

Evidence on Covalency and Monomeric Structure of (Phenylsilyl)lithiums in Ethereal Solutions from Scalar ^{29}Si - ^6Li Couplings

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There has been considerable debate concerning the electronic structures of organo lithium compounds, whether they have essentially ionic, covalent, or intermediate bonding character.¹ Theoretical computations, as they generally apply to the gaseous state, may not accurately reflect the structures in solution or in the solid state. X-ray structures of a number of organo lithiums have been determined² and have revealed structures of varying types: monomeric, dimeric, tetrameric, etc. NMR studies³ have been the most informative of the structures in solution, and particularly important evidence has recently been obtained from low-temperature observation of ^{13}C - ^6Li scalar coupling and multiplicities.^{4,5} Thus the observation in the ^{13}C NMR spectrum of a seven-line coupling pattern for C(1) of $(\text{CH}_3)_3\text{CC}\equiv\text{C}^6\text{Li}$ ($^1J[^{13}\text{C},^6\text{Li}] = 6\text{ Hz}$) in THF at 183 K showed conclusively that this compound existed as a nonfluxional cubic tetramer with a covalent character in the carbon-lithium bond.^{4a} At room temperature C(1) appears as a singlet due to rapid exchange on the NMR time scale. Similarly, on the basis of the observed ^{13}C , ^6Li coupling, *n*-butyllithium in THF has been shown to exist as an equilibrium between tetramers and dimers depending on the temperature.^{5a} For the phenylmethylolithiums (PhCH_2Li , Ph_2CHLi , Ph_3CLi), on the other hand, no coupling was observed down to 123 K,^{5b} which could be consistent with ionic species (contact or solvent-separated ion pairs) or it could arise as a result of rapid exchange mechanisms in more covalent species.

The structures of organo silyllithium compounds appear to be known with less certainty than of the alkylolithiums, though a number of NMR studies have been performed to this end.⁶ In our own NMR studies (^1H , ^{13}C , ^7Li) of (phenylsilyl)lithiums, the chemical shift data were interpreted on the basis of significant covalent silicon-lithium interaction, in less polar ethereal solvents, and as compared with the corresponding potassium derivatives.⁷ However, there has been no study of silyllithiums reported so far yielding definitive structural evidence from scalar coupling, as reported for alkylolithiums.^{4,5}

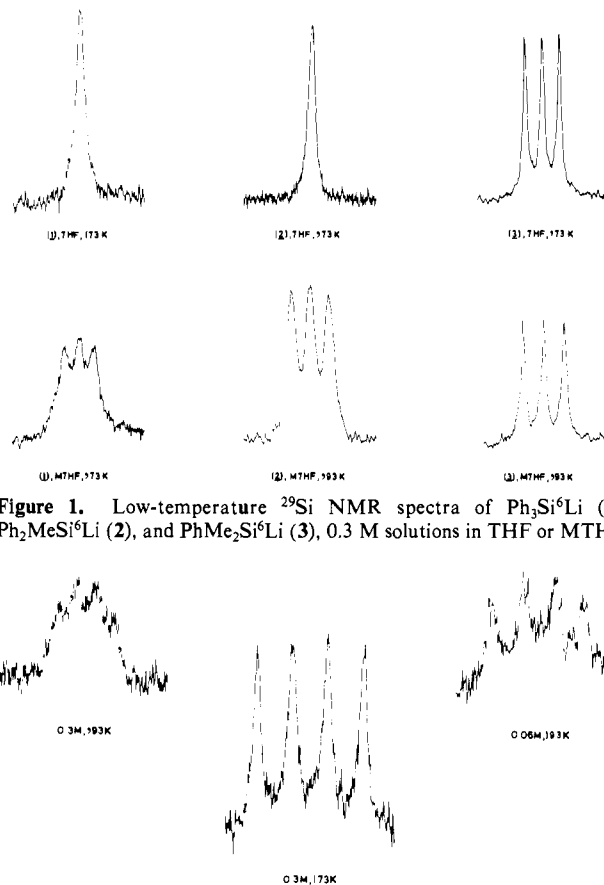


Figure 1. Low-temperature ^{29}Si NMR spectra of $\text{Ph}_3\text{Si}^6\text{Li}$ (1), $\text{Ph}_2\text{MeSi}^6\text{Li}$ (2), and $\text{PhMe}_2\text{Si}^6\text{Li}$ (3), 0.3 M solutions in THF or MTHF.

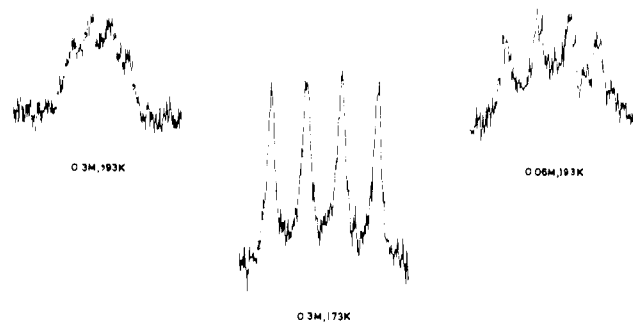


Figure 2. Low-temperature ^{29}Si NMR spectra of $\text{PhMe}_2\text{Si}^7\text{Li}$ in THF.

Table I. ^{29}Si NMR Chemical Shifts and ^{29}Si - ^6Li One-Bond Couplings of $\text{Ph}_3\text{Si}^6\text{Li}$ (1), $\text{Ph}_2\text{MeSi}^6\text{Li}$ (2), and $\text{PhMe}_2\text{Si}^6\text{Li}$ (3)^a

solvent	T, K	δ, δ^b ($^1J[^{29}\text{Si}-^6\text{Li}]$, Hz)		
		1	2	3
THF	295	-9.0	-20.6	-27.8
	233	-9.2		
	193	-9.7	-23.0	-29.1
	173	-9.7		-29.1 (18)
	158	-9.7	-23.1 (15)	
MTHF	295	-9.2	-21.3	-28.4
	233	-9.3		
	193	-9.3	-22.2 (16)	-28.7 (18)
	173	-9.3 (17)		

^a 0.3 M. Samples run in an unlocked mode on a Bruker WM-250 multinuclear NMR instrument, using Me_4Si as internal reference. ^b Negative δ values correspond to upfield shifts from Me_4Si .

We have now been able to obtain this kind of evidence, derived from the low-temperature determination of ^{29}Si - ^6Li and ^{29}Si - ^7Li scalar coupling in (phenylsilyl)lithiums at a natural abundance ^{29}Si level.

(Triphenylsilyl)lithium (1), (diphenylmethylsilyl)lithium (2), and (dimethylphenylsilyl)lithium (3) were obtained in dimethoxyethane (DME), tetrahydrofuran (THF), or 2-methyltetrahydrofuran (MTHF) solution by lithium metal⁸ cleavage of the parent disilanes, as described previously.⁷

The ^{29}Si NMR chemical shift of $\text{Ph}_3\text{Si}^6\text{Li}$ does not undergo any significant change on varying the temperature or by going to more polar ethers, $\text{MTHF} \rightarrow \text{THF} \rightarrow \text{DME}$; $\delta(^{29}\text{Si}) = -9.2, -9.0, \text{ and } -8.7$, respectively. However, in MTHF or THF the ^{29}Si signal broadens when decreasing the temperature; at 173 K in MTHF the ^{29}Si resonance resolves into a triplet (Figure 1). This implies a monomeric structure and, with the present knowledge,

(8) Lithium-6 metal purchased from Martin Marietta Energy System Inc., Oak Ridge, TN.

- (1) (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *Ibid.* **1977**, *99*, 6159. (c) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *Ibid.* **1980**, *102*, 4572. (d) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (e) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283.
- (2) (a) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333. (b) Kieft, R. L.; Novak, D. P.; Brown, Th. L. *J. Organomet. Chem.* **1974**, *77*, 299. (c) Koster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1. (d) Rewicki, D.; Dietrich, H. *Chem. Ber.* **1979**, *112*, 1380.
- (3) O'Brien, D. H. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Vol. 1.
- (4) (a) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J.; *J. Am. Chem. Soc.* **1980**, *102*, 3345. (b) Beckenbaugh, W. E.; Geckle, J. M.; Fraenkel, G. *Chem. Scr.* **1978**, *13*, 150. (c) Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1527.
- (5) (a) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (b) Seebach, D.; Gabriel, J.; Hassig, R. *Ibid.* **1984**, *67*, 1083. (c) Hassig, R.; Seebach, D. *Ibid.* **1983**, *66*, 2269.
- (6) (a) Cox, R. H.; Janzen, E. G.; Harrison, W. B. *J. Magn. Reson.* **1971**, *4*, 274. (b) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989. (c) Batchelor, R. J.; Birchall, T. *J. Am. Chem. Soc.* **1983**, *105*, 3848. (d) Sooriyakumaran, R.; Boudjouk, P. *J. Organomet. Chem.* **1984**, *271*, 289.
- (7) (a) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, U. *J. Am. Chem. Soc.* **1985**, *107*, 303. (b) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, U. *J. Chem. Soc., Chem. Commun.* **1984**, 1476.

at least a partial covalent contribution to the Si-Li bond; i.e., ^{29}Si is coupled to one ^6Li atom ($I = 1$, $^1J[^{29}\text{Si}, ^6\text{Li}] = 17$ Hz at 173 K). By increasing the temperature above 173 K, or by increasing the cation solvating power of the solvent, the ^{29}Si - ^6Li 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 $\text{PhMe}_2\text{Si}^6\text{Li}$ (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 $^1J[^{29}\text{Si}, ^6\text{Li}]$ 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 ^7Li nucleus ($I = 3/2$) yields a well-resolved quartet at 173 K in THF with $^1J[^{29}\text{Si}, ^7\text{Li}] = 51$ Hz. The ratio of the $^1J[^{29}\text{Si}, ^7\text{Li}]/^1J[^{29}\text{Si}, ^6\text{Li}]$ couplings is 2.82, i.e., close to the expected ratio of the $^7\text{Li}/^6\text{Li}$ NMR frequencies of 2.64. Evidently, quadrupole-induced relaxation is insufficient to quench the ^{29}Si - ^7Li coupling.⁴ No secondary isotope effect could be detected on the ^{29}Si chemical shift when changing from ^6Li to ^7Li .

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 ^7Li , ^{13}C , and ^{29}Si resonances for the solvent changes MTHF \rightarrow THF \rightarrow DME suggest that the same bonding characteristics prevail and that these (phenylsilyl)lithiums are monomeric in the ethereal solvents under investigation.

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Ether Cleavage following Insertion of Carbon Monoxide into the Tantalum-Silicon Bond of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{SiMe}_3)\text{Cl}_3$

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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 $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$ (1, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) to produce the silylacyl $\text{Cp}_2\text{Zr}(\eta^2\text{-COSiMe}_3)\text{Cl}$ (2).³ Here we report some initial results on the more complex CO insertion chemistry of $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3$ (3, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in the presence of ethers.

Complex 3 is prepared from Cp^*TaCl_4 and $\text{Al}(\text{SiMe}_3)_3\text{OEt}_2$ 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

(1) Staude, E.; Patat, F. In "The Chemistry of the Ether Linkage"; Patai, S., Ed.; Wiley: New York, 1967, pp 21-80.

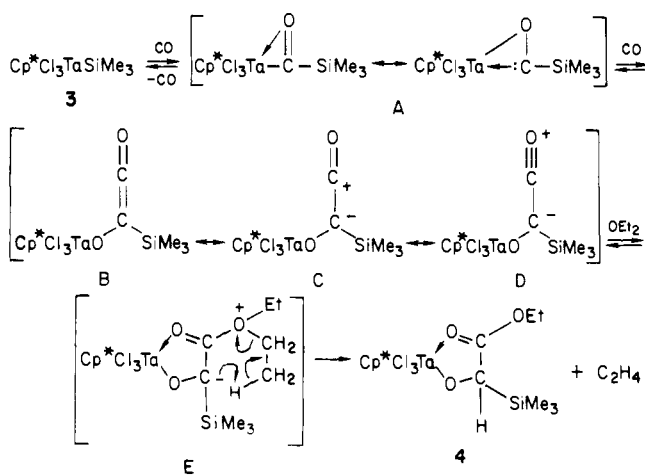
(2) Tilley, T. D. *Organometallics* 1985, 4, 1452.

(3) Tilley, T. D. *J. Am. Chem. Soc.* 1985, 107, 4084.

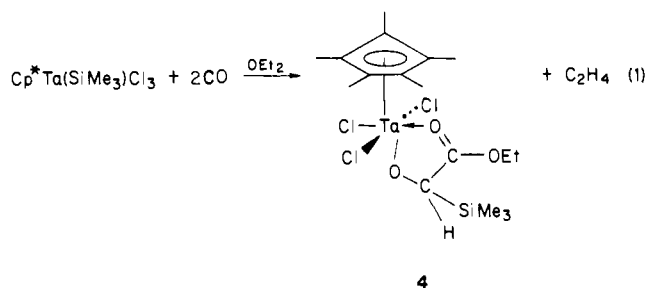
(4) Roesch, L.; Altnau, G. *J. Organomet. Chem.* 1980, 195, 47.

(5) Arnold, J.; Shina, D.; Tilley, T. D., manuscript in preparation.

Scheme I

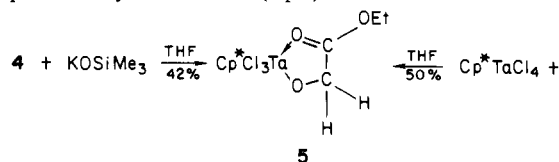


sublimation. The physical and spectral properties of this product⁶ indicate the structure shown in eq 1. The presence of ethylene



was confirmed by GC/MS analysis of the volatiles from the reaction. Use of ^{13}C 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 $\nu_{\text{C=O}}$ stretching frequency (1578 cm^{-1}) than 4 (1610 cm^{-1}) and a ^{13}C - ^{13}C coupling constant ($^1J_{\text{CC}} = 52$ Hz) consistent with adjacent sp^2 and sp^3 carbon atoms.^{7,8}

The reaction of 4 with KOSiMe_3 in tetrahydrofuran results in protodesilylation⁹ to 5⁶ (eq 2). This conversion introduces a



$\text{LiOCH}_2\text{CO}_2\text{Et}$ (2)

molecular plane of symmetry which simplifies the ^1H NMR resonance of the diastereotopic ethoxide methylene protons of 4 to a quartet. Complex 5 was independently synthesized from Cp^*TaCl_4 and $\text{LiOCH}_2\text{CO}_2\text{Et}$.

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 silylacyl analogous to 2, i.e., $\text{Cp}^*\text{Ta}(\eta^2\text{-COSiMe}_3)\text{Cl}_3$ (A). This silylacyl is expected to exhibit strong "oxycarbene" character¹⁰ due to the electron-deficient, oxophilic nature of the tantalum center. The next step involves coupling of a second CO molecule to the silylacyl

(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*: ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$, 360 MHz) δ 0.08 (d, 9 H, $^3J_{\text{CH}} = 2$ Hz, SiMe_3), 5.16 (dd, 1H, $^1J_{\text{CH}} = 137$, $^2J_{\text{CH}} = 6$ Hz, OCHSiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20 $^\circ\text{C}$, 50.3 MHz) δ 84.8 (d, $^1J_{\text{CC}} = 52$ Hz, OCHSiMe_3), 189.8 (d, $^1J_{\text{CC}} = 52$ Hz, $\text{OCHSiMe}_3\text{CO}_2\text{Et}$).

(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.