

(1*S*,2*S*,9*R*,10*R*)-Tetracyclo[8.2.1.0^{2,9}.0^{3,7}]trideca-3,6-dienyl-lithium. Tentative Evidence for a Quinternary Equilibrium Involving a Cyclopentadienide Ion

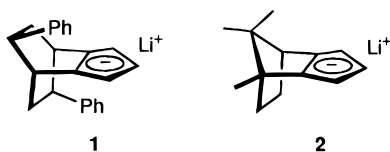
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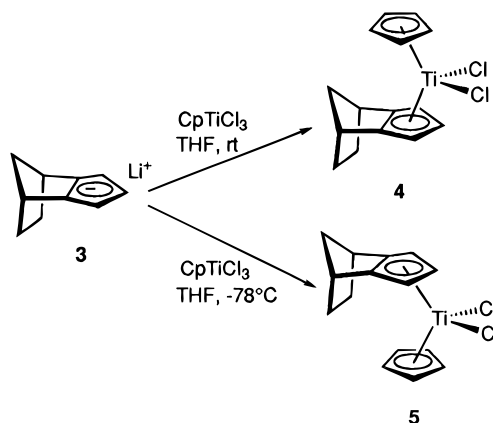
The title anion **9** was prepared starting from (+)-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol, the less reactive enantiomer from lipase-mediated transesterification with vinyl acetate, by sequential Jones oxidation, hydrogenation, condensation with cyclopropyldiphenylsulfonium ylide, Baeyer–Villiger oxidation, acid-catalyzed rearrangement, hydride reduction, and dehydration. The derived lithium cyclopentadienide **9** reacted with TiCl₃ and CpTiCl₃ to give only exo titanocenes. Comparison of cross peak intensities in ⁶Li, ¹H HOESY spectra of **9** indicates the existence of the exo-monomer at +24 °C. At –110 °C, the ⁶Li spectrum indicates the presence of five distinct species which are in mutual exchange of the lithium cation as is shown by ⁶Li, ⁶Li-EXSY. The two major species are assigned as an exo-monomer and an exo,dimer. MNDO calculations on various monomeric and dimeric solvatomers of **9** confirm the NMR findings.

Chiral metallocenes formed by the complexation of transition metals to optically active cyclopentadienyl anions have emerged in recent years as serviceable catalysts for asymmetric synthesis.² When the negatively charged Cp ligand is annulated in a C₂-symmetric manner as in **1**,³ its two faces are homotopic and only a single complex can be obtained therefrom. In C₁-symmetric examples represented by **2**,⁴ two diastereo-



meric modes of complexation are available and the task of obtaining either complex in pure condition rests on controlling π -facial selectivity. In select examples such as **3**, this fascinating type of stereoregulation may originate from electronic contributions provided by the neighboring fused bicyclic hydrocarbon framework (in this instance norbornyl).⁵ The lithium counterion responds to these forces by bonding preferentially to one or the other diastereotopic cyclopentadienide surface. Capture of the metal halide introduced subsequently

proceeds with retention of stereochemistry.⁶ The complexation of dissymmetric cyclopentadienide anions to Li⁺ generally involves dynamic equilibration between the two π -surfaces and changes in the metal's state of aggregation. Variations in reaction temperature can consequently sometimes be utilized to advantage for the stereocontrolled preparation of chiral complexes, e.g. **4** and **5**.⁷



More recently, a second means has been developed for achieving exceptional stereocontrol in the prepara-

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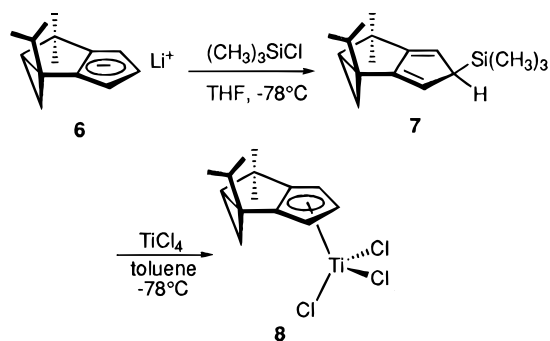
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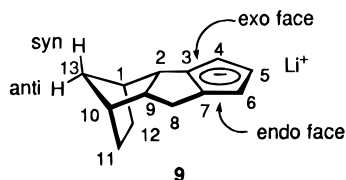
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tion of diastereomeric complexes.⁸ The targeted objective can be reached by first generating the trimethylsilyl derivatives, effecting their chromatographic separation, and exposing the individual silanes to a reactive metal halide.⁹ As shown in the **7** → **8** conversion, strict inversion of configuration accompanies formation of the metallocene.



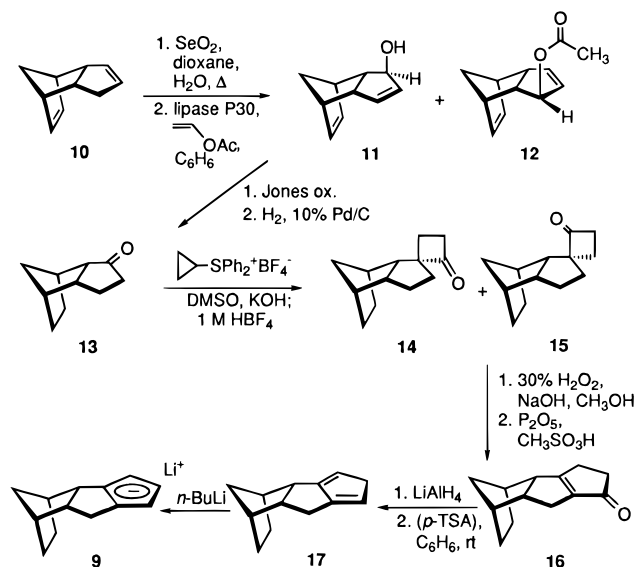
Despite these utilitarian advances, there is as yet only limited knowledge of the effects of substantive steric congestion on one face of a C_1 -symmetric cyclopentadienide species. The expectation is, of course, that the crowded surface would be avoided by attacking reagents. Under these circumstances, does lithium prefer a monomeric, dimeric, or trimeric association with the anion? What are the overall geometries of the resulting complexes and how do these features impact on their role as asymmetric catalysts? Herein we detail the first phase of our investigation into the preparation of the optically active title anion **9** and its coordination to lithium and titanium.



Results and Discussion

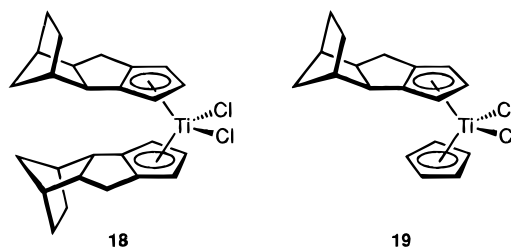
Preparation of the Optically Active Tetracyclic Anion. Selenium dioxide oxidation of (\pm)-dicyclopentadiene (**10**) according to Rosenblum¹⁰ gave the racemic exo alcohol, which was conveniently resolved by lipase-mediated transesterification with vinyl acetate.¹¹ This process provided the lesser reactive (+)-enantiomer **11** in optically pure form alongside the levorotatory acetate

12. Sequential Jones oxidation and hydrogenation of **11** produced **13**,^{12,13} which was converted into a mixture of spirocyclobutanones **14** and **15** by treatment with the



cyclopropyldiphenylsulfonium ylide.¹⁴ The stereoisomeric nature of this mixture was of no consequence since subsequent Baeyer–Villiger oxidation to the corresponding lactones and their exposure to an 8% solution of phosphorus pentoxide in methanesulfonic acid¹⁵ resulted in convergence to tetracyclic ketone **16**. Hydride reduction of **16** and dehydration of the resultant allylic alcohol with catalytic *p*-toluenesulfonic acid in benzene at rt afforded a mixture of **17** and its positional isomers. Characterization was therefore deferred until after the conversion to **9**. This white solid is indefinitely stable if stored under an inert atmosphere and away from air and moisture. The very characteristic ¹H NMR spectrum of **9** is illustrated in Figure 1.

Titanocene Formation. Treatment of **9** dissolved in anhydrous THF with TiCl₃, initially at -78°C and subsequently at the reflux temperature for 48 h, resulted in smooth conversion to the bright red complex **18**. Although somewhat less forcing conditions were



utilized when **9** was condensed with CpTiCl₃ to give **19**

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(13) The optical rotation that we have recorded for **13**, $[\alpha]_D^{20} +191.5^\circ$ (*c* 7.8, hexane) is significantly below that reported earlier for this ketone: $[\alpha]_D^{20} +260.5^\circ$ (0.925%, hexane).¹² Since our samples of **11** were of 100% ee, we assume that the reduction in optical purity materialized during the chromic acid oxidation by partial [3,3] rearrangement within the chromate ester intermediate. This conclusion is supported by the fact that the $[\alpha]_D^{20}$ of our dienone precursor, $+127.3^\circ$ (*c* 3.3, CHCl₃), is already below values recorded by others: $[\alpha]_D^{20} -150.0^\circ$ (0.954%, CH₂Cl₂)¹² and $[\alpha]_D^{33} -154^\circ$ (*c* 2.12, CH₃OH).¹¹ In future work, it is recommended that the hydrogenation precede the oxidation.

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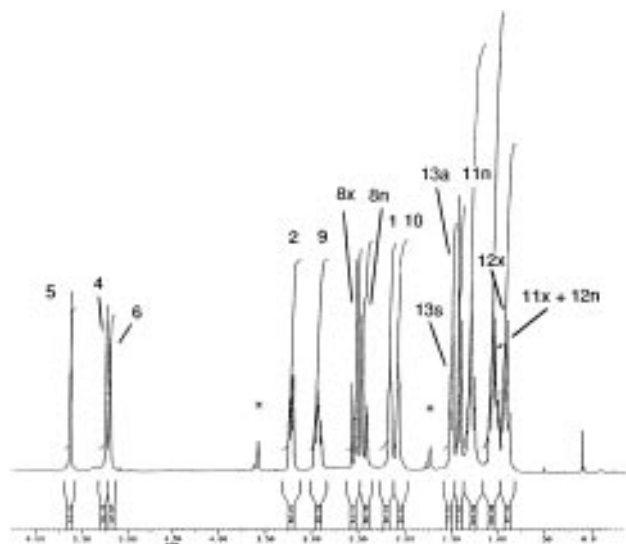


Figure 1. 300 MHz ^1H NMR spectrum of **9** recorded in THF- d_8 solution. Symbols: a = anti, s = syn, x = exo, n = endo, o = solvent signal.

(rt, 10 h), no evidence was found in either instance for the formation of isomeric titanocenes. The structural assignments to **18** and **19** are based upon the substantive steric nonequivalence of the two π -surfaces and the identical stereochemical discrimination exhibited by the Li^+ ion in THF solution as derived from the experiments to be described below.

NMR Spectroscopy of Lithium Salt 9. For the studies described in this section, material isotopically labeled with ^6Li was employed. The numbering and stereochemical assignments are depicted in **9**. As observed in related cases,⁶ the ^1H , ^{13}C , and ^6Li spectra of **9** at +24 °C in THF- d_8 show a single set of signals. The ^1H -assignment (1D-spectrum see Figure 1) was achieved by standard 2D NMR techniques. Most of the ^1H -resonances can be assigned by ^1H , ^1H -COSY. The assignment strategy for the aliphatic protons starts with the unique signal of H2, which appears as a doublet at lowest field in the aliphatic region of the spectrum. The discrimination between chemically non-equivalent protons H4 and H6 was achieved by ^1H , ^1H -COSY with delays suitable to detect long-range couplings. The ^{13}C -assignments were straightforward, and involved standard ^1H , ^{13}C -HETCOR, and COLOC techniques. The ^{13}C -chemical shifts and assignments are given in the Experimental Section.

The ^6Li -NMR spectrum of **9** in THF at +24 °C consists of a single resonance line at -7.89 ppm. This unusual upfield shift as compared to the "normal" range of lithium chemical shifts (ca. -2 ... +2 ppm) is very similar to related cyclopentadienides described earlier by our groups.⁶ The lithium cation must necessarily be positioned in a magnetically anisotropic environment where it experiences the "high field cone" of the Cp ring current effect.^{6e-j} In all of the preceding examples, the fused Cp compounds were found to exist mainly or exclusively as monomers at room temperature. Hence, we hold the same to be true for the present compound.

Stereochemical assignments of the cation location in organolithium compounds can be conveniently realized by ^6Li , ^1H -HOESY analysis.^{16,17} The HOESY spectrum obtained for **9** at +24 °C is shown in Figure 2. As expected,⁶ intense cross peaks appear at the ^1H -

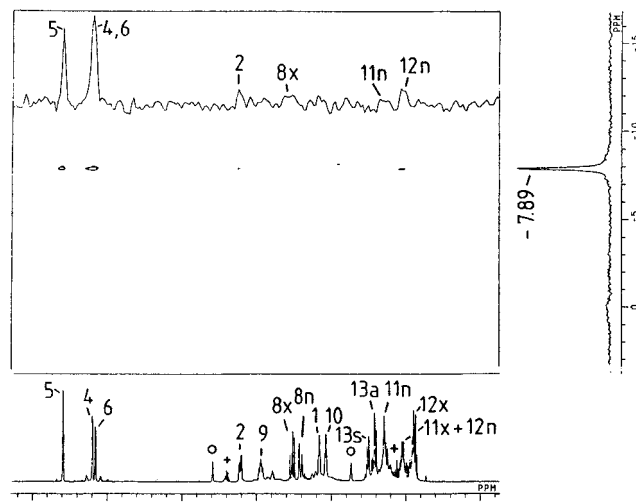


Figure 2. ^6Li , ^1H -HOESY spectrum of **9** in THF- d_8 , 0.55 M, +24 °C, mixing period 2.0 s. Inset: f_1 -slice cut at the top of the ^6Li signal. Symbols: a = anti, s = syn, x = exo, n = endo, o = solvent signal, + = signal of Et_2O (from preparation).

resonance lines of the three Cp protons. However, these signals do not allow an exo/endo assignment of lithium. Additional much weaker cross peaks involve the protons H2, H8, H11(endo), and H12(endo). This is consistent with a rapid exo-monomer/endo-monomer equilibrium at room temperature. In addition, it is safe to assume that this equilibrium must be largely on the exo-monomer side: MNDO calculations suggest that in the endo-monomer the distance between Li and the H11(endo)/H12(endo) protons is very small (2.80 Å for H12(endo)). These distances are even smaller than the separation between Li and the Cp protons. Accordingly, if large amounts of the endo-monomer were present, very intense cross peaks should be expected at the H11(endo)/H12(endo) positions in the HOESY spectrum. Hence, we construe the observed small intensities of these cross peaks to be evidence for the predominance of the exo-monomer under the measurement conditions.

The low temperature NMR spectra of **9** are of particular interest. The ^1H spectrum at -102 °C evidently is comprised of two data sets, indicating a monomer-dimer equilibrium as is well-known from previous studies.⁶ This spectrum is highly crowded in the aliphatic region. Moreover, it is impossible to deconvolute the ^1H spectrum due to line broadening at this low temperature. However, valuable information can be extracted from the companion ^6Li spectrum (cf. Figure 3). Three intense peaks are visible at -1.05,

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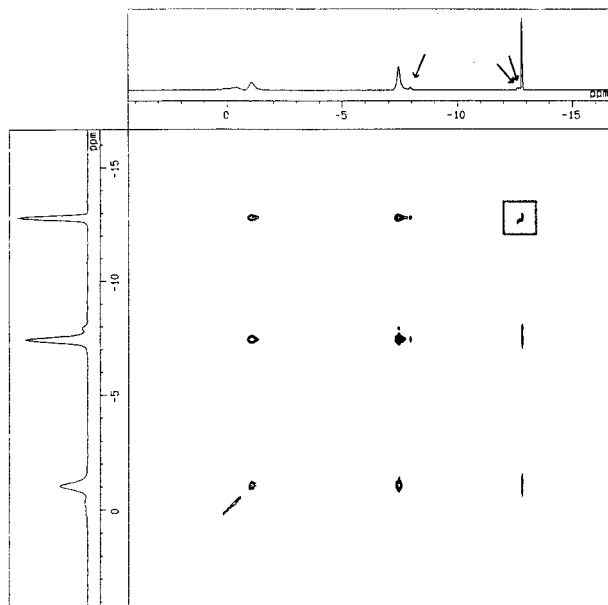


Figure 3. ^6Li , ^6Li -EXSY spectrum of **9** in $\text{THF-}d_8$, 0.55 M, -110°C , mixing time 5.0 s. The diagonal runs from the lower left to the upper right. The arrows in the 1D spectrum indicate additional small peaks. The 1D spectra are projections along both axes. The boxed area is enlarged in Figure 4.

-7.44 , and -12.80 ppm. Again, this behavior is very similar to cases observed earlier.⁶ We thus are dealing with a monomer–dimer equilibrium. The -7.44 ppm peak must represent the monomer, whereas the -1.05 and -12.80 ppm signals must be due to the dimer with two chemically nonequivalent lithium sites. The -1.05 ppm peak must be due to “external” solvated lithium, whereas the -12.80 ppm signal must originate from lithium sandwiched between two Cp rings.^{6,18} Most interesting, however, is the appearance of three additional weak signals at -7.95 , -12.61 , and -12.69 ppm. Tentatively, we ascribe these peaks to result from an additional monomeric and two additional dimeric species. Hence, a *quinternary* equilibrium consisting of a major monomer and a minor monomer, as well as of a major dimer and two minor dimers, is probably being observed. *To our knowledge, this is the first report of a quinternary equilibrium of an organolithium compound in THF solution.* These five ^6Li signals might represent the number of all theoretically expected structures: exo-monomer, endo-monomer, exo,endo-dimer, endo,endo-dimer, and exo,exo-dimer. The integral ratios of the five peaks upfield from -7 ppm are 51.3%, 2.8%, 0.6%, 0.7%, and 44.6%. These percentage numbers would reflect the molar ratios of the aggregates involved.

Further important information comes from a ^6Li , ^6Li exchange spectrum (EXSY) at low temperatures (Figures 3 and 4). As is evident, there is mutual exchange between the different lithium sites. Concerning the exchange mechanism, a detailed study has been undertaken earlier.^{6a} The same mechanism is assumed to take place in the present case. Accordingly, since there is no direct exchange between “sandwiched” and “free” lithium, the exchange cross peaks between the -1.05 and -12.80 ppm signals must originate from a stepwise

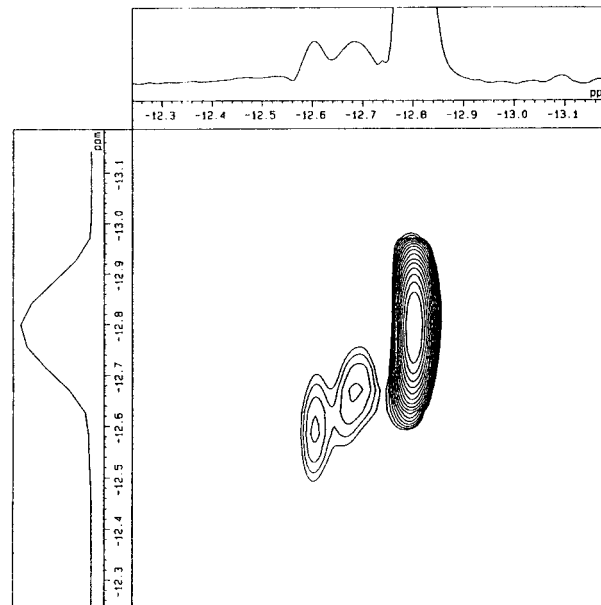


Figure 4. Enlarged plot of the boxed area of Figure 3.

process. Exchange cross peaks may also be observed for the minor monomer signal (-7.95 ppm). The exchange cross peaks of the two minor dimers are too weak to be observed in Figure 3 at the baseline threshold employed. At lower thresholds, part of these cross peaks appear slightly above the noise level under the conditions of measurement.

A ^6Li , ^1H HOESY spectrum of **9** recorded at -102°C proved to be of limited value. As noted above, the ^1H spectrum cannot be assigned unambiguously due to signal overlap and broadness of the signals. Hence, there is no direct evidence for close Li, H contacts at this temperature. However, similar to the analog spectrum at $+24^\circ\text{C}$, all cross peaks which involve the Cp protons are much more intense than any cross peak which includes the aliphatic ^1H signals. For the reasons outlined above, the exo-monomer and exo,exo-dimer are obviously being observed as the major species at low temperature. The three residual possible aggregates must constitute the minor species. This is in complete agreement with the MNDO calculations described below.

As a cautionary note we emphasize that the assignment of the minor ^6Li peaks given in this section is still tentative. At the present point we cannot completely exclude exchange phenomena with further unknown byproducts.

The presence of exo-species both at $+24^\circ\text{C}$ and at -102°C agrees nicely with the results of titanocene formation described above. In agreement with our proposed mechanism,^{6a} the metal exchange takes place with retention of the exo/endo configuration.

MNDO Calculations. The optimized geometries of several monomers and dimers of **9** were calculated by the semiempirical MNDO method (Figure 5). These isomers differ in the location of lithium and/or in the

(19) This conclusion is based on the following observation: in Figure 3 as well as in cases reported earlier (refs 6a–d), an additional minor peak is observed in the ^6Li -spectrum at *ca.* 0 ppm. This is typical for traces of hydrolysis product where initially formed LiOH is converted to its THF-solvate with a $[\text{Li}(\text{THF})_4]^+$ ion being present. As is evident from Figure 3 and the described cases mentioned earlier, there must be slow exchange between “external” lithium of a dimer of the title compound and $[\text{Li}(\text{THF})_4]^+$.

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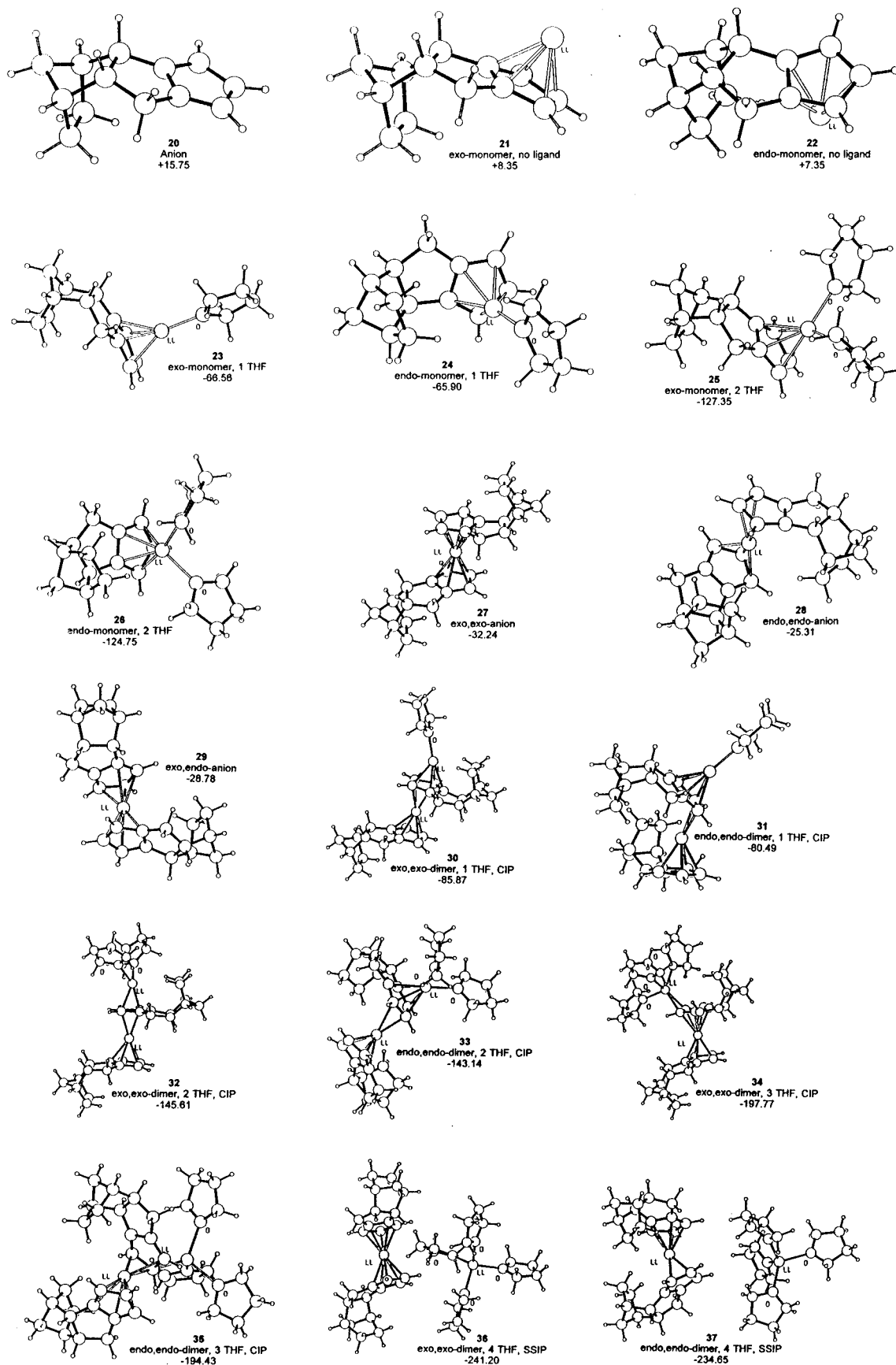
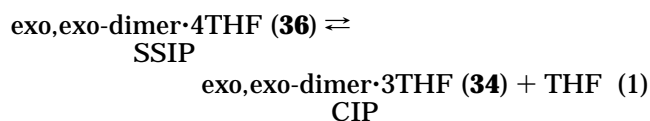


Figure 5. MNDO calculated structures of various monomers and dimers of **9**, differing in lithium location and/or in the number of THF ligands. SSIP = solvent separated ion pair. CIP = contact ion pair. Numbers are heats of formation (kcal/mol). The heat of formation of THF is -59.28 kcal/mol.

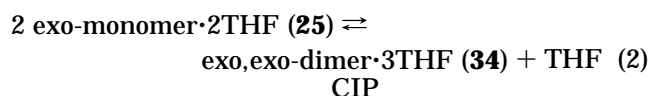
number of THF ligands. Two equations may be used to explain the behavior found experimentally for **9** in

solution. With reference to a possible SSIP/CIP equilibrium (SSIP = solvent separated ion pair, CIP =

contact ion pair), eq 1 indicates that the CIP is strongly favored energetically over the SSIP. This agrees with experimental observation. In the 1D spectrum of Figure 3, the peak at -1.05 ppm is interpreted *not* to represent the $[\text{Li}(\text{THF})_4]^+$ species. Rather, this peak must constitute the "peripheral" lithium in a CIP dimer.¹⁹ On the other hand, the dimerization of two monomers is an *exothermic* process (eq 2). This also agrees nicely



$$\begin{aligned} \Delta H &= (\Delta H_{34} + \Delta H_{\text{THF}}) - \Delta H_{36} \\ -15.85 &= (-197.77 - 59.28) + 241.20 \end{aligned}$$



$$\begin{aligned} \Delta H &= (\Delta H_{34} + \Delta H_{\text{THF}}) - 2\Delta H_{25} \\ -2.35 &= (-197.77 - 59.28) + 254.70 \end{aligned}$$

with the experimental findings. Whereas at $+24$ °C only monomers appear to be present, the equilibrium is shifted toward the species favored by enthalpy (dimer) when cooled.

Conclusions. We have shown that the title compound **9** must exist as a rapid exo-monomer/endo-monomer equilibrium at room temperature, with the exo compound being the prevailing species. At -110 °C, a quinternary mixture in THF is seen consisting predominantly of the exo-monomer and exo,exo-dimer, with the minor species presumably being the endo-monomer, the endo,endo (sandwich) dimer, and the exo,endo-dimer. MNDO calculations confirm the experimental results. Exo locations of lithium are preferred in solvated species. These findings are in agreement with the chemical behavior of **9** since exo compounds are produced upon reaction with appropriate titanium substrates. We emphasize that the NMR assignment of the minor species as described above is still tentative.

Experimental Section

(+)-(1R,2S,3R,6R,7R)-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol (11). Racemic tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol (32.50 g, 0.22 mol), obtained by the oxidation of dicyclopentadiene,¹⁰ was combined with benzene (1000 mL), vinyl acetate (189.40 g, 2.20 mol), lipase P30 (7.0 g, *Pseudomonas sp.*, Amano) at rt in a 3000 mL three-necked round-bottomed flask fitted with a gas inlet, mechanical stirrer, and septum. The progress of reaction was monitored by GC-MS. The mixture was stirred at room temperature for 16 days to achieve 56% conversion, filtered through a Celite pad (benzene wash) and concentrated to give a yellow-brown oil. The oil was placed atop a column of silica gel and eluted with 5% ethyl acetate in petroleum ether to yield (–)-acetate **12** (19.21 g, 46%). Continued elution with 20% ethyl acetate in petroleum ether afforded 13.37 g (41%) of **11**, recrystallization of which from ether-hexane gave 11.68 g (36%) of optically pure alcohol: $[\alpha]_{\text{D}}^{20} +99.8^\circ$ (*c* 5.2, CHCl_3) (lit. $+99^\circ$ (CHCl_3)).¹¹

(+)-(1R,2S,6R,7R)-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one. A solution of **11** (10.00 g, 0.067 mol, 99% ee) in ether (250 mL) was cooled to 0 °C and treated dropwise over 30 min with a mixture of sodium dichromate (29.20 g, 0.100 mol), concentrated sulfuric acid (4.9 mL), and water (30 mL) so as

to keep the reaction temperature below 10 °C. Once addition was complete, the ice bath was removed, and the mixture was stirred at 25 °C for 10 h and extracted with ether (3×100 mL). The combined ethereal phases were washed with saturated NaHCO_3 solution (200 mL) and brine (100 mL), dried, and concentrated to leave the dienone as a colorless oil which solidified on standing: 9.25 g (93%), mp 73–74 °C (from ether); $[\alpha]_{\text{D}}^{20} +127.3^\circ$ (*c* 3.3, CHCl_3).¹³

(+)-(1S,2S,6R,7R)-Tricyclo[5.2.1.0^{2,6}]decan-3-one (13). The above dienone (6.00 g, 41.0 mmol) was dissolved in ethyl acetate (75 mL) containing 10% palladium on carbon catalyst (200 mg) and hydrogenated at 40 psi. After hydrogen uptake ceased, the catalyst was removed by filtration through Celite, and the eluate was concentrated to leave **13** as a white microcrystalline solid: 5.70 g (92%), $[\alpha]_{\text{D}}^{20} +191.5^\circ$ (*c* 7.8, hexane).¹³

Spirocyclobutanone Formation. To a solution of (+)-**13** (2.00 g, 13.3 mmol) in 45 mL of dry DMSO was added cyclopropyldiphenylsulfonium tetrafluoroborate (4.28 g, 16.7 mmol) followed by powdered potassium hydroxide (1.50 g, 26.7 mmol). After 24 h, 75 mL of cold aqueous 1 M fluoroboric acid solution was introduced. The mixture was stirred for 15 min, diluted with cold water (100 mL), and extracted with CH_2Cl_2 (4×100 mL). The combined extracts were dried, filtered, and concentrated to give an orange oil, purification of which on silica gel afforded 2.02 g (80%) of a 4:1 mixture of spirocyclobutanone isomers.

For the major isomer: ¹H NMR (300 MHz, CDCl_3) δ 2.90 (dm, *J* = 7.7, 5.2 Hz, 2 H), 2.43 (br m, *J* = 6.6 Hz, 2 H), 2.19 (br s, 1 H), 2.11 (br s, 1 H), 2.07–1.92 (m, 2 H), 1.91–1.65 (m, 3 H), 1.61 (dt, *J* = 6.2, 4.3 Hz, 2 H), 1.49–1.23 (m, 5 H); ¹³C NMR (75 MHz, CDCl_3) ppm 213.5, 72.6, 58.1, 44.6, 42.9, 41.4, 41.2, 37.3, 29.9, 25.2, 24.3, 22.4.

For the minor isomer: ¹H NMR (300 MHz, CDCl_3) δ 3.00 (dm, *J* = 7.5, 5.0 Hz, 2 H), 2.39 (br m, *J* = 5.8 Hz, 2 H), 2.20 (br s, 1 H), 2.15 (br s, 1 H), 2.07–1.92 (m, 2 H), 1.91–1.65 (m, 5 H), 1.49–1.23 (m, 5 H); ¹³C NMR (75 MHz, CDCl_3) ppm 215.7, 71.5, 49.5, 45.4, 42.13, 42.10, 41.9, 40.4, 36.5, 25.8, 24.6, 22.8, 20.4.

For the mixture: IR (CHCl_3 , cm^{-1}) 1760; HRMS *m/z* (*M*⁺) 190.1358, obsd 190.1398. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 82.04; H, 9.53.

Baeyer–Villiger Oxidation of 14/15. A solution of the **14/15** mixture (1.50 g, 7.9 mmol) in 75 mL of methanol was treated with 30% hydrogen peroxide solution (4.17 g, 36.7 mmol). Sodium hydroxide solution (1.5 mL of 10 N, 15.6 mmol) was slowly introduced and stirring was maintained for 6 h. After the addition of 10% aqueous hydrochloric acid solution (110 mL) and 60 mL of water, the mixture was extracted with CH_2Cl_2 (4×75 mL). The combined extracts were washed with water, dried, and concentrated to afford, after trituration with pentane, 1.50 g (92%) of a white solid as a 9:1 mixture of lactone isomers. For the major isomer, mp 67–69 °C (from ether); IR (neat, cm^{-1}) 1759; ¹H NMR (300 MHz, CDCl_3) δ 2.54 (t, *J* = 7.9 Hz, 2 H), 2.41 (m, 1 H), 2.32 (br d, *J* = 0.9 Hz, 1 H), 2.20 (br d, *J* = 4.6 Hz, 2 H), 2.04 (m, *J* = 7.2 Hz, 3 H), 1.85 (br m, 1 H), 1.77–1.35 (m, 8 H); ¹³C NMR (75 MHz, CDCl_3) ppm 177.2, 93.4, 53.9, 42.4, 42.3, 41.8, 41.0, 37.8, 37.4, 28.5, 24.4, 22.7, 22.4; HRMS *m/z* (*M*⁺) calcd 206.1306, obsd 206.1310. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69; H, 8.80. Found: C, 75.55; H, 8.82.

(–)-(1S,2S,9R,10R)-Tetracyclo[8.2.1.0^{2,9}.0^{3,7}]tridec-3(7)-en-6-one (16). To a homogeneous solution containing 255 g (2.65 mol) of methanesulfonic acid and 25.5 g (0.18 mol) of phosphorous pentoxide was added a mixture of the above lactones (1.50 g, 7.8 mmol), and the dark red mixture was stirred for 36 h before being carefully quenched with cold (15 °C) water. After 1 h, the product was extracted into CH_2Cl_2 (3×100 mL). The combined organic phases were washed with saturated NaHCO_3 solution (2×50 mL), dried, and concentrated to give a red oil, purification of which on silica gel (elution with 10% ethyl acetate in petroleum ether) gave **16**

as a pale yellow oil (1.30 g, 95%): IR (neat, cm^{-1}) 1698; ^1H NMR (300 MHz, CDCl_3) δ 3.03 (m, 2 H), 2.69 (dt, $J = 3.8, 1.5$ Hz, 2 H), 2.45 (br s, 1 H), 2.41 (br m, 2 H), 2.24 (t, $J = 2.8$ Hz, 1 H), 2.22 (q, $J = 2.7$ Hz, 2 H), 1.50 (t, $J = 1.7$ Hz, 1 H), 1.48 (t, $J = 1.7$ Hz, 1 H), 1.34–1.28 (m, 3 H), 0.99 (br m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) ppm 205.0, 187.4, 149.1, 51.2, 49.2, 41.4, 40.9, 41.8, 38.8, 25.8, 25.2, 24.4, 21.9; HRMS m/z (M^+) calcd 188.1201, obsd 188.1203; $[\alpha]_D^{20} -1.5^\circ$ (c 0.5, CHCl_3). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.85; H, 8.71.

(1S,2S,9R,10R)-Tetracyclo[8.2.1.0^{2,9}.0^{3,7}]trideca-3,6-dienyllithium (9). Enone **16** (3.40 g, 18.1 mmol) dissolved in 20 mL of ether was added to a cooled (0 °C) slurry of lithium aluminum hydride (685 mg, 18.1 mmol) in 50 mL of the same solvent. After 3 h, the reaction mixture was warmed to 25 °C and quenched 60 min later with a saturated solution of Rochelle's salt (50 mL). The aqueous phase was extracted with ether (3 \times 50 mL), and the combined ethereal phases were dried and concentrated leaving an approximate 50:50 mixture of allylic alcohols as a gummy residue. To avoid decomposition, this material was directly dehydrated.

The residue was taken up in benzene (100 mL), and *p*-toluenesulfonic acid (0.58 g, 0.60 mmol) was added at rt. Once the alcohol was consumed as indicated by TLC, the reaction mixture was neutralized with saturated NaHCO_3 solution (50 mL), extracted with ether (3 \times 50 mL), dried, decolorized with activated carbon, filtered, and concentrated to give a light yellow oil. Rapid purification of this material on 240–400 mesh silica gel (pentane elution) afforded 1.57 g (79%) of a mixture of cyclopentadienes. For the major diene **17**: ^1H NMR (300 MHz, C_6D_6) δ 5.27 (s, 1 H), 5.11 (s, 1 H), 3.83 (s, 1 H), 3.42 (br s, 1 H), 3.04 (br s, 1 H), 2.85 (br s, 1 H), 2.68 (br s, 1 H), 2.52 (dd, $J = 15.8, 9.2$ Hz, 1 H), 2.30–2.09 (m, 3 H), 1.50–1.16 (m, 4 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 158.0, 156.2, 120.5, 120.0, 60.5, 44.0, 41.8, 40.7, 39.8, 37.5, 25.5, 24.5, 22.7; HRMS m/z (M^+) calcd 172.1252, obsd 172.1260.

The diene mixture (2.00 g, 11.6 mmol) was dissolved in ether (20 mL) and hexane (20 mL) under argon, the solution was cooled to 0 °C, and *n*-butyllithium (8.3 mL, 1.4 M in hexane, 11.6 mmol) was added. The white precipitate which formed was collected under argon after the mixture had stirred at 25 °C for 10 h and stored under nitrogen in a Schlenk tube. There was obtained 2.00 g (97%) of **9**, a white air-sensitive solid: ^1H NMR (300 MHz, $\text{THF}-d_6$) δ 5.63 (t, $J = 3.0$ Hz, 1 H), 5.23 (d, $J = 2.8$ Hz, 1 H), 5.19 (d, $J = 2.3$ Hz, 1H), 3.22 (dd, $J = 9.9, 4.9$ Hz, 1 H), 2.94 (m, 1 H), 2.53 (dd, $J = 14.3, 8.9$ Hz, 1 H), 2.43 (dd, $J = 14.3, 3.1$ Hz, 1 H), 2.17 (t, $J = 4.4$ Hz, 1 H), 2.08 (t, $J = 4.4$ Hz, 1 H), 1.51 (dt, $J = 8.9, 1.7$ Hz, 1 H), 1.40 (dt, $J = 8.0, 1.6$ Hz, 1 H), 1.29 (m, 1 H), 1.03 (m, 1 H), 0.90 (m, 1 H); ^{13}C NMR (125 MHz, $\text{THF}-d_6$) ppm 158.51 (C4 or C8), 156.62 (C8 or C4), 125.69 (C3 + C7), 106.65 (C5), 95.53 (C4), 93.93 (C6), 52.80 (C9), 48.24 (C2), 42.64 (C10), 42.36 (C1), 42.22 (C13), 27.93 (C8), 25.08 (C12), 23.00 (C11).

(+)-Bis(η^5 -[*exo*-(1S,2S,9R,10R)-tetracyclo[8.2.1.0^{2,9}.0^{3,7}]trideca-3,6-dienyl]dichlorotitanium (18). To a slurry of titanium(III) chloride (438 mg, 2.81 mmol) in 80 mL of THF at -78°C was added a solution of **9** (1.00 g, 5.61 mmol) in 10 mL of THF via cannula. After the addition was complete, the mixture was stirred for 30 min at -78°C , allowed to warm to rt, heated to reflux for 48 h, cooled to 0 °C, and quenched with concentrated hydrochloric acid (40 mL) in air for 10 min. The mixture was poured into 100 mL of ether, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 \times 50 mL). The combined organic layers were washed with brine, dried, and concentrated to leave a brown residue. Toluene (7 mL) was added, and this solution was cooled to -20°C . Subsequently collected was 503 mg (39%) of **18** as a bright red crystalline powder: ^1H NMR (300 MHz, CDCl_3) δ 6.43 (s, 2 H), 5.96 (s, 2 H), 3.39 (dd, $J = 10.0, 5.0$ Hz, 2 H), 3.13 (br m, $J = 5.9$ Hz, 2 H), 2.91 (dd, $J = 13.4, 9.6$ Hz, 2 H), 2.57 (dd, $J = 17.7, 2.9$ Hz, 2 H), 2.42 (br s, 2 H), 2.24 (br s, 2 H), 1.59 (d, $J_{\text{AB}} = 9.4$ Hz, 2 H), 1.46 (d, $J_{\text{AB}} = 9.4$ Hz, 2 H), 1.28 (br m, 6

H), 0.81 (br m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) ppm 148.0, 147.7, 117.5, 112.6, 110.7, 50.9, 48.3, 41.3, 40.9, 40.5, 28.5, 24.8, 22.4; HRMS m/z (M^+) calcd 462.1192, obsd 462.1192; $[\alpha]_D^{20} +209.4^\circ$ (c 0.12, CHCl_3).

(-)-(η^5 -Cyclopentadienyl)(η^5 -[*exo*-(1S,2S,9R,10R)-tetracyclo[8.2.1.0^{2,9}.0^{3,7}]trideca-3,6-dienyl]dichlorotitanium (19). Cyclopentadienide **9** (190 mg, 1.07 mmol) was taken up in THF (20 mL) and added to a cold (-78°C) solution of cyclopentadienyltrichlorotitanium (234 mg, 1.07 mmol) in 20 mL of THF. The reaction mixture was stirred for 2 h at -78°C , 10 h at 25 °C, filtered, and concentrated to leave a black residue. This material was dissolved in toluene (5 mL) and cooled to -20°C . The crystals originally formed and collected consisted of a mixture of **19** and CpTiCl_3 . The mother liquors were concentrated further and allowed to crystallize. Thus obtained was 61 mg (16%) of **19**: mp 168°C dec; ^1H NMR (300 MHz, CDCl_3) δ 6.56 (s, 5 H), 6.29 (s, 2 H), 6.26 (s, 1 H), 5.87 (s, 1 H), 3.29 (d, $J = 3.7$ Hz, 1 H), 3.25 (m, 1H), 2.64 (dd, $J = 17.1, 8.6$ Hz, 1 H), 2.46 (br s, 1 H), 1.79 (t, $J = 9.8$ Hz, 1 H), 1.64 (br s, 2 H), 1.55 (br s, 1 H), 1.31 (d, $J = 6.7$ Hz, 1 H), 1.29 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) ppm 164.0, 120.2, 119.8, 119.5, 119.4, 118.5, 53.2, 50.6, 45.4, 40.0, 39.4, 28.0, 24.7, 23.3; HRMS m/z (M^+) calcd 356.0409, obsd 356.0414; $[\alpha]_D^{20} -575^\circ$ (c 0.04, CHCl_3).

Nuclear Magnetic Resonance Studies. All experiments involving organolithium compounds were carried out in flame-dried glassware under an atmosphere of dry argon. NMR spectra were recorded on a Bruker AM300 (300 MHz; Figure 1), a JEOL GX400 (400 MHz; Figure 2), and a JEOL Alpha500 (500 MHz; Figures 3 and 4) spectrometer, respectively. ^1H and ^{13}C NMR spectra were referenced to the solvent signals: $\delta = 3.58$ ppm (^1H , $\text{THF}-d_7$, α -H) and $\delta = 67.4$ ppm (^{13}C , $\text{THF}-d_6$, α -C). ^6Li -NMR spectra were referenced to 1 M LiBr in THF at appropriate temperatures.

^6Li , ^1H -HOESY (Figure 2): 5 mm tube in 10 mm multinuclear probehead, 0.55M **9** in $\text{THF}-d_6$, ^1H 90° pulse width 29 μs , ^6Li 90° pulse width 28 μs , spectral widths 1216 Hz (f_2 , ^6Li) and 2627 Hz (f_1 , ^1H), 512 complex data points in t_2 , zero filled to 1024, 128 increments in t_1 , zero filled to 256, 192 transients per t_1 -increment, mixing time 2.0 s, relaxation delay 4.0 s, experimental window in t_1 and t_2 , pure absorption presentation (States method for quad-detection in f_1).

^6Li , ^6Li -EXSY (Figures 3 and 4): 5 mm tunable probehead, 0.55M **9** in $\text{THF}-d_6$, 90° pulse width 12.8 μs , spectral width 1618 Hz in both dimensions, 2048 complex points in t_2 , zero filled to 4096, 106 increments in t_1 , zero filled to 512, 4 transients per t_1 increment, mixing period 5.0 s, relaxation delay 22.0 s, Gaussian window in t_1 and t_2 , pure absorption presentation (States method for quad-detection in f_1).

Computational Studies. MNDO calculations were carried out on a Silicon Graphics Indigo workstation by using the VAMP5 software package. No symmetry constraints were imposed. The lithium parameters were those provided by Thiel and Clark.²⁰

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