cycles) and dried with 5A molecular sieves.

Cp*Cl₃TaOCH₂SiMe₃ (2a). (a) Compound **1** (0.30 g, 0.60 mmol), paraformaldehyde (0.018 g, 0.60 mmol), and dichloromethane (5 mL) were stirred for 1 day. After removal of solvent in vacuo, the yellow residue was extracted with diethyl ether (40 mL). Concentration to 5 mL followed by cooling to $-45^\circ C$ overnight gave 0.21 g (66%) of yellow crystals (mp $128-130^\circ C$). IR (Nujol, CsI, cm^{-1}): 1475 m, 1401 m, 1298 w, 1257 m, 1240 s, 1206 m, 1070 s, 1021 m, 845 br s, 768 m, 699 m, 672 m, 598 w, 558 m, 423 w, 366 m, 320 s, 282 s. Anal. Calcd for $C_{14}H_{26}Cl_3OTaSi$: C, 31.3; H, 4.99. Found: C, 31.2; H, 5.01.

(b) To a suspension of Cp^*TaCl_4 (1.50 g, 3.28 mmol) in benzene (50 mL) was added $HOCH_2SiMe_3$ (0.41 mL, 3.3 mmol), and the resulting solution was allowed to stir for 12 h. The volatiles were removed in vacuo, and the yellow residue was extracted into diethyl ether (100 mL). Concentration to 20 mL and cooling ($-45^\circ C$) of this extract gave 0.53 g (31%) of yellow crystals. The melting point and 1H NMR spectrum of this material were identical with those obtained for the product of procedure a.

Cp*Cl₃TaOCHMeSiMe₃ (2b). Acetaldehyde (34 μ L, 0.60 mmol) was added to a solution of **1** (0.30 g, 0.60 mmol) in benzene (10 mL). After 2 min, the yellow solution was evaporated to dryness. A diethyl ether extract (30 mL) of the residue was concentrated to ca. 5 mL and cooled to $-45^\circ C$. Yellow crystals (mp $109-110^\circ C$) of the product were isolated by filtration (0.19 g, 60%). IR (Nujol, CsI, cm^{-1}): 2720 w, 1291 w, 1288 w, 1243 s, 1090 m, 1035 s, 977 s, 940 m, 836 s, 751 m, 717 m, 692 w, 660 m, 559 m, 550 m, 365 m, 321 m, 287 s. Anal. Calcd for $C_{15}H_{28}Cl_3OTaSi$: C, 33.4; H, 5.23. Found: C, 33.5; H, 5.32.

Cp*Cl₃TaOCMe₂SiMe₃ (2c). Acetone (44 μ L, 0.60 mmol) was added to a solution of **1** (0.30 g, 0.60 mmol) in benzene (10 mL), and the resulting solution was stirred for 24 h. After evaporation of the volatiles, the pale green residue was extracted into diethyl ether (30 mL). The diethyl ether solution was concentrated to 5 mL and cooled ($-45^\circ C$). After 12 h the product (mp $155-156^\circ C$ dec) was isolated by filtration in 75% yield (0.25 g). IR (Nujol, CsI, cm^{-1}): 2719 w, 1475 m, 1247 s, 1101 m, 1020 w, 998 s, 881 m, 833 s, 749 m, 718 w, 688 w, 661 w, 605 w, 361 m, 317 m, 288 s. Anal. Calcd for $C_{16}H_{30}Cl_3OTaSi$: C, 34.7; H, 5.46. Found: C, 34.9; H, 5.56.

Cp*Cl₃TaOCHPhSiMe₃ (2d). Addition of benzaldehyde (62 μ L, 0.58 mmol) to a benzene (20 mL) solution of **1** (0.29 g, 0.58 mmol) caused a rapid (<2 min) color change to yellow. After removal of volatiles, the residue was extracted with diethyl ether (30 mL). The volume of the extract was reduced to 5 mL, and after the solution was cooled to $-45^\circ C$ for 10 h, yellow crystals (mp $159-161^\circ C$) of the product were isolated by filtration (0.27 g, 78%). IR (Nujol, CsI, cm^{-1}): 3050 w, 2719 w, 1595 w, 1293 w, 1241 s, 1200 m, 1152 m, 1141 m, 1068 w, 1025 br s, 918 m, 840 br s, 779 m, 760 m, 741 w, 701 s, 685 m, 648 m, 618 m, 599 m, 484 m, 367 m, 322 s, 290 s. Anal. Calcd for $C_{20}H_{30}Cl_3OTaSi$: C, 39.9; H, 5.02. Found: C, 39.9; H, 5.31.

Cp*Cl₃TaOCMePhSiMe₃ (2e). Acetophenone (0.12 g, 1.0 mmol) was added to a benzene solution (10 mL) of **1** (0.50 g, 1.0 mmol), and the resulting solution was stirred for 2 days. After evaporation of the volatiles, the pale green residue was dissolved in diethyl ether (30 mL). Concentration of this solution to 5 mL and cooling ($-45^\circ C$) afforded 0.31 g (50%) of pale green crystals (mp $160-165^\circ C$ dec). IR (Nujol, CsI, cm^{-1}): 3050 w, 2717 w, 1255 w, 1241 m, 1058 w, 1025 m, 1016 m, 970 s, 836 s, 752 w, 699 m, 621 w, 489 w, 373 w, 312 m, 288 m. Anal. Calcd for $C_{21}H_{32}Cl_3OTaSi$: C, 40.9; H, 5.24. Found: C, 40.7; H, 5.13.

Cp*Cl₃TaOC(SiMe₃)(CH₂)₄CH₂ (2f). Cyclohexanone (75 μ L, 0.73 mmol) was added to **1** (0.36 g, 0.73 mmol) in benzene (20 mL), and the resulting solution was stirred for 18 h. Removal of volatiles left a pale yellow residue that was dissolved in diethyl ether (30 mL). Filtration, concentration (to 5 mL), and cooling ($-45^\circ C$) afforded yellow platelike crystals (mp $148-150^\circ C$ dec) of the product in 70% yield (0.30 g). IR (Nujol, CsI, cm^{-1}): 2710 w, 1244 s, 1027 m, 981 s, 925 w, 832 s, 801 w, 750 m, 718 w, 680 w, 636 m, 365 m, 311 s, 285 s. Anal. Calcd for $C_{19}H_{34}Cl_3OTaSi$: C, 38.4; H, 5.77. Found: C, 37.3; H, 5.57.

(20) Neumann, H. M.; Laemmle, J.; Ashby, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 2597.

(21) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029.

(22) Breitmaier, E.; Voelter, W. *¹³C NMR Spectroscopy*, 2nd ed.; Verlag Chemie: Weinheim, New York, 1978.

Table III. Observed Rate Constants for the Reaction of **1** with Acetophenone in Benzene-*d*₆ at 34 °C (See Figure 1)

[1], M	[PhMeCO], M	10 ³ <i>k</i> _{obsd} , s ⁻¹
0.089	0.44	0.89
0.089	0.96	1.79
0.089	1.60	2.67
0.089	1.81	3.56

Cp*Cl₃TaOCH(CH=CH₂)SiMe₃ (2g). Addition of acrolein (40 μL, 0.60 mmol) to a benzene (20 mL) solution of **1** (0.30 g, 0.60 mmol) resulted in a rapid (<1 min) color change from green to yellow. After 10 min, volatiles were removed, and the product was extracted into diethyl ether (30 mL). Concentration (10 mL) and cooling (-45 °C) for 12 h gave 0.24 g (71%) of **2g** as yellow crystals (mp 163–164 °C). IR (Nujol, CsI, cm⁻¹): 3065 w, 2710 w, 1617 w, 1240 m, 1180 w, 1098 w, 1022 s, 986 m, 920 m, 837 s, 770 w, 755 m, 691 w, 615 m, 362 m, 321 m, 299 m, 275 m. Anal. Calcd for C₁₆H₂₈Cl₃OTaSi: C, 34.8; H, 5.11. Found: C, 34.8; H, 5.20.

Cp*Cl₃TaOCMe(CH=CH₂)SiMe₃ (2h). Methyl vinyl ketone (52 μL, 0.63 mmol) was added to a benzene (20 mL) solution of **1** (0.31 g, 0.63 mmol). After the solution was stirred for 12 h, volatiles were removed and the yellow residue was extracted into diethyl ether (30 mL). Concentration to 15 mL and cooling (-45 °C) gave 0.22 g (62%) of **2h** as yellow crystals (mp 158–160 °C dec). IR (Nujol, CsI, cm⁻¹): 3075 w, 2712 w, 1618 w, 1401 w, 1242 s, 1149 m, 1068 m, 1000 s, 958 m, 906 m, 865 m, 832 s, 760 m, 749 m, 690 w, 629 m, 547 w, 458 w, 367 m, 318 m, 286 s. Anal. Calcd for C₁₇H₃₀Cl₃OTaSi: C, 36.1; H, 5.34; Cl, 18.8. Found: C, 36.2; H, 5.33; Cl 18.9.

Reaction of 1 with Acetophenone-carbonyl-¹³C. A 5-mm NMR tube was charged with **1** (0.020 g, 0.04 mmol), acetophenone-carbonyl-¹³C (4.8 μL, 0.04 mmol) and benzene-*d*₆ (0.4 mL). After 3 h, examination of the ¹H NMR spectrum revealed a 40% conversion to Cp*Cl₃TaO¹³CMePhSiMe₃. The peak due to the SiMe₃ group of the product at δ 0.06 was split into a doublet (³*J*_{CH} = 1.3 Hz). The methyl peak of the product at δ 1.93 was also split into a doublet (²*J*_{CH} = 45 Hz).

Hydrolysis Reactions. 2a. Water (2 μL; excess, degassed) was added to a solution of **2a** (0.017 g) and ferrocene (0.0014 g, as internal standard) in chloroform-*d*. An unidentified yellow solid precipitated. The ¹H NMR spectrum of the solution revealed a quantitative conversion to HOCH₂SiMe₃. GC analysis of the reaction solution also confirmed the presence of the free alcohol. ¹H NMR of HOCH₂SiMe₃ (chloroform-*d*, 90 MHz, 34 °C): δ 0.06 (s, 9 H, SiMe₃), 3.38 (s, 2 H, OCH₂Si).

2b. A solution of **2b** (0.015 g) in benzene-*d*₆ (0.40 mL) was treated with excess degassed water (3 μL). A yellow solid quickly precipitated. Examination of the ¹H NMR spectrum showed quantitative conversion to HOCHMeSiMe₃; ¹H NMR (benzene-*d*₆, 90 MHz, 34 °C): δ 0.00 (s, 9 H, SiMe₃), 0.97 (d, *J* = 7 Hz, 3 H, Me), 3.18 (q, *J* = 7 Hz, 1 H, OCH).

Table IV. Temperature Dependence of Observed Rate for Reaction of **1** with Acetone in Benzene-*d*₆ (See Experimental Section)

10 ³ (1/ <i>T</i>), K	10 ³ <i>k</i> , M ⁻¹ s ⁻¹	10 ³ (1/ <i>T</i>), K	10 ³ <i>k</i> , M ⁻¹ s ⁻¹
3.53	0.818	3.28	3.66
3.78	2.19	3.19	5.38

2h. With use of the method described for **2b** above, **2h** was hydrolyzed to HOC(CH₂)MeSiMe₃; ¹H NMR (benzene-*d*₆, 90 MHz, 34 °C): δ 0.00 (s, 9 H, SiMe₃), 1.10 (s, 3 H, Me), 4.79–5.07 (m, 2 H, CHCH₂), 5.76–6.00 (m, 1 H, CHCH₂).

Cp*Cl₃Ta[η²-N(SiMe₃)NCPh₂] (3). Benzene (30 mL) was added to a flask containing **1** (1.00 g, 1.01 mmol) and Ph₂CN₂ (0.20 g, 1.0 mmol), and the resulting solution was stirred for 5 min. After removal of volatiles under vacuum, the orange residue was extracted with diethyl ether (2 × 30 mL). Concentration to ca. 30 mL and cooling (-45 °C) gave the product as orange crystals (mp 150–151 °C) in 58% yield (0.40 g). FABMS (in orthonitrophenyloctyl ether): *m/z* 652.1297 (M⁺ - HCl requires 652.1270). IR (Nujol, CsI, cm⁻¹): 3038 w, 3010 w, 1590 w, 1572 w, 1537 m, 1480 m sh, 1437 s, 1320 m, 1303 w, 1242 s, 1171 m, 1148 w, 1031 s, 1016 s, 948 m, 921 m, 836 br s, 771 m, 759 s, 701 s, 643 m, 570 m, 430 br m, 354 m, 304 m, 262 m. ¹H NMR (dichloromethane-*d*₂, 300 MHz, 23 °C): δ 0.02 (s, 9 H, SiMe₃), 2.47 (s, 15 H, C₅Me₅), 7.35–7.54 (m, 8 H, Ph), 7.67–7.75 (m, 2 H, Ph). ¹³C{¹H} NMR (dichloromethane-*d*₂, 75.5 MHz, 23 °C): δ 2.98 (SiMe₃), 13.33 (C₅Me₅), 128.0, 129.1, 131.0, 131.2, 131.5, 132.0 (Ph), 128.5 (C₅Me₅), 137.2, 137.4 (ipso Ph), 156.3 (TaNCPh₂). Anal. Calcd for C₂₆H₃₄Cl₃N₂TaSi: C, 45.3; H, 4.97; N, 4.06. Found: C, 43.8; H, 4.99; N, 4.02.

Kinetic Studies. Reactions were run in septum-sealed 5-mm NMR tubes with benzene-*d*₆ as solvent. The initial concentration of **1** was 0.089 M unless otherwise stated. Concentrations were calculated by integration of the SiMe₃ peak in **1** or **2**, using the sum of the two (which remained unchanged during the experiment) as an internal standard. All reactions were monitored for >2.5 half-lives. Pseudo-first-order conditions of excess carbonyl were employed (0.89–3.56 M) for the data shown in Figure 1 and Table III. These reactions were run in the probe of the EM 390 at 34.0 °C. The data for the Eyring plot (Figure 2, Table IV) was obtained on the GE QE-300 with a 10-fold excess of acetone (0.89 M). The resulting *k*_{obsd} were converted to second-order rate constants (*k*'s) by using the relationship *k*_{obsd} = *k*[acetone]. Figures in parentheses represent the standard deviation from unweighted least-squares analysis.

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