Oligomeric Chain Structures of Substituted (Dialkylaminomethyl)cyclopentadienyllithium Compounds: Structural Variations Characterized by Different Involvement of the Internal Amino Donor Ligands in the Solid State

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Treatment of 6-dimethylaminofulvene (**8**) with propynyllithium (**9a**) results in a clean nucleophilic addition at the electrophilic fulvene carbon atom C6 to yield the substituted lithium cyclopentadienide system $[C_5H_4CH(C{\equiv}CCH_3)N(CH_3)_2]Li$ (**10**). Likewise, the addition of *p*-tolyllithium, *n*-butyllithium, or phenyllithium resulted in the analogous substituted lithium cyclopentadienide systems $[C_5H_4CH(R)N(CH_3)_2]Li$, **11** (R = *p*-tolyl), **12** ($R = C_4H_9$), or **13** (R = Ph), respectively. These four Li−cyclopentadienide systems were characterized by single crystal X-ray structural analyses. This has revealed a series of gradually different oligomeric $[C_5H_4CH(R)N(CH_3)_2]Li$ structural aggregate types in the solid state. Compound **10** crystallizes with 1 equiv of THF that is coordinated to Li. The metal is η^5-coordinated to the Cp ligand and κN-bonded to the $-N(CH_3)_2$ substituent of the next ligand (Li−N 2.181(7) Å), thereby constructing an oligomeric chain of a (THF)Li(η^5-Cp)(L-κN) type. The compound **11** crystallizes without incorporation of solvent. Here the oligomeric chain is constructed by η^5-Cp coordination to lithium and again κN-bonding of the $-N(CH_3)_2$ donor of the adjacent ligand to the metal center. In the solvent-free system **11** the resulting Li−N linkage (2.032(5) Å) is much shorter than in **10**. In **12** a beginning coordination of the lithium atom to both its neighboring Cp rings is observed. A Li cation is η^5-coordinated to one face of the C_5H_4 ring system, whereas another lithium atom in the oligomeric chain structure is bonded in a η^2-fashion from the other face, assisted by κN-coordination of the attached dimethylamino substituent. Eventually, two very different coordination geometries around lithium are characteristic for the oligomeric chain structure of **13**: atom Li1 is rather symmetrically η^5-coordinated in a metallocene fashion to two cyclopentadienides, whereas the adjacent Li2 atom is coordinated to two $-N(CH_3)_2$ groups, assisted by a weaker η^2- to η^4-Cp coordination to the attached Cp ring systems. Supporting quantum chemical calculations have revealed rather shallow minima and easy conversions between these structural types. The $[C_5H_4CH(R)NR_2']^-$ ligand is thus suited to experimentally realize a whole family of novel oligomeric $(CpLi)_n$ structural types.

Introduction

Cyclopentadienyllithium compounds are valuable and extensively used reagents in organic and organometallic synthesis.[1,2] The structural features of such reagents have been explored to a considerable extent, e.g., using dynamic NMR spectroscopy in solution or X-ray diffraction in the solid state.[3] A variety of specific structural motifs have been revealed from these studies, identifying the essential structural types that seem to be involved in the structural chemistry of ^{R}CpLi species and related compounds.[4]

In principle, ^{R}Cp−lithium reagents seem to adopt structures under specific conditions that belong to five

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[‡] Performed the X-ray crystal structure analyses.

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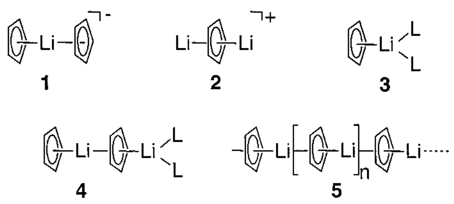
Scheme 1



different general types.[4,5] Two of them are charged, namely, the anionic sandwich compound [bis(cyclopentadienyl)lithium]$^-$ (**1**) and the cationic inverse sandwich [di(lithium)cyclopentadienide]$^+$ (**2**, see Scheme 1).[6] Both formally contain η^5-coordinated cyclopentadienide ligands, but due to the very high electrostatic component of the Cp−Li bond,[7] this situation is probably not electronically equivalent to the ubiquitous (η^5-Cp)M bonding situation in the organometallic chemistry of the d- and f-block elements. The addition of donor ligands L can lead to the stabilization of the ^{R}CpLi monomer in the form of, for example, the ligand-stabilized ^{R}CpLi(L)$_2$ species (**3**) and related arrangements.[8] Lower ^{R}CpLi/L ratios can result in the formation of dimetallic "super-sandwich" system, e.g., of the type [(^{R}Cp)Li(^{R}Cp)LiL$_2$] (**4**), several stable examples of which were isolated and structurally characterized.[9] Eventually, a limiting variation of this structural type is reached in the oligomeric (^{R}CpLi)$_n$ systems (**5**), linear or almost linear oligomeric or polymeric organometallic materials that contain strings of alternating μ-η:$^5\eta^5$- ^{R}Cp$^-$ units and intercalating Li$^+$ ions.[10,11]

Oligomeric systems, such as **5**, are of a great principal interest since they represent novel structural types of organometallic aggregates. Systems such as **5** are quite common in ^{R}Cp−sodium or −potassium chemistry[4] and increasingly also encountered and structurally characterized in organometallic ^{R}Cp−lithium chemistry.[10−12] We and others[13] have synthesized Cp anion equivalents that bear pendant substituents that contain a donor functionality. In the corresponding substituted Cp−lithium structural chemistry this will result in a competition of the two different ligand types, namely, the core cyclopentadienide anion and its pendant neutral donor ligand, about the lithium cation. We have prepared a variety of differently substituted [CpCR^{1}R^2-NMe$_2$]Li systems, crystallized them, and characterized their resulting oligomeric chain structures in the solid state by single-crystal X-ray analyses. This has revealed a varying degree of involvement of the −NMe$_2$ donor ligand in this structural competition situation, which is described in this article.

Results and Discussion

Formation of the (C$_5$H$_4$CR^{1}R^{2}NMe$_2$)Li Building Blocks. For this study we have employed a series of (*N*,*N*-dimethylaminomethyl)cyclopentadienyllithium systems [C$_5$H$_4$CHRNMe$_2$]$^-$Li$^+$ (**10**−**13**) that bear different substituents R at the "pseudo-benzylic" position directly adjacent to the cyclopentadienyl ring system. The variation of these substituents has caused small detailed alterations in the specific oligomeric chain structure exhibited by these complexes in the crystal. The synthetic scheme followed here was based on aminofulvene chemistry developed by K. Hafner et al.[14,15] Dimethylformamide was O-methylated by treatment with dimethyl sulfate under solvent-free conditions to generate the activated cationic reagent **6**. Subsequent addition of sodium cyclopentadienide (**7**) in THF gave 6-dimethylaminofulvene (**8**, 76% isolated). Compound **8** was then treated with a variety of organolithium reagents (**9a**−**d**) that all added cleanly to the positively polarized, "carbonyl-like" carbon atom C6 of the fulvene[16] to directly furnish the corresponding substituted lithium cyclopentadienide systems (**10**−**13**).

Addition of propynyllithium (**9a**) to the fulvene **8** in THF gave lithium (1-(dimethylamino)-2-butynyl)cyclo-

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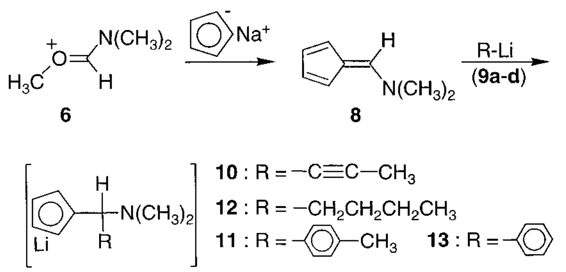
Scheme 2



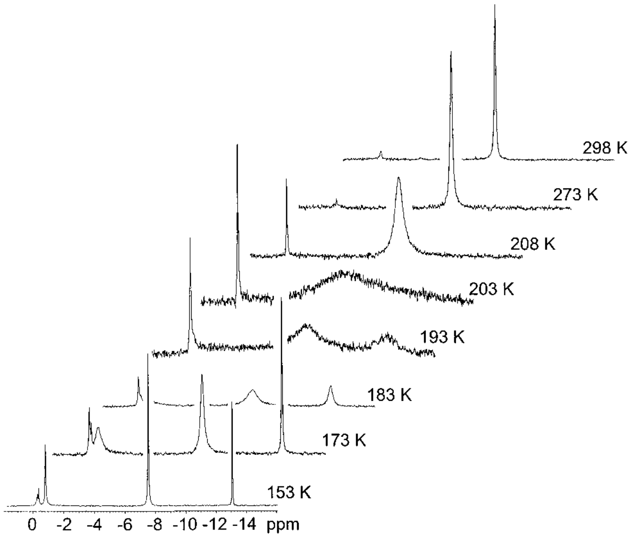
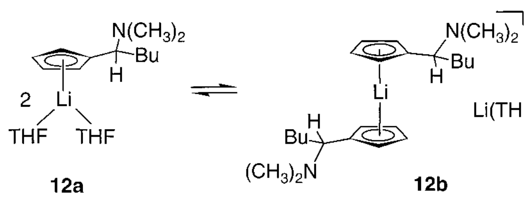


Figure 1. Temperature-dependent ^{7}Li NMR spectra of the equilibrating **12a**/**12b** pair of lithium cyclopentadienides (194 MHz, 1:1 THF/THF-d_8).

pentadienide (**10**), which was precipitated from the solution by the addition of pentane and isolated as a pale brown amorphous solid in 61% yield. The lithium complex **12** was prepared by addition of a pentane solution of *n*-butyllithium to **8** in THF. Removal of the solvent in vacuo in this case gave **12** as a viscous oil. This was eventually solidified by vigorous stirring with pentane to give **12** as an amorphous solid, isolated in 95% yield. The aryl-substituted analogues **11** and **13** were synthesized analogously by treatment of the fulvene **8** with 1 molar equiv of *p*-tolyllithium or phenyllithium, respectively, and isolated as amorphous solids in ≥90% yield after treatment with pentane (Scheme 2).

The lithium (aminomethyl)cyclopentadienides show dynamic temperature-dependent NMR spectra under suitable conditions.[3] The 1-(dimethylaminopentyl)cyclopentadienyllithium system **12** may serve as a typical example. In tetrahydrofuran solution it shows a single ^{7}Li NMR resonance (δ −8.0) at 298 K (Figure 1). Lowering the temperature rapidly results in broadening of this signal and splitting into a 1:1 pair of singlets at δ −0.8 and −13.0 (at 153 K) and a remaining singlet at δ −7.8. These three signals are found under these specific conditions in a 1:2:1 ratio. From a comparison with literature data it is clear that the large central signal belongs to a monomeric, THF-solvated [$C_5H_4CH(NMe_2)CH_2CH_2CH_2CH_3$]Li species (**12a**), and the remaining equal intensity pair of signals is due to the ligand disproportionated [$(C_5H_4CH/NMe_2)R)_2Li]^-/[Li(THF)_n]^n$ ion pair system (**12b**) (see Scheme 3). Consequently, only simple (ligand averaged) ^{1}H and ^{13}C NMR spectra are monitored of **12** at high temperature [δ 5.80, 5.92 (C_5H_4, ^{1}H), δ 102.5, 104.7 (*C*H), 117.5 (*C*) (C_5H_4, ^{13}C NMR)], whereas decoalescence is observed upon lowering the temperature, eventually giving rise to the much more complicated NMR spectra of the **12a**/**12b** mixture at low temperature (for details see the Experimental Section and the Supporting Information).

Scheme 3



The dynamic $2[C_5H_4CH(NMe_2)R]Li \rightleftharpoons [(C_5H_4CH(NMe_2)R)_2Li]^-/[Li(THF)_n]^+$ equilibrium is substituent and concentration dependent. Under typical conditions of the NMR measurement a **10a**:**10b** ratio of 14:1 (^{7}Li NMR signals at δ −0.4, −7.3, and −13.0 in a 1:14:1 ratio at 163 K) was found for the propynyl-substituted system, whereas only the monomer (i.e., **13a**) was found in the solution of the lithium [1-(dimethylaminobenzyl)cyclopentadienide] system **13** in solution at low temperature (^{7}Li NMR, 194 MHz, 153 K).

Oligomeric Structures of the Substituted Lithium [1-(Dimethylaminoalkyl)cyclopentadienides] in the Crystal. Single crystals suited for X-ray crystal structure analyses were obtained from the systems **11**−**13**, albeit under quite different conditions. In addition to the different steric demands introduced by the series of substituents R, these variations of the specific conditions of the crystallization processes resulted in the generation of a family of oligomeric [$(C_5H_4CH(NMe_2)R)Li]_n$-type structures that show a series of remarkable structural alterations.

Single crystals of **10** were obtained from a deuterated benzene/THF (1:1) mixture during 5 days at ambient temperature. The crystalline material contained 1 molar equiv of tetrahydrofuran coordinated to lithium (**10**·THF).

Complex **10** shows an oligomeric chain structure in the crystal. The lithium atom of each [$C_5H_4CH(NMe_2)C\equiv CCH_3$]Li subunit is η^5-coordinated to the Cp ring system. The Li−C(cyclopentadienide) distances are in a very close range between 2.302(7) (Li−C9) and 2.376(7) Å (Li−C12). The substituent at the Cp ring system (C4−C8 1.502(4) Å) contains a hydrogen atom at C4 and an unperturbed propynyl moiety (C2−C3 1.186(5) Å, dihedral angle C9−C8−C4−C3 −161.9(3)°) and a $-N(CH_3)_2$ group that is oriented away from the Cp face that is coordinated to the lithium atom (θ C9−C8−C4−N5 70.8(4)°). The coordination environment of the lithium atom is complemented by a single κ-O-coordinated tetrahydrofuran ligand (Li−O13 2.023(6) Å) and the nitrogen atom of the $-CHR-NMe_2$ substituent of the *next* $C_5H_4CHRNMe_2$ ligand (Li−N5$^\#$ 2.181(7) Å). The individual bonding angles at the central lithium atom are found at 123.6° (O13−Li−Cp(centroid)), 135.1° (N5$^\#$−Li−Cp(centroid)), and 97.8(3)° (O13−Li−N5$^\#$). The sum of these bonding angles (356.5°) indicates a close to trigonal planar coordination geometry at lithium. The separation between Li and the next Cp ring (C8$^\#$−

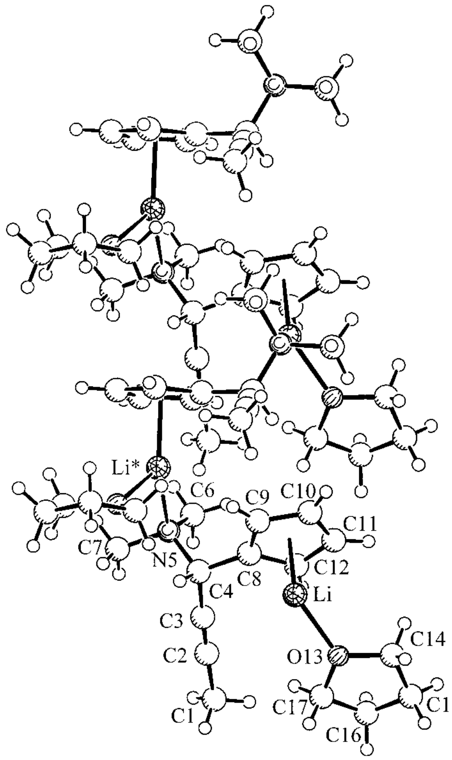


Figure 2. View of the oligomeric chain structure of **10** showing four identical independent units aggregated. Selected bond lengths (Å) and angles (deg): Li–C8 2.349(7), Li–C9 2.302(7), Li–C10 2.308(7), Li–C11 2.354(7), Li–C12 2.376(7), Li–N5 2.181(7), Li–O13 2.023(6), C1–C2 1.469(5), C2–C3 1.186(5), C3–C4 1.487(5), C4–N5 1.505(4), C4–C8 1.502(4), N5–C6 1.471(4), N5–C7 1.471(4); C1–C2–C3 177.6(4), C2–C3–C4 178.3(4), C3–C4–N5 112.3(3), C3–C4–C8 112.0(3), C4–N5–C6 111.3(3), C4–N5–C7 109.7(3), C6–N5–C7 109.2(3), C4–N5–Li 110.3(3), C6–N5–Li 111.0(3), C7–N5–Li 105.2(3), N5–Li–O13 97.8(3).

C12#) is beyond a significant bonding distance (3.108–5.041 Å). Therefore, the chain structure of **10** is to be regarded as a variant of the general ligand-stabilized neutral mononuclear CpLi(L)$_2$ structural type (**3**, see Scheme 1), except that one of the donor ligands, here the –NMe$_2$ group, is covalently attached to the next cyclopentadienide ring, which consequently results in the donor-ligand-connected oligomeric chain structure that is observed of compound **10** (Figure 2). Connecting the chiral subunits of **10** does not, however, just result in an oligomeric analogue of the structural type **3**, but has stereochemical consequences. Oligomerization of **10** in the crystal has resulted in a stereochemically regular "pseudo-isotactic" chain structure: the (R*)$_n$ diastereomeric associated chain structure is observed.[17]

Diffusion of pentane vapor into a solution of **11** in ether at room temperature furnished single crystals of the [C$_5$H$_4$CH(p-tolyl)NMe$_2$]Li compound that were used for the X-ray crystal structure analysis. The single crystals were donor ligand free; the ether solvent had not become incorporated into the eventually obtained crystalline material. Again, an oligomeric chain structure was observed. The coordination geometry around lithium in **11** is very similar to that found in **10**. We notice a close to (μ-κN:η^5-C$_5$H$_4$CH(R)NMe$_2$) coordination with five close Li1–C(21–25) contacts in the independent unit between 2.164(5) and 2.220(4) Å and a very short Li1–N2 bond of 2.032(5) Å. The lithium atom is only very weakly associated with the next Cp ring [Li1*–C21 3.154 Å, Li1*–C22 2.995 Å; the remaining Li1*–C(23–25) separations are even larger at 4.055, 4.707, and 4.263 Å]. The overall *configuration* at the oligomeric chain of **11** (Figure 3) is meso-like, similar to that found in the achiral relative **12** (see below), but the *conformational* arrangement of the (here: symmetry-equivalent) subunits of **11** along the chain is slightly different from that of **12** (the symmetry-equivalent units in **11** are interconverted by a screw axis combined with a glide plane operation).

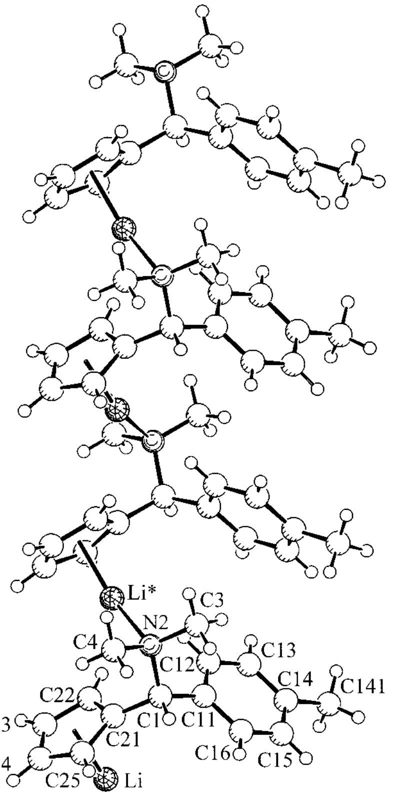


Figure 3. View of the oligomeric chain structure of **11** showing the μ-κN:η^5-coordination of the substituted Cp ligand. Selected bond lengths (Å) and angles (deg) of **11**: Li–C21 2.220(5), Li–C22 2.220(4), Li–C23 2.186(5), Li–C24 2.164(5), Li–C25 2.183(5), Li–N2 2.032(5), C1–N2 1.504(3), C1–C11 1.502(3), C1–C21 1.505(3), N2–C3 1.472(3), N2–C4 1.464(3); N2–C1–C11 112.1(2), N2–C1–C21 110.0(2), C11–C1–C21 112.1(2), Li–N2–C1 114.4(2), Li–N2–C3 115.6(2), Li–N2–C4 99.0(2), C1–N2–C3 110.7(2), C1–N2–C4 109.1(2), C3–N2–C4 107.0(2).

Keeping the oil that was primarily obtained from the synthesis of **12** (see above) for several weeks at ambient temperature (in an inert atmosphere) eventually resulted in the formation and recovery of clear crystalline plates that turned out to be single crystals suited for the X-ray crystal structure determination. This crystalline material also turned out to be solvent free, and it contained oligomeric chains of **12** in a meso, i.e., alternating (R*S*)$_n$, arrangement. Consequently pairs of connected adjacent independent molecular entities of **12** were found that were further connected in an

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[17] The crystal is racemic and contains equal amounts of the enantiomeric (R*)$_n$ and (S*)$_n$ chains.

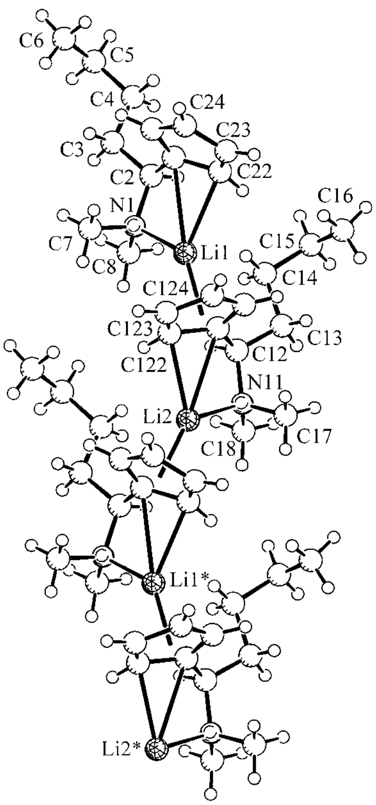

Figure 4. Asymmetric unit of **12**. Selected bond lengths (Å) and angles (deg): Li1−C121 2.300(4), Li2*−C21 2.294(4), Li1−C122 2.267(3), Li2*−C22 2.272(4), Li1−C123 2.242(4), Li2*−C23 2.241(4), Li1−C124 2.243(4), Li2*−C24 2.234(4), Li−C125 2.277(4), Li2*−C25 2.264(4), Li1−C21 2.710(3), Li2−C121 2.694(3), Li1−C22 2.486(4), Li2−C122 2.461(4), Li1−N1 2.106(4), Li2−N11 2.095(4), N1−C2 1.506(2), N11−C12 1.502(2), C2−C21 1.511(2), C12−C121 1.508(3), N1−C7 1.465(3), N11−C17 1.470(3), N1−C8 1.471(2), N11−C18 1.472(2), C2−C3 1.528(3), C12−C13 1.522(3); Li1−N1−C2 103.8(1), Li2−N11−C12 104.1(1), Li1−N1−C7 100.6(2), Li2−N11−C17 100.0(2), Li1−N1−C8 117.9(2), Li2−N11−C18 118.3(2), C2−N1−C7 112.2(2), C12−N11−C17 112.2(2), C2−N1−C8 111.6(2), C12−N11−C18 112.1(2), C7−N1−C8 110.1(2), C17−N11−C18 109.6(2), N1−C2−C21 107.7(1), N11−C12−C121 107.7(1), N1−C2−C3 114.4(2), N11−C12−C13 114.6(2), C3−C2−C21 114.2(2), C13−C12−C121 114.3(2).

analogous manner with symmetry-equivalent units to form the oligomeric chain structure.

In the crystal the lithium atom Li1 exhibits five close contacts to the cyclopentadienyl carbon atoms of the adjacent [C_5H_4CH(butyl)NMe_2] ligand (C121−C125) in the range 2.242(4)−2.300(4) Å. In addition to this η^5-C_5H_4−X coordination, lithium atom Li1 is connected strongly to the nitrogen atom of the other [C_5H_4CH(butyl)NMe_2] ligand (Li1−N1 2.106(4) Å); the crystallographically independent, but chemically equivalent Li2−N11 distance in **12** amounts to 2.095(4) Å (Figure 4). The remaining coordinative saturation of the lithium atom in **12** comes from an additional contact to the second Cp ring. This interaction is much less pronounced than with the first Cp ligand and much less symmetric. Lithium atom Li1 exhibits only two short contacts to the C21−C25 ring system, to which the strongly coordinating −N(1)Me_2 group is connected via C2. The strongest contact exists between Li1 and C22 (2.486(4) Å) and Li1 and the adjacent ring atom C21 (2.710(3) Å). The remaining Li1−C(23−25) separations are much larger (3.377(4), 3.959(4), 3.635(4) Å) and probably insignificant with regard to stabilizing the Li center in **12**. Thus, to a first approximation the oligomeric chain structure contains [κN-μ-η^2:η^5-C_5H_4CH(butyl)NMe_2] ligands that connect the individual lithium atoms in **12**. In some respect, the structural arrangements found for **12** (and **11**) in the crystal seem to represent an intermediate stage in a range of possible transition structures between a donor-stabilized ^{R}CpLi(L_2) type (such as **3** or **10**) and the symmetrical oligomeric supersandwich (**5**).[18] Consequently, the chain structure of **12** deviated markedly from linearity with Cp(centroid C(21−25))−Li1−Cp(centroid C(121−C125)) amounting to 139.7° and Li1−Cp(centroid C(121−125))−Li2 being 137.5°.

Single crystals of **13** were grown from the neat oil of this organolithium compound at −30 °C. The compound is obtained free of external donor ligands. The structure of **13** is again oligomeric, but distinctly different from those reported above. Two independent [C_5H_4CH(Ph)NMe_2)Li units are found in the asymmetric unit, which are aggregated to form an oligomeric supersandwich-type supramolecular structural arrangement. The angles of the Cp planes within the asymmetric unit and between the asymmetric units inside the chain structure amount to 8.9° (C8−C12/C28−32), 8.9° (C8−C12/C28$^\#$−C32$^\#$), 0.0° (C28−C32/C28$^\#$−C32$^\#$), and 0.0° (C8−C12/C8$^\#$−C12$^\#$). The individual lithium atoms are intercalated between these planes, but in structurally different ways. The metal atom Li1 is almost symmetrically η^5-coordinated to two cyclopentadienides. The Li1−C(8−12) distances are found in a very close range between 2.29(2) and 2.37(2) Å, and the Li1−C(28−32) bond lengths are in the same overall range between 2.27(2) and 2.32(1) Å. The other lithium atom (Li2) is located between the next pair of Cp ligands [C28−C32 and C8$^\#$−C12$^\#$], but this lithium atom is also strongly bonded to a pair of −NMe_2 nitrogen atoms that belong to these two C_5H_4CH(Ph)NMe_2 ligands. The corresponding metal−nitrogen distances amount to 2.20(2) (Li2−N2) and 2.62(2) Å (Li2−N1). Both interactions are probably weaker than the Li−N bonds in the other members (i.e., **10**−**12**) of this structural series, but they are strong enough to pull the lithium atom considerably out of the idealized collinear supersandwich arrangement (see Figure 5, resulting in angles Li1−Cp[centroid C(28−32)]−Li2 of 150.2° and Cp[centroid C(28−32)]−Li2−Cp[centroid C(8$^\#$−12$^\#$)] of 126.2°.

Consequently, this coordinative shifting of the lithium atom Li2 from the central supersandwich vector weakens the corresponding Cp(28−32)−Li and Cp(8$^\#$−12$^\#$)−Li bonding. The latter interaction is governed by only two short contacts (Li2−C8$^\#$ 2.26(2), Li2−C12$^\#$ 2.30(2) Å), whereas three metal−carbon separations within this subunit are markedly longer (Li2−C9$^\#$ 2.57(2), Li2−C10$^\#$ 2.79(2), Li2−C11$^\#$ 2.64(2) Å). This characteristic distortion is even more pronounced for the Li2−C(28−32) interaction, which is influenced by the markedly stronger Li2−N1 (vs Li2−N2) interaction. Consequently, only two reasonably short Li2−C28 (2.32(2) Å) and Li2−C32 (2.49(2) Å) contacts are found, whereas

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[18] The terminal ethyl groups of the *n*-butyl substituents in **12** are disordered, but the core structural units are not affected.

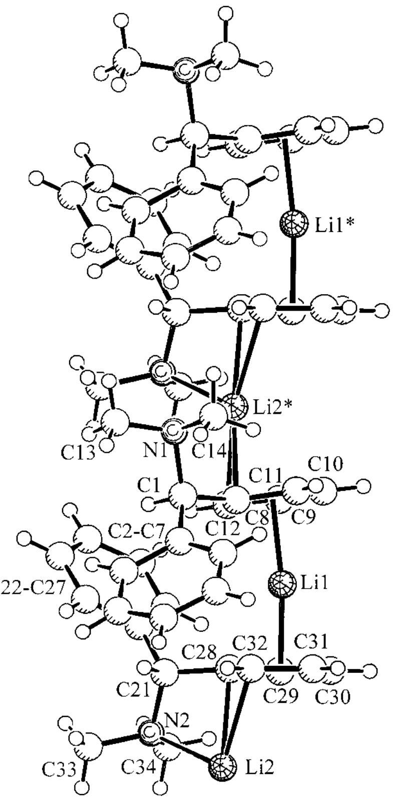

Figure 5. Side views of the distorted supersandwich structure of **13**. Selected bond lengths (Å) and angles (deg): Li1−C8 2.33(1), Li1−C28 2.30(1), Li1−C9 2.37(2), Li1−C29 2.32(1), Li1−C10 2.35(2), Li1−C30 2.29(2), Li1−C11 2.31(1), Li1−C31 2.27(2), Li1−C12 2.29(2), Li1−C32 2.28(1), Li2−C8* 2.26(2), Li2−C28 2.32(2), Li2−C12* 2.30(2), Li2−C32 2.49(2), Li2−N2 2.20(2), Li2−N1* 2.62(2), N1−C1 1.54(1), N2−C21 1.48(1), C1−C8 1.52(1), C21−C28 1.51(1), N1−C13 1.41(1), N2−C33 1.46(1), N1−C14 1.42(1), N2−C34 1.46(1); Li2*−N1−C1 84.4(6), Li2−N2−C21 90.8(6), Li2*−N1−C13 133.3(7), Li2−N2−C33 125.3(8), Li2*−N1−C14 103.5(6), Li2−N2−C34 106.4(8), C1−N1−C13 109.8(7), C21−N2−C33 112.0(6), C1−N1−C14 111.7(7), C21−N2−C34 114.6(6), C13−N1−C14 110.9(7), C33−N2−C134 107.4(6), N1−C1−C8 109.1(6), N2−C21−C28 108.8(6).

the remaining Li2−C29 (2.91(2) Å), Li2−C30 (3.36(2) Å), and Li2−C31 (3.14(2) Å) separations are markedly larger.

It is evident from these data that the structure of **13** is unique in that sense that it contains in some form most of the general ^{R}CpLi structural elements that are depicted in Scheme 1, namely, the ^{R}Cp−Li−^{R}Cp linear metallocene substructure, the ^{R}Cp−Li−^{R}Cp−Li(L)$_n$ substructure, and (in a distorted form) the polymeric supersandwich arrangement. The observed chain structure of **13** actually is stereochemically characterized as the chiral (R*,R*)$_n$ (isotactic) diastereomer, but the overall arrangement in the crystal is achiral; that is, a racemic mixture of the enantiomeric chain structures is present.

Computational Analysis Using Model Systems. To elucidate the bonding situation in these lithium cyclopentadienide oligomers further, we have investigated such systems by quantum chemical calculations using the PM3 algorithm for monomers, dimers, and trimers and the DFT method B3LYP/6-31G*//B3LYP/6-31G* for the monomers. Previous work from our laboratory[12a] has convincingly shown that PM3 including the lithium parameters developed by Anders et al. is a very suitable tool for the analysis of such lithium cyclopentadienides.[19,20] The MOPAC93 program[21] and GAUSSIAN98[22] were used throughout.

The study was performed on three levels of structural complexity. First, monomeric subunits of the chains were calculated to get information on the unperturbed bonding parameters around lithium. Second, parts of the crystallographically characterized chains containing two or three monomers were taken as starting geometries for the structural simulation in the gas phase. Third, the trimeric structures obtained were taken as models for general ensembles of monomers; thus, by replacing of the individual substituents by simple methyl groups, an energetic and structural comparison of the experimentally observed structural types in the lattice for the gas phase was undertaken.

The oligomeric structure of compound **10** is different from **11**−**13** with regard to the extra molecule of THF, which coordinates to lithium within the chain. Due to this extra coordination, **10** is relatively saturated with respect to coordination. This is easily seen in the calculated structure of the monomer, which is dominated by η^5-coordination to Cp and the Li-oxygen interaction to THF. In the best calculated structure there is no intramolecular bonding interaction to the amino group within the molecule, probably because a coordination to nitrogen would decrease the bonding to Cp due to strain within the forming chelate. Hence, the coordination site of the amino group is for energetic reasons not used for coordination within a molecule but as an additional donor group to the next monomer. This type of coordination avoids steric strain, allows for optimal Li−Cp interaction, and helps to build up the observed polymeric chain structure.

Different from the experimentally observed structure (η^5-Cp/κO/κN′), the PM3 structure shows (η^2-Cp/κO/κN′) coordination around lithium, indicating a balanced donor situation with decreased Cp−Li interaction. In the X-ray crystal structure analysis of **10**, relatively long C−Li distances (2.302−2.376 Å) are indicative of the weakening of this interaction. Furthermore, the calculationally optimized structure is by far not as well organized as the one in the crystalline phase, reflecting the additional conformational freedom of this isolated trimer in the gas phase.

The calculated structures of compounds **11** and **12** show structural features similar to **10**: however, the lacking additional THF donor group leads to a closer connection of the individual monomers with each other.

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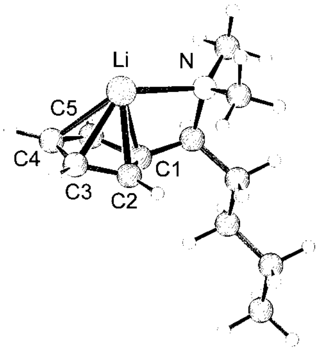

Figure 6. Calculated molecular structure of monomeric **12** (B3LYP/6-31G*//B3LYP/6-31G*). Distances to Li: Li−N 2.2662 Å, Li−C1 2.0545 Å, Li−C2 2.1520 Å, Li−C3 2.2651 Å, Li−C4 2.456 Å, Li−C5 2.1151 Å.

The monomers of **11**, **12**, and **13** each show five short lithium contacts to Cp and an additional weak interaction with N. According to B3LYP/6-31G* calculations this additional contact to nitrogen lowers the energy of the system only by ca. 2 kcal/mol, as calculated for two conformers with a syn- and an anti-positioned amino group with respect to the lithium cation. Again, the contact to nitrogen weakens the interaction to the Cp ring, as is seen from the C−Li bond distances. In contrast, PM3 prefers the isomer without Li−N contact by 0.6 kcal/mol and finds even better minima with Li−H_3C−N contact, probably an artifact of the method.

Several dimers and trimers of **11**, **12**, and **13** have been studied computationally. They result from rotamers with regard to the Cp units with and without Li−N contacts. In general, PM3 finds minima of lower energy for structures with intense Cp−Li interaction (η^5-Cp−Li−η^5-Cp) compared to structures that involve Li−nitrogen contacts simultaneous with η^2- or η^3-coordination to Cp. Thus, for the gas phase, diverse structural behavior is predicted from the calculations. The absence of crystal lattice forces allows the formation of structures with many Cp−Li interactions, sometimes with additional coordination to nitrogen. All the trimeric structures are highly twisted with respect to the lithium atom alignment, thus using the conformational freedom offered by the gas phase. In the crystal however, the formation of long polymeric structures leads to a high degree of order, where Cp units and the nitrogen donor atoms all contribute to lithium coordination, resulting in the experimentally observed four types of crystal structures. As anticipated, the absence of crystal forces leads to a huge number of rotamers and other isomers of the oligomers; structural preferences of the computational models (PM3 and B3LYP/6-31G*) also contribute to the structural diversity. As a result, all three types of structures **11**−**13** fall into a very narrow energetic range (<2 kcal/mol) if one compares the calculated heat of formations of trimeric model compounds that carry methyl groups instead of the tolyl (**11**), butyl (**12**), or phenyl (**13**) groups independent of their respective conformational and configurational properties.

Conclusions

The four $[C_5H_4CH(R)N(CH_3)_2]Li$ examples all exhibit polymeric chain structures in the solid state, and all four are structurally different. In all the examples of this structural family the Cp ring system and its attached $-CHRN(CH_3)_2$ substituent are used as active ligands for constructing the polymeric $(LiCpX)_n$-type chain structure. In each case the Cp ring is η^5-coordinated to a lithium atom and the $-N(CH_3)_2$ nitrogen donor ligand is used to make up a connection to the next lithium atom. The structures vary from one another by the relative coordination symmetry and the gradual change in the involvement of the second Li atom to coordinate the Cp ring from the other face. The quantum chemical calculations have revealed that the resulting changes in energy are minute and that it is expected that these structural types are easily interconverted, and, hence, their actual presence may be determined by crystal packing forces and/or small steric substituent effects. In **10** the additional Li coordination from the second face is totally absent. This system must actually be regarded as a variation of an ordinary $CpLi(L)_2$ example, whose oligomeric nature merely results from the covalent attachment of one of the donor ligands to the Cp ring. Complex **11** is principally of the same type, but here the ensuing Li−N interaction inside the oligomeric chain appears to be much stronger. Complex **12** already resembles a $(CpLi)_n$-type supersandwich structure, except that the nitrogen donor ligand seems to compete with its own Cp system about the Li atom, which results in a "mixed" η^2-Cp/κN coordinative situation. Eventually, compound **13** comes close to an oligomeric $(CpLi)_n$ supersandwich, but here the attached pendant $-CH(R)N(CH_3)_2$ donors pairwise act together to pull a lithium atom from the center line toward the side, but without completely interrupting the Li−Cp interaction: residual η^2-Cp to η^4-Cp bonding is observed. The other crystallographically independent Li atom in **13** resides between two Cp rings in a sandwich (η^5-Cp−Li−η^5-Cp) arrangement. This diversity of chemically related structures demonstrates that an individual location of a specific structural subtype within a large family of energetically similar coordination types of oligomeric $(^{R}CpLi)_n$ systems can be realized by attaching a $-N(CH_3)_2$ donor ligand by a one-carbon (sp^3-CHR) linker and thus make such structural variants experimentally observable in the crystal.

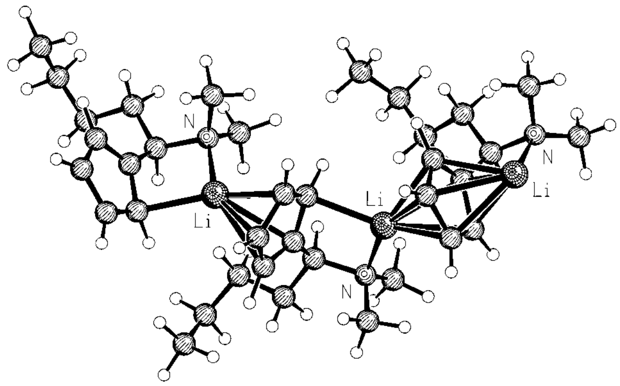

Figure 7. Calculated molecular structure of trimeric **12** (PM3).

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. NMR spectra were measured using a Bruker AC 200 P, Bruker ARX 300, or Varian Unity Plus 600 NMR spectrometer ($\Xi(^{13}C) = 25.14$, $(^{7}Li) = 38.86$ MHz). Most assignments were based on a series of 2D NMR experiments. (6-Dimethylamino)fulvene (**8**) was prepared analogously as described by K. Hafner et al.[14] Propynyllithium was prepared by treatment of propyne with *n*-butyllithium in liquid ammonia according to a literature procedure.[23]

Preparation of Lithium (1-(Dimethylamino)-2-butynyl)cyclopentadienide (10). A solution of 1.32 g (10.9 mmol) of 6-(dimethylamino)fulvene (**8**) in 100 mL of tetrahydrofuran was added dropwise to a suspension of 500 mg (10.9 mmol) of propynyllithium in 50 mL of THF at room temperature. The mixture was stirred for 2 days at ambient temperature. The solvent was then removed in vacuo. Pentane (100 mL) was added and the mixture stirred for a day to solidify the product. The resulting solid (**10**) was collected by filtration, washed with pentane (30 mL), and dried in vacuo to yield 1.1 g (61%) of **10** as a pale brown powder. ^{1}H NMR (599.9 MHz, benzene-d_6/THF-d_8 1:1): δ 6.12 (m, 2H, C_5H_4, α-C*H)*, 5.98 (m, 2H, C_5H_4, *β*-C*H*), 4.65 (m, 1H, C*H*[N]), 2.33 (s, 6H, $N(CH_3)_2$), 1.70 (s, 3H, $-C{\equiv}C-CH_3$). ^{13}C NMR (150.8 MHz, benzene-d_6/THF-d_8 1:1): δ 117.9 (C_5H_4, ipso-C), 104.4 (C_5H_4, α-*C*H), 102.8 (C_5H_4, *β*-*C*H), 79.7, 78.4 ($-C{\equiv}C-$Me), 58.8 ($-C$H[N]), 41.7 (N(CH$_3$)$_2$), 3.3 ($C{\equiv}C-CH_3$). ^{7}Li NMR (77.8 MHz, THF-d_8, 300 K): δ −7.5 (s), (163 K): −0.4 (br), −7.3 (br s), −13.0 (br, rel int 1:14:1).

X-ray Crystal Structure Analysis of 10. Single crystals were obtained from a benzene-d_6/THF-d_8 (1:1) solution after 5 days at ambient temperature: formula $C_{15}H_{22}NOLi$, $M = 239.28$, yellow crystal 0.35 × 0.15 × 0.10 mm, $a = 9.512(2)$, $b = 7.519(1)$, $c = 20.443(5)$ Å, $\beta = 103.23(2)°$, $V = 1423.3(5)$ Å^3, $\rho_{calc} = 1.117$ g cm^{-3}, $\mu = 5.19$ cm^{-1}, no absorption correction ($0.839 \le T \le 0.950$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 1998 reflections collected ($\pm h, +k, -l$), $[(\sin\theta)/\lambda] = 0.55$ Å^{-1}, 1936 independent ($R_{int} = 0.065$) and 1444 observed reflections [$I \ge 2\sigma(I)$], 167 refined parameters, $R = 0.072$, $wR_2 = 0.207$, max. residual electron density 0.40 (−0.27) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Lithium (1-Dimethylaminopentyl)cyclopentadienide (11). A 26.1 mL sample of a 1.6 M solution of *n*-butyllithium in pentane (41.8 mmol) was added dropwise at −40°C to a solution of 5.05 g (41.7 mmol) of 6-(dimethylamino)fulvene (**8**) in 40 mL of THF. The mixture was allowed to slowly warm to room temperature and then stirred overnight. Solvent was removed in vacuo to give a dark brown viscous oil. Addition of 100 mL of pentane followed by stirring for several hours gave **8** as a pale brown solid. The solvent was decanted off and the product dried in vacuo to yield 7.33 g (95%) of **11**. ^{1}H NMR (200 MHz, benzene-d_6/THF-d_8 3:1): δ 5.92, 5.80 (m, each 2H, C_5H_4), 3.52 (m, 1H, C*H*[N]), 2.18 (s, 6H, $N(CH_3)_2$), 1.92, 1.68, 1.43 (m, each 2H), 0.89 (t, 3H, *n*-butyl). ^{13}C NMR (75.5 MHz, benzene-d_6/THF-d_8 3:1): δ 117.5 (ipso-C of C_5H_4), 104.7, 102.5 (CH of C_5H_4), 65.4 (CH[N]), 41.7 (N(CH$_3$)$_2$), 34.0, 31.0, 23.2 (CH_2 of *n*-butyl), 14.7 (CH_3 of *n*-butyl). ^{7}Li NMR (THF/THF-d_8 1:1, 313 K): δ −8.0 (s) (153 K), −0.8 (s), −7.8 (s), −13.0 (s, rel int 1:2:1).

X-ray Crystal Structure Analysis of 11. Single crystals were grown from the oil of the product **8** during several weeks in the form of large colorless plates: formula $C_{15}H_{18}NLi$, $M = 219.24$, yellow crystal 0.35 × 0.15 × 0.10 mm, $a = 10.232(1)$, $b = 13.373(3)$, $c = 10.025(1)$ Å, $\beta = 109.04(1)°$, $V = 1296.7(3)$ Å^3, $\rho_{calc} = 1.123$ g cm^{-3}, $\mu = 4.75$ cm^{-1}, empirical absorption correction via ψ scan data ($0.851 \le T \le 0.954$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 2809 reflections collected ($+h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2663 independent ($R_{int} = 0.079$) and 1406 observed reflections [$I \ge 2\sigma(I)$], 157 refined parameters, $R = 0.055$, $wR_2 = 0.137$, max. residual electron density 0.24 (−0.23) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Lithium (Dimethylamino-*p*-tolylmethyl)cyclopentadienide (12). 6-(Dimethylamino)fulvene (**8**, 2.0 g, 16.5 mmol) were suspended in 50 mL of ether. At −40 °C a solution of 1.62 g (16.5 mmol) of *p*-tolyllithium in 50 mL of ether was added. The mixture was warmed to room temperature and then stirred overnight. Solvent was then removed in vacuo. The resulting oil was solidified by stirring with 50 mL of pentane to give the product **12** as a yellow solid (3.25 g, 90% yield). ^{1}H NMR (599.8 MHz, THF-d_8, 298 K): δ 7.39, 6.99 (AA′XX′, ^{3}J = 7.8 Hz, 4H, *p*-tolyl), 5.63, 5.55 (m, each 2H, C_5H_4), 3.87 (s, 1H, CH[N]), 2.24 (s, 3H, *p*-tolyl CH_3), 2.02 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (150.7 MHz, THF-d_8, 298 K): δ 147.2, 134.9 (ipso-C of *p*-tolyl), 129.1, 128.4 (o-, m-CH of *p*-tolyl), 122.8 (ipso-C of C_5H_4), 104.0, 102.6 (CH of C_5H_4), 74.8 (CH[N]), 45.3 ($N(CH_3)_2$), 21.0 (p-tolyl CH_3). ^{7}Li NMR (233.18 MHz, THF-d_8, 298 K): δ −7.5 (br).

X-ray Crystal Structure Analysis of 12. Single crystals were obtained by diffraction of pentane into a saturated solution of **12** in diethyl ether at ambient temperature: formula $C_{12}H_{20}NLi$, $M = 185.23$, yellow crystal 0.30 × 0.30 × 0.10 mm, $a = 9.226(1)$, $b = 18.413(4)$, $c = 14.370(2)$ Å, $\beta = 101.45(1)°$, $V = 2392.6(7)$ Å^3, $\rho_{calc} = 1.028$ g cm^{-3}, $\mu = 4.25$ cm^{-1}, empirical absorption correction via ψ scan data ($0.974 \le C \le 0.999$), $Z = 8$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4235 reflections collected ($\pm h, +k, -l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 4064 independent ($R_{int} = 0.037$) and 2973 observed reflections [$I \ge 2\sigma(I)$], 300 refined parameters, $R = 0.052$, $wR_2 = 0.147$, max. residual electron density 0.22 (−0.24) e Å^{-3}, disorder at C6 (0.72(1):0.28(1)) and in the group C14, C15, and C16 (0.55(1):0.45(1)), refined with split positions, hydrogens calculated and refined as riding atoms.

Preparation of Lithium (1-Dimethylaminobenzyl)cyclopentadienide (13). A 56.6 mL sample of a 0.99 M solution of phenyllithium in diethyl ether (56.6 mmol) was added dropwise at −40°C with stirring to a suspension of 6.85 g (56.5 mmol) of the fulvene **8** in 60 mL of ether. The mixture was warmed to room temperature and then stirred overnight. Solvent was removed from the resulting dark violet solution in vacuo to give a sticky oil, which was solidified by stirring with pentane (100 mL) during 12 h. The solvent was decanted off and the residue dried in vacuo to yield 10.7 g (92%) of **13**. ^{1}H NMR (benzene-d_6/THF-d_8 3:1): δ 7.69 (m, 2H), 7.12 (m, 2H), 6.96 (m, 1H, Ph), 6.09 (br s, 4H, C_5H_4), 4.20 (s, 1H, CH[N]), 2.34 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (benzene-d_6, THF-d_8 3:1): δ 150.2 (ipso-C of Ph), 128.4, 128.1, 125.4 (Ph), 123.0 (ipso-C of C_5H_4), 103.9, 102.9 (CH of C_5H_4), 74.8 (CH), 45.3 ($N(CH_3)_2$). ^{7}Li NMR (THF/THF-d_8 1:1, 153 K): δ −7.92.

X-ray Crystal Structure Analysis of 13. Large needlelike single crystals crystallized during several weeks from the oil of **13**: formula $C_{14}H_{16}NLi$, $M = 205.22$, orange crystal 0.30 × 0.15 × 0.10 mm, $a = 8.254(4)$, $b = 18.961(4)$, $c = 15.376(5)$ Å, $\beta = 94.23(4)°$, $V = 2400(2)$ Å^3, $\rho_{calc} = 1.136$ g cm^{-3}, $\mu = 4.83$ cm^{-1}, no absorption correction ($0.982 \le T \le 0.999$), $Z = 8$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3250 reflections collected ($+h, -k, \pm l$), $[(\sin\theta)/\lambda] = 0.53$ Å^{-1}, 3003 independent ($R_{int} = 0.064$) and 1239 observed reflections [$I \ge 2\sigma(I)$], 293 refined parameters, $R = 0.083$, $wR_2 = 0.199$, max. residual electron density 0.68 (−0.27) e Å^{-3}, thermal parameters of Li2 indicate disorder, not refined, hydrogens calculated and refined as riding atoms.

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(23) Jäger, V.; Viehe, H. G. *Houben-Weyl: Methoden der Organischen Chemie*; Thieme: Stuttgart, 1977; p 4. Auflage, Vol. 5/2a, pp 123−124, 351−367, 391.

Data sets were collected with Enraf-Nonius CAD4 diffractometers, equipped with sealed tube generators. Programs used: data collection EXPRESS (Nonius B.V., 1994), datareduction MolEN (K. Fair, Enraf-Nonius B.V., 1990), structure solution SHELXS-86 and SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-93 and SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics SCHAKAL (Keller, E. Unversität Freiburg, 1997) and DIAMOND (Brandenburg, K. Universität Bonn, 1997).

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Supporting Information Available: Details of the X-ray crystal structure analyses and the quantum chemical calculations, including MOPAC93 and GAUSSIAN98 archive entries. This material is available free of charge via the Internet at http://pubs.acs.org.

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