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A donor-functionalized, silyl-substituted pentadienyllithium: structural insight from experiment and theory†

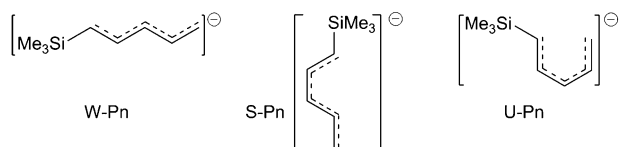
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A donor-functionalized, silyl-substituted pentadienyllithium has been synthesized and characterized by crystallography and NMR spectroscopy. The pentadienyl negative charge was found to be partially localized, which DFT revealed to be due to the polarizing power of the lithium cation.

Silyl-substituted allyl and pentadienyl (Pn) anions are widely used as organometallic ligands^{1,2} and in organic synthesis.^{3–7} Electrophilic quenching of silyl-allyl^{3,4} and silyl-pentadienyl^{6,7} anions are fundamental reactions that can be used as a synthetic strategy to allow complex molecules to be constructed from simple starting materials. However, because these nominally delocalized carbanions possess multiple reactivity sites, their addition to electrophiles produces mixtures of regioisomers. With pentadienyllithiums, reactions can occur at the α -, γ - or ε -carbons, and the Pn anion can exist in the W-, S- or U-conformations.



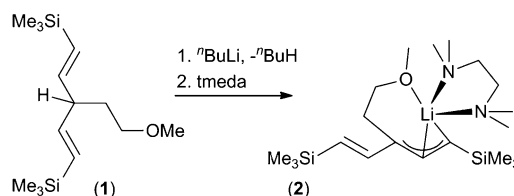
The stereochemistry of the pentadienyl species depends on the solvent, the alkali metal cation and on temperature.^{5,6} Depending on which conformation forms, different diene stereoisomers are obtained on electrophilic quenching.

The large structure–reactivity manifold available to silyl-substituted pentadienyllithiums is a potential barrier towards their wider use in synthesis, therefore strategies that could lead to better structural definition, and therefore to selective reactivity, are desirable. Extensive studies of silyl-substituted allyllithiums

in which the silyl-allylic group contains a Lewis base functionality have shown that the internal donor-functionalities can position lithium in close proximity to one of the two reactive allyl carbons. This results in either partial or complete localization of the formal allyl negative charge on one carbon atom, rendering it more reactive.^{4,8} In some instances, the reactions of functionalized allyl carbanions with electrophiles occur with improved regioselectivity.

To date, no studies of donor-functionalized silyl-pentadienyl complexes of alkali metals have been reported. To explore the possibility that the nominally delocalized charge in a pentadienyl anion might be localized by a pendant donor group, we have synthesized a methoxy-functionalized silyl-pentadienyllithium (**2**), and have studied its structure by crystallography, NMR spectroscopy, and by computation.

Deprotonation of **1** with ⁿBuLi followed by addition of *N,N,N',N'*-tetramethylethylenediamine (tmeda) produced an orange solution, which, upon concentration and storage at –5 °C, gave orange crystals of **2** (Scheme 1). Compound **2** crystallizes as two unique molecules in the asymmetric unit (**2a** and **2b**). The structure of **2a** is described in detail below, and key bond lengths and angles for the similar structures of **2a** and **2b** are shown in the ESI.† The structure of **2a** (Fig. 1) reveals a W-shaped C(1)–C(5) pentadienyl conformation, with both SiMe₃ substituents adopting the *exo* stereochemistry, (*exo,exo*)-W-**2**. The pentadienyl group η^2 -bonds to Li(1) to produce Li(1)–C(1) and Li(1)–C(2) distances of 2.368(4) and 2.446(4) Å, respectively; the Li(1)–C(3) distance of 2.798 Å is too long to allow for an η^3 -Pn coordination mode. Coordination of the pendant ether to lithium results in a Li(1)–O(1) distance of 1.986(4) Å. A bidentate tmeda ligand also coordinates to lithium, with Li(1)–N(1) and Li(1)–N(2) distances of 2.132(4) and 2.192(4) Å, respectively, such that Li(1) is in a distorted tetrahedral environment.

Scheme 1 Synthesis of complex **2**.

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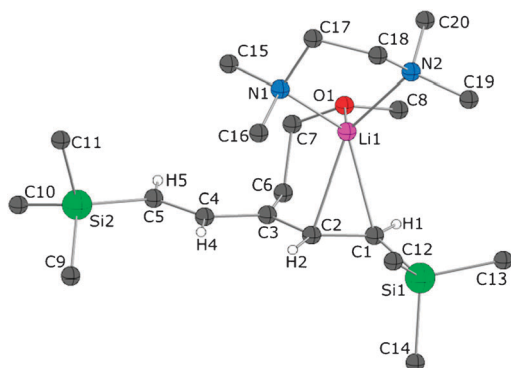


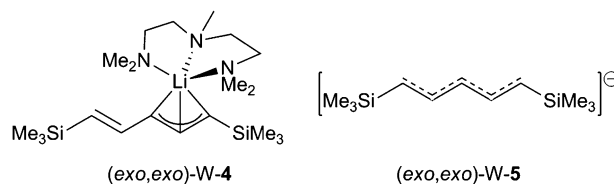
Fig. 1 Molecular structure of complex **2a**. For clarity, only the pentadienyl hydrogen atoms are shown.

The pentadienyl C–C distances in **2a** lie in the range 1.360(3)–1.430(3) Å, and within this range the C(1)–C(2) and C(2)–C(3) distances are essentially identical at 1.400(3) Å, respectively, whereas the C(3)–C(4) and C(4)–C(5) distances are relatively long and short at 1.430(3) and 1.360(3) Å, respectively. These C–C bond lengths suggest that **2a** is a partially localized vinyl-substituted allyllithium rather than a fully delocalized pentadienyllithium. Additional support for the vinyl-substituted allyl structure is obtained by comparing the Si(1)–C(1)–C(2)–C(3) and Si(2)–C(5)–C(4)–C(3) torsional angles of 169.1(2)° and 179.09(19)°, respectively, *i.e.* C(1) is in a pyramidal environment whereas C(4) and C(5) are planar.

Complex **2** is the first crystallographically characterized pentadienyllithium and the first structurally authenticated donor-functionalized pentadienyl complex of any metal. In contrast to **2**, the magnesium complex [Mg(tmeda)(2,4-dimethyl-2,4-pentadienyl)₂] and the polymeric potassium pentadienyl [K(tmeda)(2,4-dimethyl-2,4-pentadienyl)]_∞ both have their pentadienyl carbons arranged in the U-conformation.^{6d,10} The structures of pentadienyllithiums have only previously been determined in solution by NMR spectroscopy (see below) or by inference from the stereochemistry of products in electrophilic quenching reactions.^{5–7} The ligand hapticity in a pentadienyl-lithium, and the extent to which the negative charge is delocalized, have not been determined by experiment. *Ab initio* calculations by Streitwieser and a DFT study by Merino have, however, furnished insight into the structure of pentadienyl-lithium, [Li(C₅H₇)] (**3**).¹¹ The lowest energy structure of gas-phase **3** was found to be the U-shape, and in each local minimum the lithium cation was coordinated to three or more carbons. This contrasts to the structure of η²-W structure of **2**. The inclusion of solvent effects *via* the conductor-like screening model (COSMO) does not change the preference for the U-shape of **3**.^{11b} Interpreting the structure of **2** as a vinyl-substituted allyl agrees well with Streitwieser's calculations on **3**.^{11b}

The lack of experimental data to compare to the structure of **2** prompted us to carry out a DFT study of: **2**; the intermolecularly solvated model complex [(pmdeta)Li{1,5-(Me₃Si)₂C₅H₅}] (**4**) (pmdeta = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine); and the pristine 1,5-bis(trimethylsilyl)pentadienyl anion [1,5-(Me₃Si)₂C₅H₅][−] (**5**).

The Amsterdam Density Functional Software was used in all cases.^{12–14} Geometry optimizations on **2** were calculated



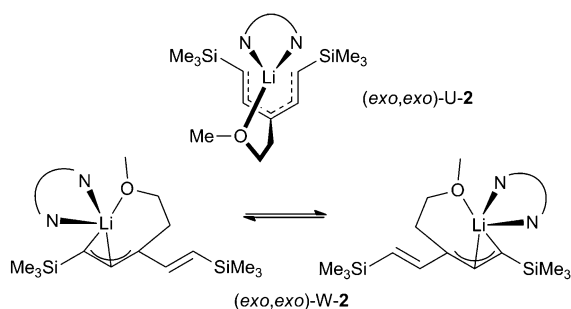
at the BP86/TZ2P and the BP86/QZ4P levels of theory. Calculations on **2** under toluene solvation conditions used the COSMO model.¹⁵

Although the Li–N distances to the tmeda ligand in **2** are slightly overestimated, the calculated geometric parameters agree well with the experimental data at both levels of theory, justifying use of BP86/TZ2P for other calculations on **4** and **5**. The optimized structure of **2** and pertinent bond lengths and angles are given in Fig. S4 (ESI†). Complex (*exo,exo*)-W-**2** is the lowest energy form of **2**, with (*exo,endo*)-S-**2**, (*exo,exo*)-S-**2**, and (*exo,exo*)-U-**2** being +10.4, +3.1 and +5.3 kcal mol^{−1} less stable (Fig. S5, ESI†). Toluene solvation produces small changes in the energies of the isomers of **2**, hence (*exo,exo*)-W-**2** remains the most stable.

The calculations on **2** were used to determine initial structures for the geometrical optimization of the model complex [(pmdeta)Li{1,5-(Me₃Si)₂C₅H₅}] (**4**). The trend in stability for **4** is the same as for **2**, hence (*exo,exo*)-W-**4** is the most stable, (*exo,endo*)-S-**4** and (*exo,exo*)-S-**4** are +5.9 and +1.5 kcal mol^{−1} less stable, and (*exo,exo*)-U-**4** is +4.7 kcal mol^{−1} less stable. The structure of (*exo,exo*)-W-**4** is similar to the crystallographic structure of **2**, consisting of a W-shaped pentadienyl group and a four-coordinate lithium cation (Fig. S5, ESI†). Whereas **2** shows η²-Pn coordination to lithium, the calculated gas-phase structure of (*exo,exo*)-W-**4** contains an η³-bonded pentadienyl ligand with Li–C distances in the range 2.325–2.515 Å (average 2.401 Å). However, the pentadienyl C–C distances in (*exo,exo*)-W-**4** are similar to those found in the experimental structure of **2** (range 1.374–1.426 Å), indicating a partially localized vinyl-substituted allyl structure.† Since the pentadienyl C–C distances in the gas-phase structure of metal-free [(*exo,exo*)-1,5-(Me₃Si)₂C₅H₅][−], (*exo,exo*)-W-**5**, are essentially equal in length at 1.393 and 1.406 Å (Fig. S6, ESI†), it can be concluded that partial localization of the pentadienyl negative charge in (*exo,exo*)-W-**2** and (*exo,exo*)-W-**4** is intrinsic to the pentadienyllithium unit, and stems from the polarizing nature of the Li⁺ cation.

Our calculations on **2** show that different isomers may be only slightly higher in energy, such that their structures could be observed experimentally. This prompted us to examine **2** by variable-temperature ¹H NMR spectroscopy.

The ¹H NMR spectrum of **2** in toluene-*d*₈ at 300 K (Fig. S2, ESI†) consists of a singlet at δ = 2.89 ppm and two mutually coupled triplets (³J = 5.3 Hz) at 2.65 and 3.48 ppm, which are due to the CH₂CH₂OMe group. A singlet due to the trimethylsilyl substituents was observed at 0.29 ppm. Two mutually coupled doublets at 3.64 and 6.80 ppm with ³J = 17.5 Hz indicate *trans* stereochemistry pentadienyl protons, *i.e.* C(1/5)–H and C(2/4)–H, respectively (Fig. 1). The resonances due to tmeda occur as singlets at 1.90 (CH₃) and 1.70 ppm (CH₂). The ¹³C NMR spectrum of **2** was fully assigned



Scheme 2 Proposed solution phase structures of **2**.

(see ESI[†]), with the resonances for the pentadienyl carbons C(1/5), C(3) and C(2/4) occurring at 76.91, 99.97 and 151.07 ppm, respectively. A single resonance in the ⁷Li spectrum of **2** was observed at −0.77 ppm. These observations imply an element of symmetry within the solution-phase structure of **2**, *i.e.* the Pn carbons adopt the U-conformation, or that a rapid equilibration of the unsymmetrical W- or S-shaped conformations is occurring. The ¹H NMR spectrum of **2** was then recorded at 273, 243, 213, 203 and 193 K, and no major changes were observed, except for line-broadening near the freezing point of the solvent (Fig. S3, ESI[†]).

The conformational flexibility of alkali metal pentadienyls is well known.^{6,17} Nakamura found that S-shaped 1,3,5-tris(trimethylsilyl)pentadienyllithium (**6**) is fluxional in THF. Insight into the solution-phase structure of **2** can be obtained by comparing the ¹H NMR spectra of **2** with those of **6**. Around room-temperature, the ¹H NMR spectra of **2** and **6** exhibit two doublets due to the pentadienyl protons. On cooling to 203 K, each doublet in the spectrum of **6** decoalesces into two doublets, whereas those in the spectrum of **2** are unchanged to 193 K. This suggests that, in toluene, complex **2** either exists as (*exo,exo*)-U-**2** or that a fluxional process with a very low activation barrier involving the other conformations is occurring. Although we do not find evidence for preservation of the crystallographic structure of (*exo,exo*)-W-**2** in solution, the combined experimental and computational data suggest a fluxional structure in toluene (Scheme 2).

However, because minor environment changes can eventually determine the actual structure, the small differences in energy between the calculated structures of **2** do allow for fluxionality involving the W-, S- or U-conformations.

In summary, we have reported the first example of a donor-functionalized metal pentadienyl complex and the first crystal structure of a pentadienyllithium. Our crystallographic studies confirm earlier theoretical predictions that the pentadienyl negative charge is not fully delocalized, but is in fact a partially localized vinyl-substituted allyl anion. This effect is not due to the influence of the pendant donor functionality, but is due to the polarizing ability of the lithium cation. Solution-phase fluxionality in the structure of **2** is a distinct possibility, however if such a dynamic process is occurring, the activation barrier is too low to enable unambiguous conclusions to be drawn.

Our ongoing research will develop donor-functionalized pentadienyllithiums in which the functionality is incorporated into the terminal silyl groups, which could lead to complete

localization of the negative charge. Versions of **2** in which the donor-functionality may be less conducive to solution-phase fluxionality are also being studied, and will be reported in the future. Our ongoing research will also develop the donor-functionalized ligand in **2** for use in coordination chemistry with other metals.

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