at least a partial covalent contribution to the Si–Li bond; i.e., $^{29}$Si is coupled to one $^6$Li atom ($I = 1$, $^1J[^{29}$Si,$^6$Li] = 17 Hz at 173 K). By increasing the temperature above 173 K, or by increasing the cation solvating power of the solvent, the $^{29}$Si–$^6$Li coupling is progressively averaged due to lithium exchange.

On decreasing the number of phenyl rings attached, the $^{29}$Si resonances of the silyl anions are successively shifted upfield (Table I). More interesting is the finding that the exchange rate is decreased by increased methyl substitution, and a well-resolved triplet can be observed for PhMe$_2$Si$^6$Li (3) at 173 K even in THF (Figure 1). The bimolecular nature of the exchange process is manifested by the finding that the collapse of the coupling upon warming is slightly concentration-dependent (Figure 2). The $^1J[^{29}$Si,$^6$Li] couplings observed for 1–3 are rather constant (16–18 Hz, Table I), which implies a similar bonding/hybridization of the Si atom throughout this series.

A low-temperature experiment with 3 using the more quadrupolar $^7$Li nucleus ($I = {}^3/_2$) yields a well-resolved quartet at 173 K in THF with $^1J[^{29}$Si,$^7$Li] = 51 Hz. The ratio of the $^1J$-[$^{29}$Si,$^7$Li]/$^1J[^{29}$Si,$^6$Li] couplings is 2.82, i.e., close to the expected ratio of the $^7$Li/$^6$Li NMR frequencies of 2.64. Evidently, quadrupole-induced relaxation is insufficient to quench the $^{29}$Si–$^7$Li coupling.[4] No secondary isotope effect could be detected on the $^{29}$Si chemical shift when changing from $^6$Li to $^7$Li.

Though dissociation of the Si–Li bond at higher temperatures or in the more solvating media cannot definitively be excluded, the minor shift changes of the $^7$Li, $^{13}$C, and $^{29}$Si resonances for the solvent changes MTHF → THF → DME suggest that the same bonding characteristics prevail and that these (phenylsilyl)lithiums are monomeric in the ethereal solvents under investigation.

## Ether Cleavage following Insertion of Carbon Monoxide into the Tantalum–Silicon Bond of (η5-C5Me5)Ta(SiMe3)Cl3

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Ethers are usually regarded as unreactive compounds; the ether linkage normally is cleaved only under extreme conditions.[1] In the course of investigating the chemical reactivity of early-transition-metal silyls,[2,3] we have discovered an ether cleavage reaction which takes place under unusually mild conditions.

Recently we described the insertion of CO into the metal–silicon bond of Cp$_2$Zr(SiMe$_3$)Cl (1, Cp = η5-C$_5$H$_5$) to produce the silaacyl Cp$_2$Zr(η2-COSiMe$_3$)Cl (2).[3] Here we report some initial results on the more complex CO insertion chemistry of Cp*Ta(SiMe$_3$)Cl$_3$ (3, Cp* = η5-C$_5$Me$_5$) in the presence of ethers.

Complex 3 is prepared from Cp*TaCl$_4$ and Al(SiMe$_3$)$_3$·OEt$_2$[4] in pentane.[5] When pressurized with CO (10–100 psi, room temperature), dark green diethyl ether solutions of 3 gradually turn red over a few minutes to a few hours, depending on the CO pressure. An orange-yellow powder (4) can be isolated in 35–50% yield by concentration and cooling of the reaction solution or by

**Scheme I**



sublimation. The physical and spectral properties of this product[6] indicate the structure shown in eq 1. The presence of ethylene
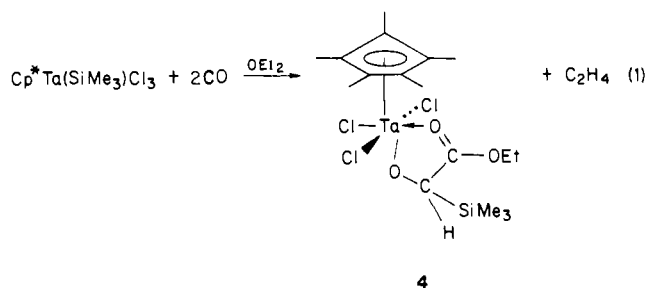


was confirmed by GC/MS analysis of the volatiles from the reaction. Use of $^{13}$CO in the reaction clearly identified the chelate ring carbon atoms of 4 as those derived from carbon monoxide. The labeled compound 4* exhibits a lower $\nu_{C=O}$ stretching frequency (1578 cm$^{-1}$) than 4 (1610 cm$^{-1}$) and a $^{13}$C–$^{13}$C coupling constant ($^1J_{CC}$ = 52 Hz) consistent with adjacent sp$^2$ and sp$^3$ carbon atoms.[7,8]

The reaction of 4 with KOSiMe$_3$ in tetrahydrofuran results in protiodesilylation[9] to 5[6] (eq 2). This conversion introduces a
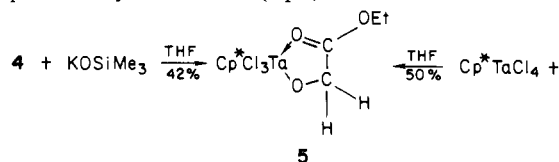


molecular plane of symmetry which simplifies the $^1$H NMR resonance of the diastereotopic ethoxide methylene protons of 4 to a quartet. Complex 5 was independently synthesized from Cp*TaCl$_4$ and LiOCH$_2$CO$_2$Et.

A proposed mechanism for the formation of 4 is given in Scheme I. The coupling of two CO molecules by the tantalum silyl 3 appears to proceed via initial insertion to produce a silaacyl analogous to 2, i.e., Cp*Ta(η2-COSiMe$_3$)Cl$_3$ (A). This silaacyl is expected to exhibit strong "oxycarbene" character[10] due to the electron-deficient, oxophilic nature of the tantalum center. The next step involves coupling of a second CO molecule to the silaacyl

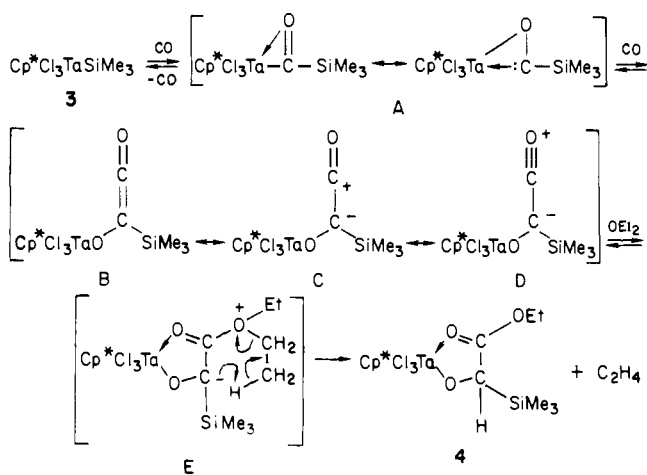(1) Staude, E.; Patat, F. In "The Chemistry of the Ether Linkage"; Patai, S., Ed.; Wiley: New York, 1967, pp 21–80.
(2) Tilley, T. D. *Organometallics* 1985, *4*, 1452.
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(5) Arnold, J.; Shina, D.; Tilley, T. D., manuscript in preparation.

(6) See supplementary material for characterization data.
(7) Brietmaier, E.; Voelter, W. "$^{13}$C NMR Spectroscopy"; Verlag Chemie: Weinheim, New York, 1978.
(8) For 4*: $^1$H NMR (C$_6$D$_6$, 20 °C, 360 MHz) δ 0.08 (d, 9 H, $^3J_{CH}$ = 2 Hz, SiMe$_3$), 5.16 (dd, 1H, $^1J_{CH}$ = 137, $^2J_{CH}$ = 6 Hz, OC*H*SiMe$_3$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 20 °C, 50.3 MHz) δ 84.8 (d, $^1J_{CC}$ = 52 Hz, OC*H*SiMe$_3$), 189.8 (d, $^1J_{CC}$ = 52 Hz, OCHSiMe$_3$CO$_2$Et).
(9) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Chem. Soc.* 1982, *104*, 6809.
(10) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* 1980, *13*, 121. See: (b) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1985, *107*, 4440.
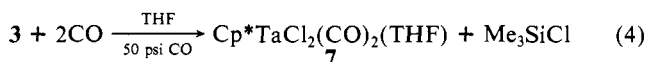
ligand (or insertion of CO into the Ta–COSiMe₃ bond) to produce a ketene intermediate, analogous to the transitory ketene Cp*₂Th[OC(CO)CH₂CMe₃]Cl formed from CO and the acyl Cp*₂Th(η²-COCH₂CMe₃)Cl.[11] The SiMe₃ and oxygen substituents should stabilize resonance structures C and D, imparting significant electrophilic character to the ketene α-carbon.[12] Nucleophilic attack by ether may be promoted by concurrent Ta–O bonding (E). Zwitterionic species similar to E have been proposed as intermediates in analogous reactions in which ethers are cleaved by arynes.[13] We are unaware of any such reactions involving ketenes, however. A mechanism involving ether cleavage by an acidic tantalum center seems unlikely, since this would be expected to produce a stable Ta–OCH₂CH₃ derivative.[1] Further studies on the mechanism of this reaction are in progress.

The formation of silaacyl intermediate A was observed by NMR and IR spectroscopy. A benzene-$d_6$ solution of 3 absorbed 1 mol of CO to produce an orange solution containing two new signals in the ¹H NMR at 2.15 and 0.42 ppm; if ¹³CO is used, the peak at 0.42 ppm appears as a doublet ($^3J_{CH} = 2.4$ Hz). The acyl carbon atom of A* appears as a singlet at 351 ppm in the ¹³C NMR spectrum.[3] The C–O stretching frequency of A (1462 cm⁻¹; 1428 cm⁻¹ for ¹³C-labeled A*) is relatively low.[11a] Complex A is stable for hours at room temperature in solution but rapidly reacts further in the presence of excess CO. Attempts to isolate A have so far proven unsuccessful.

Also consistent with the mechanism in Scheme I is the reaction of 3 with CO (50 psi) and 2-methyltetrahydrofuran (as solvent or with 1 equiv in pentane, eq 3), leading to the ring-opened product product 6.[6]

$$3 + 2CO \xrightarrow{66\%} \text{Cp*Cl}_3\text{Ta} \cdots \text{6} \qquad (3)$$
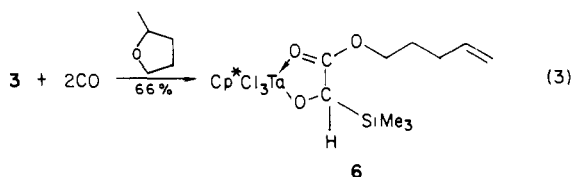
In tetrahydrofuran as solvent, no evidence for the analogous CO insertion chemistry was obtained. Instead, the products appear to result from a ligand-induced reductive elimination of Me₃SiCl (identified by GC/MS) to form the Ta(III) product 7[6] (eq 4).

$$3 + 2CO \xrightarrow[\text{50 psi CO}]{\text{THF}} \text{Cp*TaCl}_2(\text{CO})_2(\text{THF}) + \text{Me}_3\text{SiCl} \qquad (4)$$
$$\underset{7}{}$$

Apparently the β-hydrogens of tetrahydrofuran are not sterically accessible for abstraction via a mechanism analogous to Scheme I. Alternatively, diethyl ether and 2-methyltetrahydrofuran, being poorer ligands toward tantalum(V), cannot induce elimination of Me₃SiCl.[14]

**Supplementary Material Available:** Spectroscopic and analytical data for 4–7 (1 page). Ordering information is given on any current masthead page.

(11) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393. (b) Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696.

(12) We thank a reviewer for comments regarding the ketene intermediate's structure. A further possibility with respect to activation of the ketene toward nucleophilic attack is an interaction of the terminal oxygen with a Lewis acid center,[11a] since unsaturated Ta species are expected to be present in solution.

(13) (a) Franzen, V.; Joscheck, H. I.; Mertz, C. *Ann.* **1962**, *654*, 82. (b) Hellmann, H.; Eberle, D. *Ann.* **1963**, *662*, 188. (c) Hayashi, S.; Ishikawa, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 642. (d) Richmond, G. D.; Spendel, W. *Tetrahedron Lett.* **1973**, 4557.

(14) In the reaction involving diethyl ether (eq 1) traces of tantalum carbonyl species were detected (by ir), implying that loss of Me₃SiCl and ether cleavage are competing reaction pathways which are heavily influenced by the ether solvent.

# Tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane, a [1.1.1]Propellane Derivative, and a New Route to the Parent Hydrocarbon

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Recently Wiberg has shown that the heat of hydrogenation of [1.1.1]propellane (1) leading to bicyclo[1.1.1]pentane (2a) is
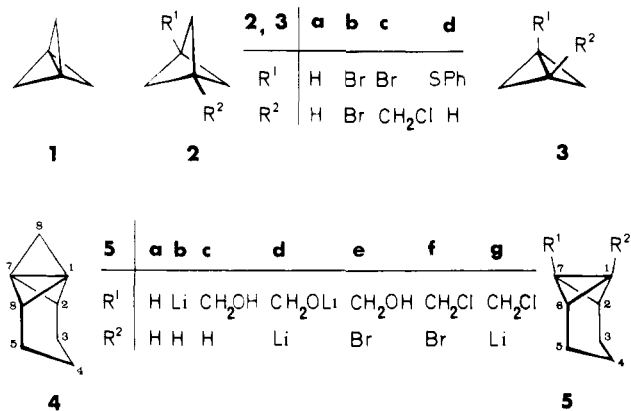


virtually the same as the one of cyclopropane affording propane.[1,2] As a consequence, formation of 1 by reduction of 1,3-dibromobicyclo[1.1.1]pentane (2b) is an energetically feasible reaction, as has been demonstrated by Wiberg and Walker.[3] It is interesting to note that bicyclo[1.1.1]pentane (2a) and bicyclo[1.1.0]butane (3a) have similar strain energies (66.6 kcal/mol[4] vs. 63.9 kcal/mol[5]). This suggests that it might be possible to construct the [1.1.1]propellane framework starting from a properly substituted bicyclo[1.1.0]butane derivative, as 3c. In this paper we wish to report our results on the synthesis of tetracyclo-[5.1.0.0^{1,6}.0^{2,7}]octane (4), a derivative of 1. In addition, we present a facile route to 1.

Tricyclo[4.1.0.0^{2,7}]heptane-1-methanol (5c),[6] obtained in 70% yield from 5a after metalation to 5b by *n*-butyllithium (BuLi) in ether at room temperature for 24 h and subsequent addition of formaldehyde, was converted to 5d by 2 equiv of BuLi in ether, followed by bromination of 5d with *p*-toluenesulfonyl bromide[7] giving rise to a 55% yield of 7-bromotricyclo[4.1.0.0^{2,7}]heptane-1-methanol (5e): ¹H NMR (CCl₄) δ 1.40 (broadened s, 6 H), 1.90 (br s, 1 H), 2.80 (s, 2 H), 4.10 (s, 2 H); ¹³C NMR (CDCl₃) δ 19.8 (t, 2 C), 20.3 (t), 22.1 (s), 26.0 (s), 49.0 (d, 2 C), 62.2 (t); HRMS calcd for C₈H₁₁⁷⁹BrO 201.9993, found 201.999. Anal. C, H. 1-Bromo-7-chloromethyltricyclo[4.1.0.0^{2,7}]heptane (5f) was prepared from 5e by refluxing the carbinol with 1.1 equiv of triphenylphosphine in carbon tetrachloride for 12 h (yield 65–90%):[8] ¹H NMR (CCl₄) δ 1.42 (narrow m, 6 H), 2.75 (broadened s, 2 H), 3.88 (s, 2 H); ¹³C NMR (CCl₄/C₆D₆) δ 19.5 (t, 2 C), 20.1 (t), 21.8 (s), 27.1 (s), 44.5 (t), 49.3 (d, 2 C); HRMS calcd for C₈H₁₀⁷⁹Br³⁵Cl 219.96545, found 219.965.

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(3) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239–5240.

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(5) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397.

(6) Properties of 5c: bp 31–32 °C (10⁻³ torr); ¹H NMR (CDCl₃) δ 1.40 (m, 7 H), 2.25 (t, 1 H), 2.50 (m, 2 H), 4.00 (d, 2 H); ¹³C NMR (CDCl₃) δ 8.9 (d), 19.7 (s), 20.4 (t, 2 C), 20.9 (t), 42.6 (d, 2 C), 63.2 (t); MS (70 eV), *m/e* 124 (13%, M⁺).

(7) For previous use of *p*-toluenesulfonyl bromide as brominating reagent, see: Szeimies-Seebach, U.; Schöffer, A.; Römer, R; Szeimies, G. *Chem. Ber.* **1981**, *114*, 1767–1785.

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