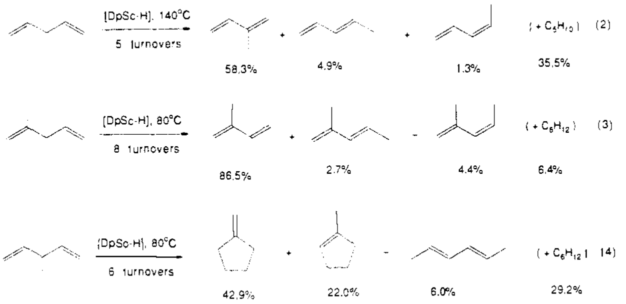
bocation and lithio or Grignard reagent reported by Roberts et al.[8] Similar mechanisms have been proposed by Miller et al. for $\{NiCl_2(PBu_3)_2/AlCl(CH_2CHMe_2)_2\}$-catalyzed skeletal rearrangements of 1,4-dienes,[9] by Atkins, Johnson, et al. for some homoallylcobalt complexes,[10] and by Flood et al. for some cyclobutylmethylplatinum derivatives.[11]

Catalytic reactions can also be performed with DpSc–H when excess 1,4-pentadienes (eq 2–4) are introduced, although after several turnovers significant amounts of hydrogenation products are formed, most likely accompanied by metalation of the Dp ligands. The remarkable catalytic conversion of 3-methyl-1,4-pentadiene to methylenecyclopentane and its isomer, methyl cyclopentene, is readily accommodated as shown in Scheme II.



These observations implicate the reverse of olefin insertion into Sc–C bonds, namely β-alkyl elimination,[12] as a relatively facile process in this system. The scope of these transformations[13] as well as the factors responsible for the high selectivity of the catalytic rearrangements[14] are presently under study.

Acknowledgment. This work was supported by the USDOE Office of Energy Research, Office of Basic Energy Sciences (Grant no. DE-FG03-85ER13431), and by the Shell Company Foundation which are gratefully acknowledged. We thank Professors Dennis Dougherty and John Roberts and Dr. Jay Labinger for helpful discussions.

Supplementary Material Available: Table consisting of ^1H and ^{13}C NMR spectral, analytical, infrared, and GC data together with a description of a representative experiment (5 pages). Ordering information is given on any current masthead page.

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(13) On the basis of these rather limited results the branching reaction appears to be restricted to α, ω (diterminal) dienes. With an internal double bond simple isomerization to the linear, conjugated diene results (e.g., for 1,4-hexadiene; footnote 5). Apparently, unfavorable steric interactions greatly slows addition of Sc–H to the internal olefin relative to addition to terminal olefin and precludes the intramolecular cyclization (via insertion of an internal olefin into a DpSc–C bond) required for branching (step B, Scheme II).

(14) For example, in eq 2 the equilibrium concentrations are estimated as the following: 1,4-pentadiene (0.05%), *cis*-piperylene (40.5%), *trans*-piperylene (27.6%), and isoprene (31.8%) at 413 K (Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; pp 330–334). The relative percentages of these isomers obtained are as follows: 1,4-pentadiene (<0.03%), *cis*-piperylene (2.0%), *trans*-piperylene (7.6%), and isoprene (90.4%) at 413 K.

Solid-State and Solution Structure of Dilithium Trimethyl((phenylsulfonyl)methyl)silane, a True Dilithiomethane Derivative[†]

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The dilithiosulfones $Li_2[C(R^1)-SO_2R^2]$ (**1**) represent potential dilithioalkane derivatives of the type $Li_2C(R^1)R^2$ (**2**)[1] with a preparative useful functional group and are therefore of particular synthetic and structural interest.[2] Despite many reports of their formation based on chemical evidence,[3] only recently with the title compound **1a** ($R^1 = SiMe_3$, $R^2 = Ph$) the first dilithiosulfone could be isolated and unequivocally characterized by ^{13}C and ^1H NMR spectroscopy.[4]

We now report results of a combined X-ray and NMR investigation which show that **1a** is a *true geminal dilithio compound* of the type **2** in the solid state as well as in solution. No such structural informations on compounds of this type were previously available.[1,5]

Metalation of trimethyl((phenylsulfonyl)methyl)silane (**3**) with 2 equiv of *n*-butyllithium (*n*-BuLi) in tetrahydrofuran (THF) at −90 °C to 25 °C in the *presence of Li_2O gave prismoide crystals* of the sparingly soluble $(\mathbf{1a})_6 \cdot Li_2O \cdot (thf)_{10}$ complex.[4] The X-ray structure analysis[6] shows a hexamer (C_i) with six THF molecules and one Li_2O molecule (Figure 1). Four THF molecules lie between the hexamers. Around the unique O atom in the center of symmetry is an octahedral array of Li atoms, two of which (Li5 and Li5A) make no contact to the dianionic C atoms C1A, C1B, and C1C and symmetry-related C1AA, C1BA, and C1CA. Six dianions of **1a** featuring three different conformations in regard to the C(α)–S bond are grouped around the Li octahedron and linked together through four-membered O–Li–O–Li and six-membered Li–C–Li–O–S–O rings, among others. The *three different dianionic C atoms are each coordinated at least to two Li atoms* with the coordination geometry and connectivity shown in Figure 2. C1C and C1A are both weakly bound, if at all, to

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[†] Dedicated to Professor Klaus Hafner on the occasion of his 60th birthday.

(1) Maercker, A.; Theis, M. *Top. Curr. Chem.* **1987**, *138*, 1 and references therein.

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(4) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 696.

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(6) Crystal data for $(\mathbf{1a})_6 \cdot Li_2O \cdot (thf)_{10}$ are given in the Supplementary Material.

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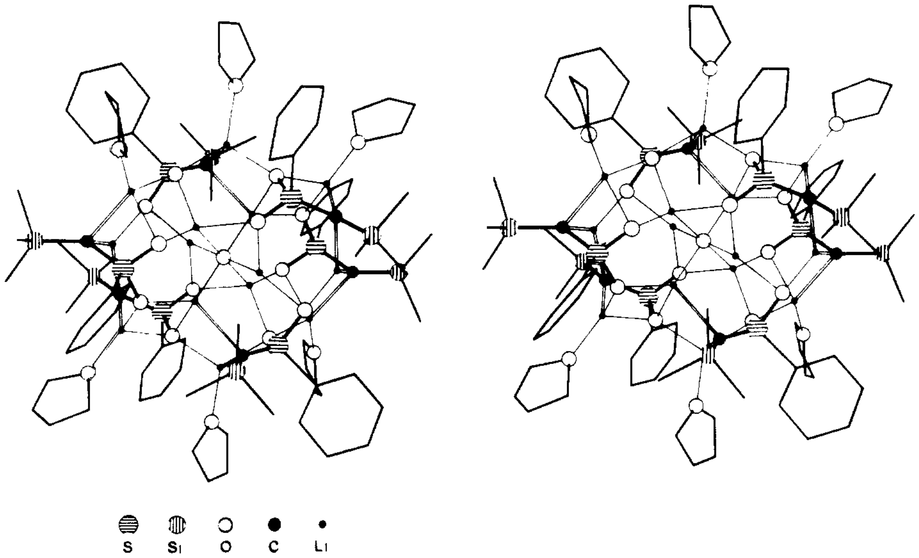


Figure 1. Stereoscopic view of the $(\mathbf{1a})_6 \cdot Li_2O \cdot (thf)_{10}$ complex. Methyl groups have been omitted.

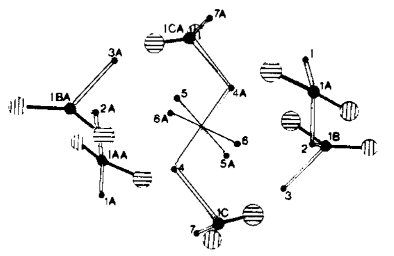


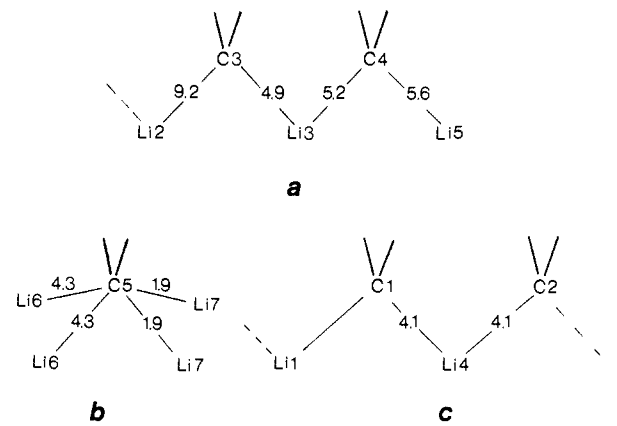
Figure 2. Coordination geometry and connectivity of the Li and dianionic C atoms in the $(\mathbf{1a})_6 \cdot Li_2O \cdot (thf)_{10}$ complex showing the atomic numbering scheme. Selected interatomic distances (Å): Li1–C1A, 2.18; C1A–Li2, 2.25; Li2–C1B, 2.19; C1B–Li3, 2.34; Li4–C1C, 2.51; C1C–Li7, 2.23; C1A–Li6, 3.08; Li6–C1C, 2.83.

a third bridging Li atom, i.e., Li6. The remaining coordination sites of the two Li atoms of C1C, i.e., Li4 and Li7, are occupied only by the O atoms of the THF molecules and sulfonyl groups, whereas C1A and C1B are linked in a chain of one bridging and two terminal Li atoms having normal C–Li bond distances (Figure 2). The latter two Li atoms are also coordinated further only by O atoms. Each of the dianionic C atoms bears a Li atom (Li1, Li3, and Li7) which is coordinated in a four-membered C–Li–O–S ring by a sulfonyl O atom;[7] all of the latter make contact to at least two Li atoms. Noteworthy, the calculated structure of monomeric **1b** ($R^1 = H$, $R^2 = CH_3$)[8] bears resemblance to unit B of Figure 2.

Lithiation of **3** (90% ^{13}C) with 1.9 equiv of *n*-BuLi (95% ^6Li) in THF at −90 °C to 0 °C *without Li_2O gave octahedral crystals of* **1a**[9] which are *readily soluble* thus allowing an NMR investigation of its structure and aggregation in solution. Low-temperature ^{13}C as well as ^6Li NMR spectroscopy and in particular ^6Li–^{13}C shift correlation experiments[10] established that the dilithiomethane structure of **1a** also prevails under these conditions.

The ^1H decoupled ^{13}C NMR spectrum of α-^{13}C and ^6Li labeled **1a** in THF-d_8 (*c* 0.36 M) at room temperature shows a single line for the dianionic carbon which broadens with decreasing temperature and finally (−28 °C) splits into two signals of equal intensity at δ 51.36 and 49.92 ppm. Upon further lowering the temperature to about −60 °C three new signals appear at δ 54.53, 53.88, and 38.16 ppm, whose intensity increases on expense of the previous ones while cooling down to −103 °C (Figure 3a,b).

Chart I. Proposed Partial Structures for Aggregates of **1a** at −103 °C Showing the $^1J(^{13}C,^6Li)$ Values in Hz



These temperature-dependent transformations are completely reversible, thereby indicating the existence of intra- and/or interaggregate exchange processes. The dynamic behavior of **1a** is thus characterized by two processes with slightly different barriers.

In the slow exchange limit all five ^{13}C signals of relative intensity 3:1:1:1:1 are split by $^{13}C,^6Li$ spin–spin coupling (Figure 3b), indicating that now also C–Li bond exchange is slow. However, from the two dynamic processes present only the first one is completely frozen out on the NMR time scale. The second process still leads to noticeable line-broadening for signals 1 and 2. Measurements at still lower temperatures were so far prevented by freezing of the solution.

The ^1H decoupled ^6Li NMR spectrum of **1a** at −103 °C features seven signals, which are likewise split by $^{13}C,^6Li$ coupling, and four additional singlets (Figure 3c), one of which (δ 0.37 ppm) was identified as belonging to the monolithio species $Li[Me_3Si{-}C(H){-}SO_2Ph]$.[4] Selective $^6Li\{^{13}C\}$ double resonance and two dimensional double quantum based shift correlation experiments[11] were then used to establish the $^6Li,^{13}C$ connectivities (Figure 3d). In addition, the multiplicities of the ^6Li signals were confirmed by ^6Li spin echo spectroscopy with gated ^{13}C decoupling[11] and, albeit less successful, by $J(^{13}C,^6Li)$-resolved 2D spectroscopy.[11] In this way a triplet structure for the ^6Li signals 3 and 4 and a doublet structure for the ^6Li signals 5, 6, and 7 were firmly established, while the multiplicity of the ^6Li signals 1 and 2 is still doubtful. The absence of $^{13}C,^{13}C$ coupling in the $^1H,^6Li$ decoupled ^{13}C spectrum as well as the absence of cross peaks in a $^6Li,^6Li$

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[7] See also: Gais, H.-J.; Dingerdissen, U.; Krüger, C.; Angermund, K. *J. Am. Chem. Soc.* **1987**, *109*, 3775.

[8] Streitwieser, A., Jr.; Bors, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1397.

[9] By using 2.1 equiv of *n*-BuLi, however *lanceoid crystals* of **1a** were obtained which are also readily soluble in THF.

[10] Moskau, D.; Brauers, F.; Günther, H.; Maercker, A. *J. Am. Chem. Soc.* **1987**, *109*, 5532.

[11] Moskau, D.; Günther, H., unpublished results.

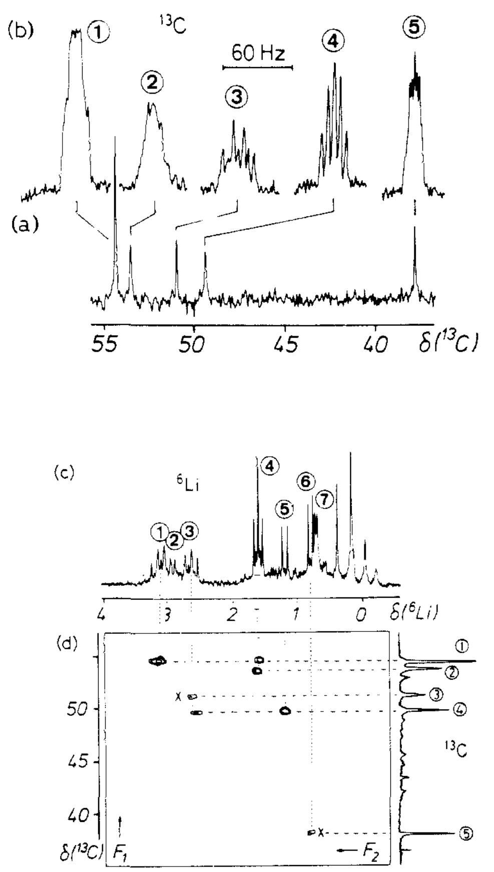

Figure 3. (a) ^{13}C NMR (100.61 MHz) spectrum of ^{13}C and ^{6}Li labeled **1a** with ^{1}H and ^{6}Li broadband decoupling at −103 °C; internal reference TMS. (b) Multiplets of the ^{6}Li coupled ^{13}C spectrum. (c) ^{1}H decoupled ^{6}Li NMR (58.86 MHz) spectrum of ^{13}C and ^{6}Li labeled **1a** with fine structure due to scalar ^{6}Li,^{13}C coupling: −103 °C, external reference 1 M LiBr in THF-d_8. (d) ^{6}Li,^{13}C shift correlation for **1a** based on the pulse sequence[10] $90^\circ_x(^6\mathrm{Li})-\Delta-90^\circ_x(^{13}\mathrm{C})-t_1/2-180^\circ_x(^6\mathrm{Li})-t_1/2-90^\circ_\phi(^{13}\mathrm{C}),t_2(^6\mathrm{Li})$; the standard BRUKER phase program for the selection of double quantum coherences was used; spectral windows were 500 Hz ($^6\mathrm{Li}{=}F_2$) and 4 kHz ($^{13}\mathrm{C}{=}F_1$), digital resolution after zero-filling 2.0 and 7.8 Hz, respectively; 128 t_1 increments of 0.125 ms, 24 transients, Δ = 50 ms (optimized for $J(^{13}\mathrm{C},^6\mathrm{Li}) = 10$ Hz), relaxation delay 6 s, acquisition time 0.512 s, total experimental time 5.6 h; window functions exp(F_2) and sin F_1. The probehead was tuned to ^{6}Li excitation and observation, ^{13}C excitation, ^{1}H decoupling at 400 MHz, and ^{19}F lock at 384 MHz; the ^{19}F resonance of $C_2F_4Br_2$ was used as external lock. Correlations 2/3 and 7/5 (X) were obtained by selective ^{13}C decoupling experiments.

COSY experiment[12] established that no direct contact exists between different dianionic carbons or between different ^{6}Li sites. In this way subspectra composed of the following ^{13}C and ^{6}Li signals could be recognized: (a) C(3),C(4),Li(2),Li(3), Li(5); (b) C(5),Li(6),Li(7); (c) C(1),C(2),Li(4). Simulation of subspectra (a) and (b) using the scalar coupling constants extracted directly from the line splittings gave good agreement with the experimentally observed ^{13}C as well as ^{6}Li multiplets.

On the basis of these results it is possible to propose partial structures **a**, **b**, and **c** for the aggregates of **1a** present in THF solution at −103 °C (Chart I). Especially revealing is the arrangement **a**, which includes besides Li(2), Li(3), and Li(5) C(3) and C(4). A similar chain of three Li and two C atoms is found in the solid-state structure of the $(\mathbf{1a})_6\cdot\mathrm{Li_2O}\cdot(\mathrm{thf})_{10}$ complex (Figure 2).

A feature of particular interest is the first experimental demonstration of C atoms in organolithium compounds in solution which carry two different Li atoms, a bonding situation which gives rise to two different ^{13}C,^{6}Li coupling constants (**a** and **b**). All substructures are characterized by a high ^{6}Li/^{13}C ratio, a fact which clearly establishes that **1a** is a true dilithiomethane derivative also in solution.

Note Added in Proof: X-ray structure analysis of the *octahedral crystals* of **1a** shows a chiral $(\mathbf{1a})_4\cdot(\mathrm{thf})_7$ complex (C_2) with a C–Li chain of the type (Li5–C4–Li3–C3)$_2$Li2.

Acknowledgment. We express our gratitude to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support of this work.

Supplementary Material Available: Crystal data and crystallographic data for $(\mathbf{1a})_6\cdot\mathrm{Li_2O}\cdot(\mathrm{thf})_{10}$ and tables of atomic positional and thermal parameters and bond distances and angles (9 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Electronic Properties of Phosphazene Substituents on Ferrocene

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There has been considerable debate over the last 20 years about the electronic structure of phosphazenes.[1-5] Although the bonding arrangements are still not fully understood, we present here some thermodynamic data from ferrocene-substituted phosphazenes[6-8] which lend new insights into the electronic structure of these materials. Variations in the shifts in the oxidation potential of ferrocene (280–780 mV) are detected with changes in both ferrocene bonding to the phosphazene (pendent versus transannular) and the nature of the remaining cosubstituents on the phosphazene ring. These shifts indicate that phosphazenes are highly electron-withdrawing units. Oxidation products of ten of these species are stable on the time scale of seconds, and, in fact, one species with an oxidation potential shifted 740 mV has an unusual stability for the ferricenium ion. Cosubstituents attached to the phosphazene ring determine the electron-withdrawing properties of the phosphazene and, hence, control the oxidation potential of the ferrocene unit. Electron-withdrawing properties are equally controlled by cosubstituents attached to any phosphorus atom of the phosphazene ring.

The oxidation–reduction chemistry of a wide variety of ferrocenyl cyclic phosphazenes was studied by using cyclic voltammetry at platinum disk electrodes (radius = 2.03 mm). All these compounds displayed diffusion-controlled electrochemistry under the conditions employed. Table I lists the oxidation peak potentials for 15 ferrocenyl phosphazenes. Four examples of the cyclic phosphazenes studied are shown below to illustrate their structure.

Although the oxidation peak potentials varied with the mode of attachment of the ferrocenyl unit and the cosubstituents present on the phosphazene, all were oxidized at considerably more positive

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