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Reviews

Functionalized Alkali Metal Cyclopentadienides: Structural and Chemical Features[†]

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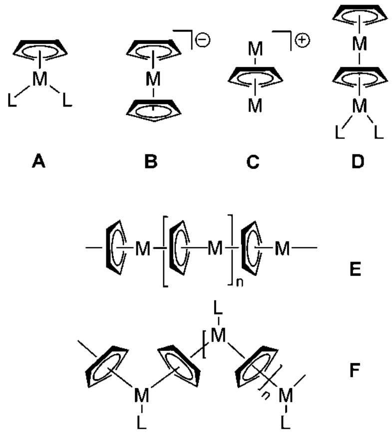
Synthetic routes to alkali metal cyclopentadienides that bear various organic functional groups on their five-membered carbocyclic ring systems are presented and discussed using selected examples. These include carbonyl addition reactions of cyclopentadienides to, for example, alkyl isocyanates to eventually yield carboxamide-substituted cyclopentadienide systems. These and related routes have been used to, for example, prepare peptide-substituted Cp anions. Fulvene routes are very useful for the synthesis of alkenylcyclopentadienides, of imino-Cp compounds, of aminomethyl- or phosphinomethyl-Cp derivatives, and even their respective dianionic analogues. Many of the new functionalized lithium cyclopentadienide examples were structurally characterized. Many of them form well-defined extended oligomeric structures that make specific use of the functional groups in the construction of the supramolecular complex framework. Eventually, first examples of specific carbon−carbon coupling reactions are presented and discussed that take place at the active lithium cyclopentadienide stage, which may lead to the development of a selective functional group chemistry at the alkali metal cyclopentadienides.

Introduction

The alkali metal cyclopentadienides feature a remarkable structural diversity. Their structures range from donor ligand stabilized neutral monomers (**A**) to charged metallocene anions (**B**) or cationic "inversed sandwich" structures (**C**), and eventually to supersandwich (**D**) or multinuclear sandwich oligomers or polymers (**E**, **F**).[1,2] It is probably the pronounced electrostatic nature of the alkali metal/cyclopentadienide interaction that makes such a structural variability energetically attractive.[3] Coulombic interaction seems to govern the structural and also the chemical properties of these classes of often very reactive organometallic compounds to a large extent.[4]

Chart 1



The alkali metal cyclopentadienides are mostly used as reagents in organometallic synthesis. There is an increasing demand for specifically functionalized d- and f-metal Cp−X complexes that bear a variety of functional groups at their Cp rings. In many cases such substituents cannot be attached at the stage of the readily assembled transition metal complex framework because of a lack of suitable synthetic methods. In many cases of sensitive (Cp−X) d- or f-metal compounds it is even difficult to carry out selective chemical functional group conversions at the Cp periphery because of the incompatibility of such systems with typical reaction conditions of organic

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[†] Dedicated to Professor Klaus Hafner on the occasion of his 80th birthday.

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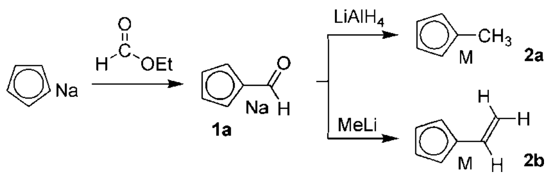
Scheme 1

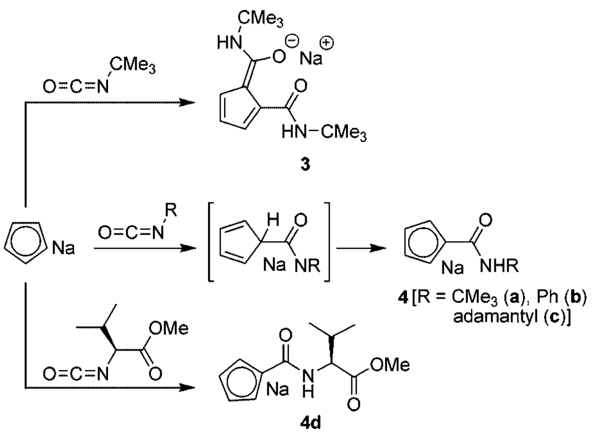


chemistry.[5,6] Therefore, in many cases suitable and desired functional groups must necessarily be introduced at the ligand stage. The resulting ring-substituted alkali metal cyclopentadienides then are employed in the final transmetalation step. This poses a variety of problems and questions regarding the availability of alkali metal cyclopentadienides that bear various organic functional groups at the Cp framework, their stability, and their handling, and also the influence and potential determination of the structural and chemical features of the alkali metal CpX systems by their substituents. In this account we wish to highlight some of these topics, mostly using examples from our own experimental work, and try to deduce some principles that may govern the structural assembly of functionalized alkali metal cyclopentadienides, and consequently determine some of their essential chemical features.

Syntheses. Functionalized cyclopentadienides can be prepared by a variety of methods. Quite recently, metal-catalyzed cross-coupling followed by deprotonation has become of some importance.[7] However, the majority of examples seem to have been prepared by variants of either of two methods, namely, by carbonyl addition or via fulvene routes. We will illustrate this by selected examples.

(a) Carbonyl Addition Routes. Rausch et al. have introduced a very useful method for attaching carbonyl functionalities to the cyclopentadienide core.[5] Typically, an alkali metal cyclopentadienide is reacted with an ester under carefully controlled conditions to yield the respective monofunctionalized product. Treatment of, for example, NaCp with ethyl formate gave formylcyclopentadienide (**1a**), whereas Na[Cp-CO$_2$R] was derived from the analogous reaction of diethyl carbonate. Some of these systems are very useful reagents for transmetalation. However, further derivatization sometimes met with difficulties. Thus, treatment of sodium formylcyclopentadienide (**1a**) with LiAlH$_4$ or methyllithium gave rise to the unexpected formation of the product **2a** (full reduction) or **2b** (partial reduction) (see Scheme 1), respectively.[8] Therefore, advanced methods of carbonyl addition were sought. These were found useful in this chemistry.

Scheme 2



Treatment of NaCp with *tert*-butylisocyanate resulted in the rapid attachment of a pair of carboxamide groups to yield the fulvenoid system (**3**),[9,10] which was successfully transmetalated to early transition metals as a κO,O′-chelate ligand (Zr).[9] At late transition metals (Ru, Fe) it served as a doubly CONHR-functionalized η^5-Cp-ligand.[11] The reaction can be stopped in some cases at the stage of the 1:1 addition product (**4**). The respective [Cp-CONHR]Na reagent (**4a**, R = CMe$_3$; **4b**, R = Ph; **4c**, R = adamantyl) was transmetalated by reaction with CpTiCl$_3$ to give the respective titanocene complex that featured the η^5-Cp-CONHR ligand.[12]

Similar reactions were carried out with isocyanates derived from amino acids or small peptides. The addition of sodium cyclopentadienide to the $O{=}C{=}N{-}R$ function in this case opened a very favorable way to amino acid- or peptide-functionalized Cp derivates (e.g., **4d**), some of which were used for the synthesis of the corresponding functionalized ferrocene derivates (see Scheme 2).[12]

From peptide chemistry we adapted a method to attach amino acid-derived functional substituents at cyclopentadienides. Hydroxybenztriazole-activated N-protected amino acids (**6**) [e.g., derived from *N*,*N*-dibenzylalanin (**5a**) or *Z*-protected proline (**5b**), see Scheme 3] were simply reacted with a cyclopentadienide carbon nucleophile to directly yield the respective amino acid C-functionalized cyclopentadienide reagents (**7**), which were successfully employed in the syntheses of the respective ferrocene or ruthenocene derivatives.[13]

Fluorenyllithium (**8**) adds to *tert*-butylisocyanate to yield the 9-carboxamido derivate **9**, which was subsequently reduced to **10**. Its treatment with strong base under various specific reaction conditions resulted in the formation of an interesting array of functionalized fluorenyllithium derivates.[14] A major pathway

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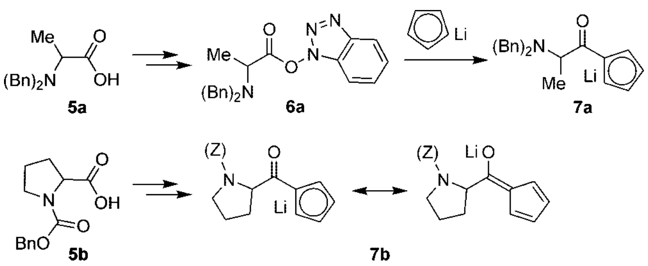
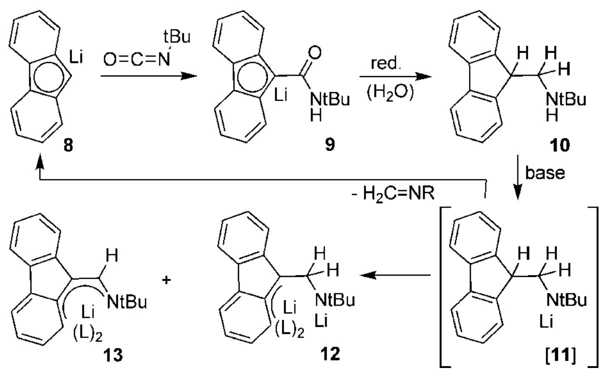
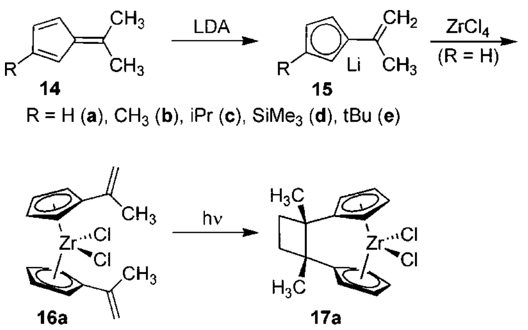
Scheme 3



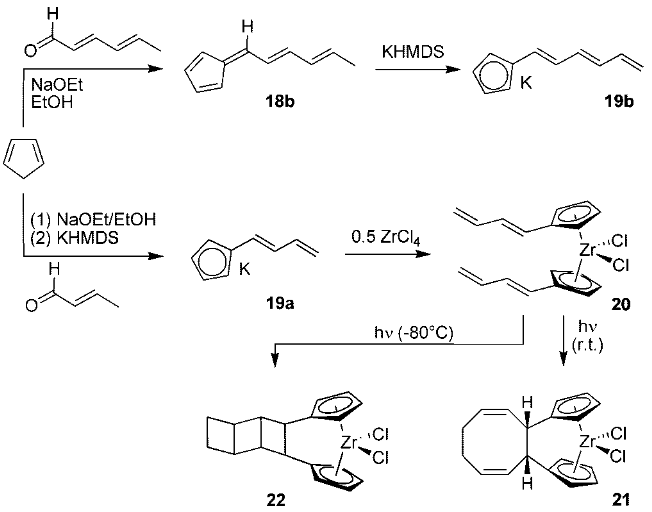
Scheme 4



Scheme 5



Scheme 6



is probably initiated by N-deprotonation. Depending on the specific reaction conditions chosen, the resulting monoanionic intermediate [**11**] then reacts further by competing formation of the fragmentation product **8**,[15] the product of a second deprotonation reaction (**12**), and/or the "monoanionic" product **13**. Formation of **13** required lithium hydride elimination (see Scheme 4).

(b) Fulvene Routes. Since the pioneering work by Ziegler et al., the specific chemical features of pentafulvenes have been used for the selective synthesis of cyclopentadienides.[16] Pentafulvenes are carbon electrophiles, and their C−H bonds in the α-position to the C6 carbon center are acidic. Cyclopentadienides can thus be prepared from suitably alkyl-substituted pentafulvenes by either nucleophilic addition or H^+ abstraction.[17]

We have used the latter reaction for the preparation of alkenylcyclopentadienides. Deprotonation of 6,6-dimethylpentafulvene (**14a**) by LDA yielded 1-methylethenylcyclopentadienide (**15a**). Transmetalation to zirconium gave **16a**. Subsequent photolysis of the functionalized bent metallocene rapidly resulted in a complete conversion to the ansa-zirconocene complex (**17a**). This intramolecular photochemical [2+2] cycloaddition reaction represents one of the best ansa-metallocene syntheses by C−C coupling at the bent metallocene stage (Scheme 5).[18,19]

The deprotonation route can even be used with ease to prepare butadienyl- (**19a**) or hexatrienyl-substituted cyclopentadienides (**19b**). Use of $K[N(SiMe_3)_2]$ as a base was advantageous in both cases. Transmetalation of **19a** gave the respective zirconocene complex (**20**). Its photolysis at ambient temperature resulted in a rapid and complete conversion to the formal [4+4] cycloaddition product (**21**). The stepwise mechanism of the formation of **21** was elucidated by photolysis at low temperature. At −80 °C, the competing photochemical formation of the organometallic ladderane derivate (**22**) was observed (see Scheme 6).[20,21]

Amide addition to the electrophilic fulvene carbon center C6 is observed in the "non-enolizable" cases. A typical example is

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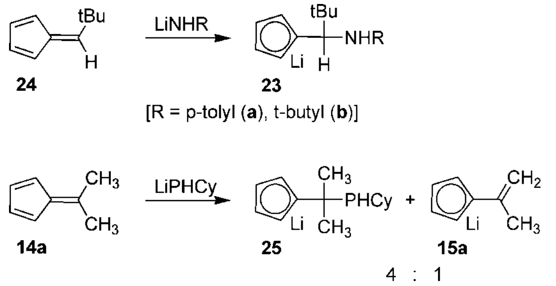
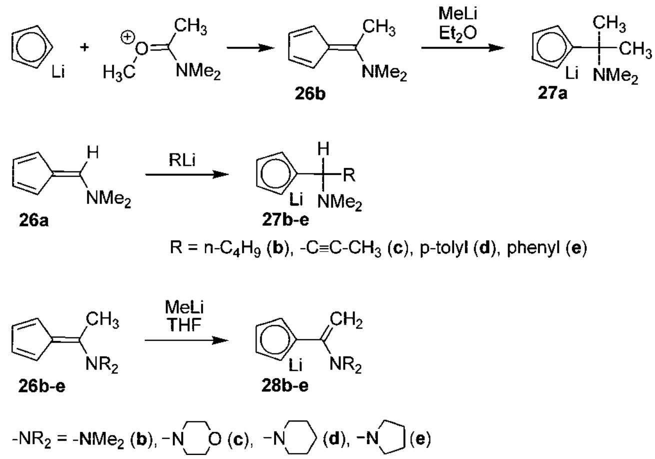
Scheme 7



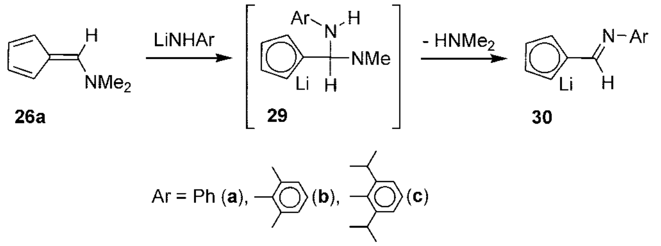
Scheme 8



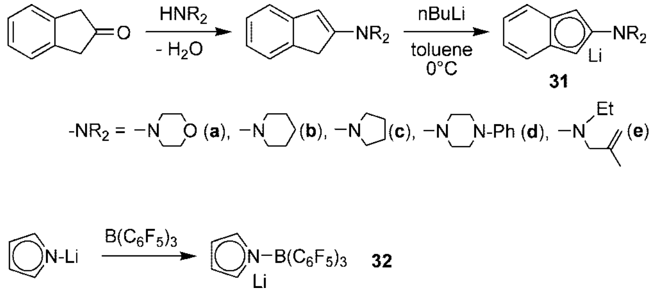
the formation of **23** from 6-*tert*-butylfulvene (**24**) and LiNHR reagents [R = *p*-tolyl, *tert*-butyl].[22,23] The corresponding secondary LiPH(cyclohexyl) reagent is less basic than the corresponding amides. Therefore, we have observed predominant C-addition to yield **25** even when a CH-acidic pentafulvene (e.g., **14a**) was employed.[24,25]

Aminofulvenes are readily synthesized by treatment of a cyclopentadienide with an activated carboxamide.[26] The subsequent reaction of 6-dimethylamino-6-methylfulvene (**26b**) with methyllithium represents an exceptional case: treatment with MeLi in ether results in selective methyl anion addition to yield the aminoalkyl-substituted cyclopentadienide (**27a**),[27j] whereas the usual deprotonation reaction takes place by adding methyllithium in THF at low temperature to furnish the unique enamino-functionalized cyclopentadienide system (**28b**). The latter is also obtained by treatment of **26b** with a variety of amide bases (see Scheme 7).[27] The "non-enolizable" aminofulvene (**26a**) cleanly adds a variety of alkyl- or aryllithium nucleophiles, as expected, to yield the respective substituted

Scheme 9



Scheme 10



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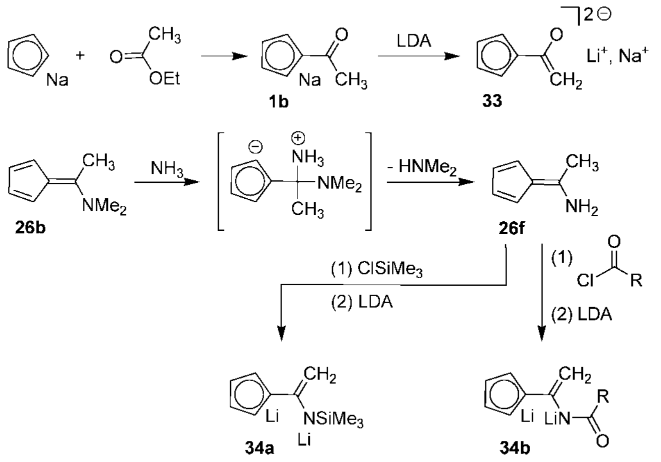
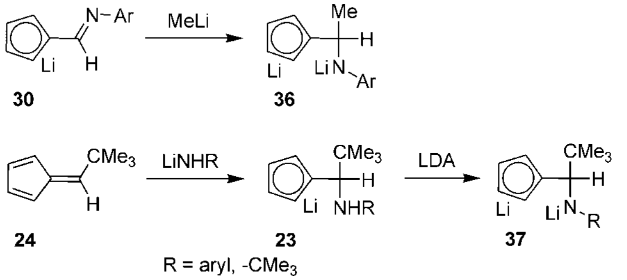


Scheme 12



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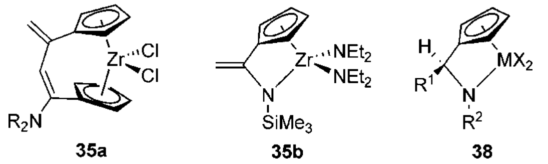
Scheme 13



dimethylaminomethyl cyclopentadienides (**27b**−**e**).[28] The enamino-Cp anion synthesis can be carried out in the presence of a variety of amino functionalities. The resulting [enamino-Cp]Li reagents (**28b**−**e**) were transmetalated to the group 4 metals. The corresponding metallocenes underwent a clean acid-catalyzed Mannich-type reaction to yield the unique fully unsaturated amino-butadien-1,3-diyl-bridged ansa-metallocenes (**35a**, see Scheme 13).[29]

6-Dimethylaminofulvene (**26a**) readily reacts with a variety of lithium anilide reagents. In this case the initial amide nucleophile addition results in the formation of an unstable intermediate (**29**) that readily eliminates dimethylamine to yield the unique formimidoylcyclopentadienide products (**30**, see Scheme 9).[23,30]

Eventually, enamine formation[31] has enormeously helped to synthesize aminocyclopentadienides and aminoindenides, i.e., LiCpX systems that have amino functions directly bonded to the five-membered ring framework. Such systems (**31**) are simply prepared by formation of the enamines starting from the respective cyclopentenone or indanone precursors (see Scheme 10), followed by deprotonation.[32] Such systems had previously been synthesized by a more tedious route involving Cp-anion attack on suitably derivatized hydroxylamines.[33] The addition of B(C_6F_5)$_3$ to pyrrolyllithium gave a hetero-Cp derivative (**32**) featuring the nitrogen center inside the five-membered ring.[34,35]

(c) Dianionic Systems. Doubly negatively charged functionalized cyclopentadienides are valuable reagents for the synthesis of interesting transition metal catalyst precursors (e.g., the "constrained geometry" Ziegler–Natta catalysts).[36,37] A simple way to synthesize such systems starts from Rausch's acetylcyclopentadienide (**1b**). Treatment of the readily available compound **1b** simply with LDA results in a clean deprotonation at the still acidic α-position to yield the enolato-cyclopentadienide product (**33**). The dianionic reagent **33** was employed in transmetalation to, for example, titanium, to give interesting binuclear homogeneous Ziegler–Natta catalyst precursors.[8]

A related reaction sequence started from 6-dimethylamino-6-methylfulvene (**26b**). Amine exchange by treatment with liquid ammonia under pressure yielded the corresponding −NH$_2$-substituted pentafulvene (**26f**). This was N-acylated or N-silylated. Subsequent treatment with 2 molar equiv of LDA resulted in clean double deprotonation reactions to yield the respective substituted enamido-cyclopentadienide products (**34a**, **34b**).[38] Transmetalation of **34a** to Zr using the $Cl_2Zr(NEt_2)_2(THF)_2$ reagent[39] gave the first C$_1$-bridged group 4 metal "constrained geometry" catalyst system (**35b**, see Scheme 13). Transmetalation of **34b** to group 4 metal systems gave larger ring systems involving coordination of the carboxamide oxygen atom.[8]

Methyllithium addition to the reactive formimidoylcyclopentadienides opened a very favorable direct pathway to the "dianionic" (1-ethylamido)cyclopentadienides (**36**). Amide anion addition to the "non-enolizable" 6-*tert*-butylfulvene substrate (**24**) followed by NH deprotonation opened a very useful complementary alternative route to the system **37** (see Scheme 12).[22,23] Both these "dianionic" systems showed very interesting structural properties (see below). They were used for the synthesis of a series of C$_1$-bridged "constrained geometry" systems (**38**, see Scheme 13).

Nucleophilic addition (e.g., by methyllithium) to a C6 carbon atom of the bis-fulvene derivative **39** generates a cyclopentadienide (**40**) in the usual way. However, in this specific case this is not stable under the applied reaction conditions but rapidly adds intramoleculary to the remaining fulvene entity to eventually yield the unsymmetrically bridged bis(cyclopentadienide) systems **42** after deprotonation (see Scheme 14).[40–42]

Structures of the Functionalized Cyclopentadienides. Due to the prevailing Coulombic interaction that characterizes the alkali metal Cp bond,[3] there seems to be a high tendency to form aggregated structures of such systems in the solid state.[1,2] However, this is counterbalanced by the addition of donor ligands or donor solvent molecules that may lead to a relative stabilization of smaller units or even monomeric structures. At this point it is the question of the involvement of the various pendant functional groups in the determination of the favorable structures of the overall systems, especially so since a number of these substituents may serve as powerful stabilizing donor ligands themselves. The structural influence of the various attached functional groups of the functionalized alkali metal cyclopentadienides, especially of their lithium derivates, shall

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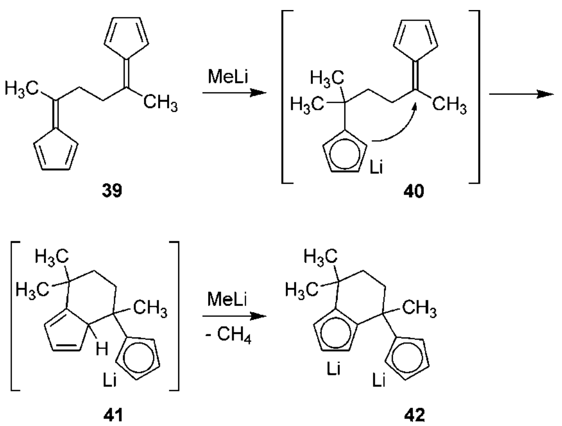
Scheme 14



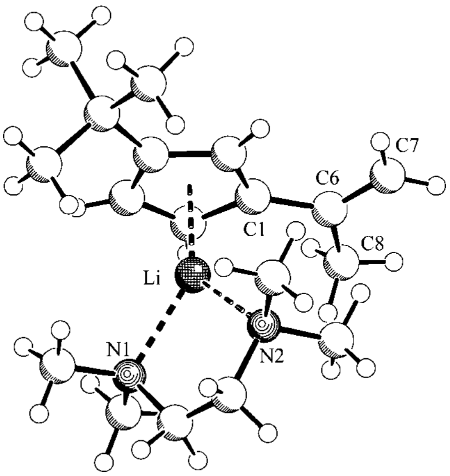


Figure 1. Molecular structure of **15e**·tmeda.

be discussed and illustrated using selected typical examples from the many systems whose syntheses were described in the preceding sections of this account.

(a) Monomeric and Dimeric Structures. Lithium [3-*tert*-butyl-(1-methylethenyl)]cyclopentadienide (**15e**, see Scheme 5) was treated with tetramethylethylenediamine. Single crystals of the resulting (**15e**·tmeda) adduct were obtained, and its structure was determined by X-ray diffraction.[43] The compound features discrete monomeric units in the crystal (see Figure 1). Lithium is rather uniformly η^5-coordinated to the functionalized Cp ring with Li−C(Cp) distances being found in a narrow range between 2.257(5) and 2.299(5) Å. The alkenyl substituent is oriented coplanar with the Cp ring [bond lengths C1−C6: 1.469(4) Å, C6−C7: 1.332(4) Å, Li−N1: 2.155(4) Å, Li−N2: 2.125(5) Å].

The structure of Li(OEt$_2$) [pyrrolyl-B(C$_6$F$_5$)$_3$] (**32**·OEt$_2$, see Scheme 10) in the crystal is conceptually related (see Figure 2).[34] It also features independent monomeric molecular units in the crystal. One stabilizing diethyl ether donor ligand is present [bond length O42−Li: 1.830(7) Å, angle O42−Li−pyrrolyl (centroid): 136.0°]. The lithium atom is rather symmetrically η^5-coordinated to the pyrrolyl-B(C$_6$F$_5$)$_3$ ligand [Li−N1: 2.281(7) Å, Li−C5/C2: 2.350(8)/2.423(8) Å, Li−C4/C3: 2.492(9)/2.533(9) Å], and there seem to be some supporting Li−F(C) interactions[44] from two of the −C$_6$F$_5$ ligands at boron [Li−F16: 2.041(7) Å, Li--F26: 2.467(8) Å], which has resulted in an overall pseudotetrahedral coordination environment of the central lithium atom.

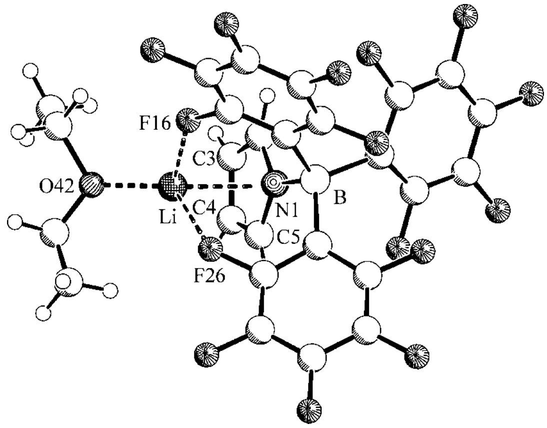


Figure 2. View of the molecular structure of **32**·OEt$_2$.

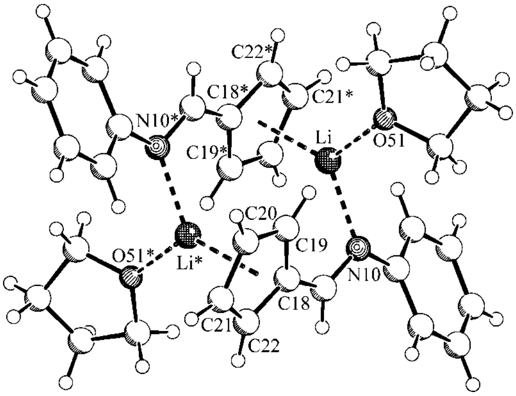


Figure 3. Projection of the cyclodimeric structure of (**30a**·THF)$_2$.

The *N*-phenylformimidoyl-substituted Li-cyclopentadienide (**30a**, see Scheme 9) exhibits a cyclodimeric structure in the crystal.[30] The lithium atom is coordinated to the nitrogen atom of the *E*-configured formimidoyl group [Li1−N10: 2.077(4) Å, N10−C17: 1.294(3) Å], and it bears one THF ligand [Li−O51: 1.961(5) Å]. The coordination sphere around Li is completed by a η^5-interaction with the Cp ring of the second (symmetry-equivalent) [Cp−CH=NPh(Li)] subunit in the dimer [e.g., Li*−C18: 2.408(5) Å, Li*−C19: 2.401(5) Å, Li*−C20: 2.378(5) Å, Li*−C21: 2.372(5) Å, Li*−C22: 2.397(5) Å] (Figure 3).

Formally the *N*-*tert*-butylformimidoylfluorenyllithium compound **13** (see Scheme 4)[14] is structurally related to the imidoylcyclopentadienides **30**. However, there are some remarkable structural differences in detail. As expected, the lithium atom in **13**(OEt$_2$)$_2$ is coordinated to nitrogen (Li−N11: 2.031(7) Å) and to the pair of ether oxygen atoms (Li−O20: 1.939(7) Å, Li−O30: 1.947(7) Å). In this case the coordination sphere of lithium is completed by a rather strong interaction with the fluorenyl carbon atoms C8, C8A, and C9 and the iminoylcarbon atom C10 (Li−C8: 2.654(7) Å, Li−C8A: 2.810(7) Å, Li−C9: 2.862(7) Å, Li−C10: 2.645(7) Å; N11−C10: 1.306(4) Å,

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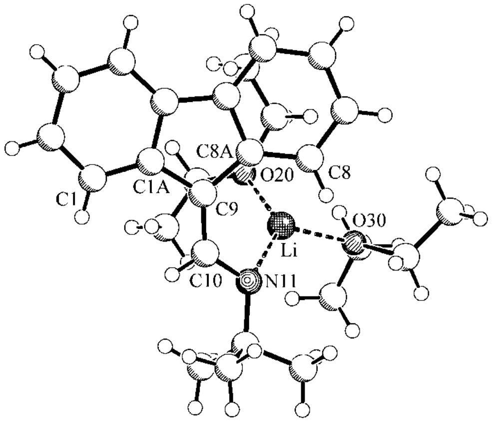

Figure 4. View of the η^5-azapentadienyllithium derivative **13**$(OEt_2)_2$.

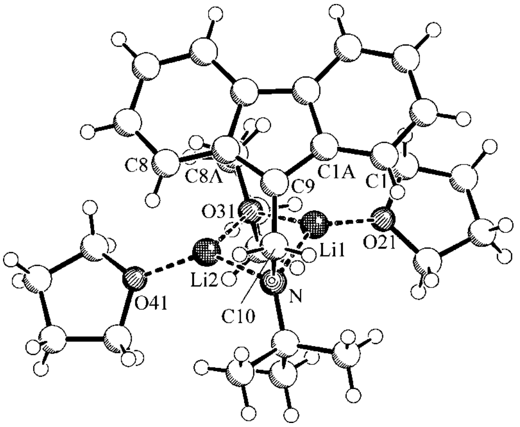

Figure 5. Molecular structure of **12** $(THF)_3$ in the crystal.

C10−C9: 1.399(4) Å). This makes compound **13** a rare example of an open U-shaped η^5-azapentadienyllithium complex (see Figure 4).[14]

Single crystals of the fluorenylamido dilithium compound **12** (see Scheme 4) were obtained from THF. The compound crystallizes with three tetrahydrofuran molecules [**12**$(THF)_3$]. It features a pair of lithium atoms that are slightly unsymmetrically bonded to the fluorenylamide unit, so that both lithium atoms have contact to N (Li1−N: 1.969(4) Å, Li2−N: 1.984(4) Å, C10−N: 1.474(3) Å). Each lithium atom has a terminal THF ligand bonded (Li1−O21: 1.923(4) Å, Li2−O41: 1.915(4) Å), and there is a bridging THF ligand shared between them (Li1−O31: 2.082(4) Å, Li2−O31: 2.041(4) Å). In addition, Li1 shows some interaction with the fluorenyl carbon atoms C9 and C1A (Li1−C9: 2.368(4) Å, Li1−C1A: 2.544(4) Å). The other lithium atom (Li2) features a much weaker interaction with the fluorenyl nucleus (Li2−C8: 2.648(5) Å, Li2−C8A: 2.823(5) Å).[14]

The Li−Cp interaction is lost if the aryl substituent in the arylformimidoyl-CpLi derivatives becomes more bulky. Crystallization of both the *N*-2,6-dimethylphenyl- and *N*-2,6-diisopropylphenyl-substituted examples from THF gave monomeric [Ar-N═CHCpLi·3THF] samples (**30b**·3THF, **30c**·3THF, see Scheme 9 and Figures 6 and 7).[30] Compound **30b**·3THF features a pseudotetrahedral coordination geometry around lithium comprising three THF ligands [Li−O21: 1.957(5) Å, Li−O31: 1.940(4) Å, Li−O41: 1.944(4) Å] and the imine nitrogen [Li−N7: 2.018(4) Å]. The central ArN═CHCp unit is *Z*-configurated. Its N═C double bond is slightly elongated (N7−C6: 1.309(3) Å),[45] and the adjacent C6−C1 bond is rather short at 1.402(3) Å. The attached C_5H_4 ring is oriented away from the lithium atom. It has no contact with it. There is a small but apparently systematic fulvene-like bond alternation inside the C_5H_4 framework [C1−C2/C5: 1.419(3)/1.417(3) Å; C2−C3/C4−C5: 1.369(3)/1.361(3) Å; C3−C4: 1.411(4) Å] (see Figure 6).

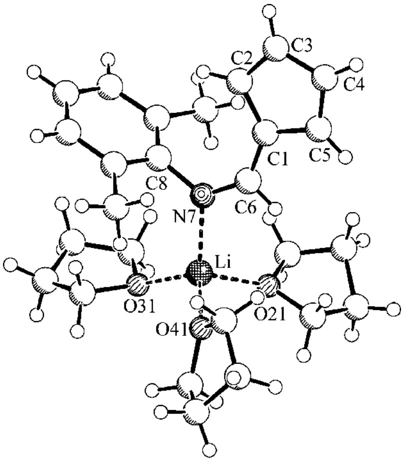

Figure 6. Molecular structure of **30b**·3THF.

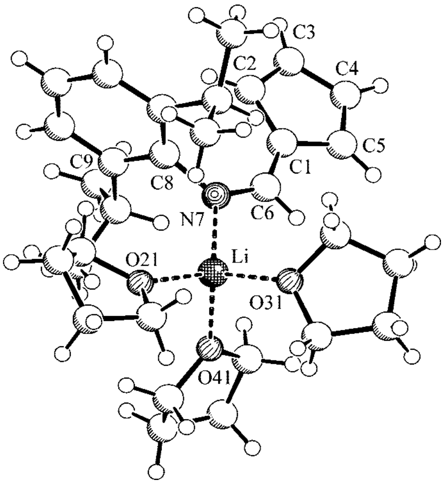

Figure 7. Molecular structure of **30c**·3THF.

The compound **30c**·3THF, featuring the even more bulky 2,6-diisopropylphenyl substituent at the imine nitrogen atom, shows a similar structure in the crystal [Li−N7: 2.006(3) Å, O−Li−O(av): 104.6(1)°, N7−C8: 1.429(2) Å, N7−C6: 1.308(2) Å, C1−C6: 1.404(2) Å, dihedral angles C9−C8−N7−C6: 96.8(2)° C1−C6−N7−C8: −0.3(2)°] (see Figure 7).

[Bn_2-Ala-Cp]Li (**7a**, see Scheme 3) features a remotely related structure in the solid state.[13] A dimeric THF adduct (**7a**·THF)$_2$ is obtained by crystallization from tetrahydrofuran. Again, the C_5H_4 unit is remote from the Li atom, and it shows some fulvenoid character [e.g., short C1−C6(A;B) bond: 1.381(5); 1.405(5) Å, elongated C6−O1(A;B) linkages (1.291(4); 1.279(4) Å), and a pronounced bond length alternation inside the five-membered ring]. The lithium atoms in the near C_2-symmetric dimer are bonded to the "acyl" oxygens [Li−O1(A;B): 1.908(7)/1.958(7) Å; 1.910(6)/1.966(7) Å] and the alanine nitrogen center [Li−N1(A;B): 2.431(7); 2.147(6) Å]. The pseudotetrahedral coordination environment is completed by the addition of a THF

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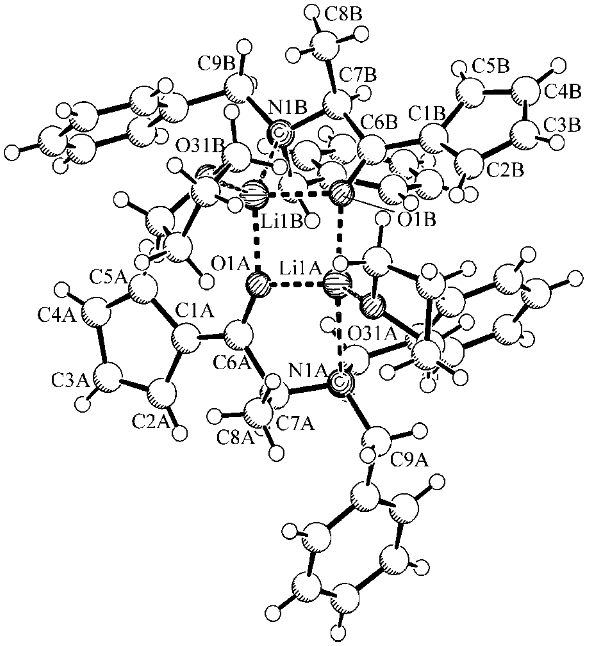

Figure 8. Molecular structure of the (**7a**·THF)$_2$ dimer.

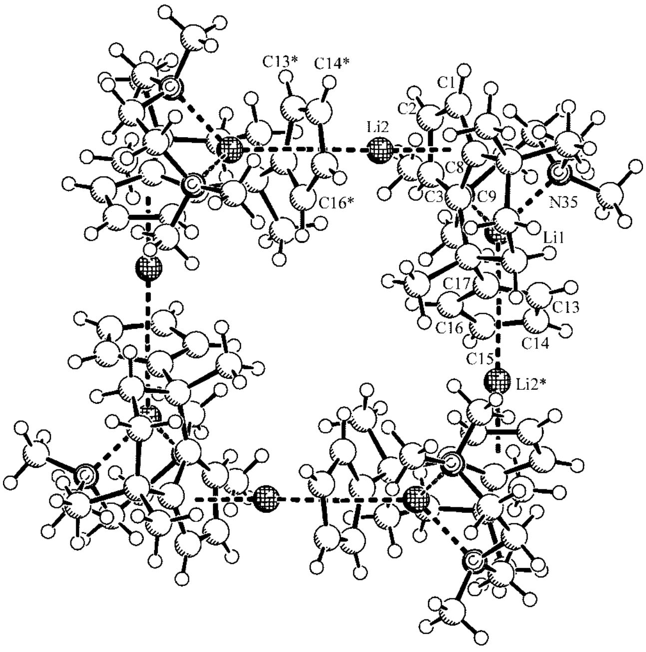

Figure 9. Molecular structure of **42**·tmeda.

donor ligand to each Li [Li−O31(A;B): 1.972(6); 1.934(7) Å] (see Figure 8).

(b) Oligomeric and Polymeric Structures. The anellated bis-cyclopentadienide system **42** (see Scheme 14) shows a unique cyclotetrameric structure.[40] It is constructed of four Li−Cp′−Li−Cp′-type supersandwich subunits[46] that are arranged in a pseudosquare-tetrameric framework (see Figure 9). The apical Li atom of the supersandwich is stabilized by a tmeda ligand. The Li1···Li2* separation (4.048 Å) is typical for a supersandwich structure. Li1 is uniformly η^5-coordinated to the pendent-Cp anion equivalent [Li1−C13 to C17 found in a range between 2.318(11) and 2.378(13) Å]. Li2 is bonded to the opposite ("outside") face of the pendant Cp ring and forms a lithiocene anion structure by additional coordination to the pendent Cp ring of the monomeric subunit. Inside the lithiocene anion substructure[47] the coordination of Li2 to the anellated Cp ring is short but unsymmetrical [Li2−C1–3/8,9 range: 2.212(12) to 2.348(11) Å]. The remaining Li2−C13 to C17 bonds again are found in a narrow range (2.343(11)−2.379(12) Å).

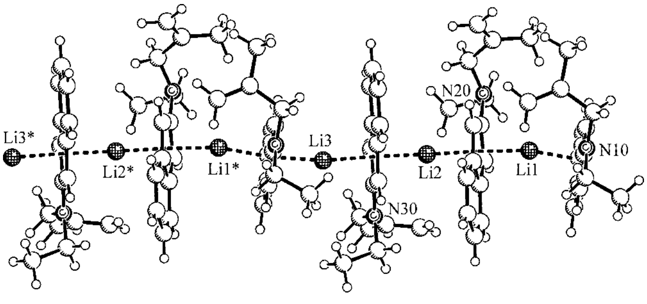

Figure 10. View of a section of the polymeric supersandwich chain structure of compound **31e** in the crystal.

Compound **31e** (see Scheme 10) exhibits a polymeric supersandwich structure in the crystal (see Figure 10).[32] The *tert*-amino substituent that is directly adjacent to the planar five-membered ring is not directly involved in the bonding to lithium. The Li−C(Cp) distances in **31e** were found in a narrow range between 2.237(7) and 2.389(7) Å. There is a very uniform bonding of the lithium to either Cp ring.

The enaminocyclopentadienide **28b** (see Scheme 8)[48] features a very similar structure in the solid state.[49] Inside each of the −RCp−Li−CpR subunits the Li−C(Cp) distances were found in a range between 2.248(5) and 2.408(45) Å. The attached enamino substituents are rotated only slightly from coplanarity with the central five-membered Cp-ring systems (see Figure 11). This orients the enamino nitrogen atoms in a sufficiently distant position to inhibit any direct Li···N interaction. In compound **28b** the enamino moiety behaves as an electronically inactive substituted olefinic substituent.

This is different with the substituted lithium aminomethylcyclopentadienides.[27] Their structures seem to be strongly influenced by interaction of the lithium cation with both the core cyclopentadienyl and the pendant *tert*-amino functionalities. With a strongly interacting intramolecular amino group there

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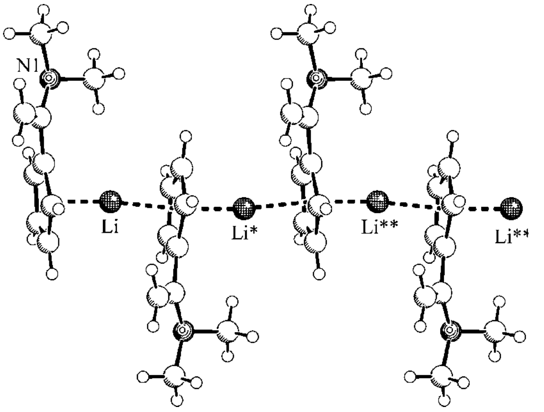
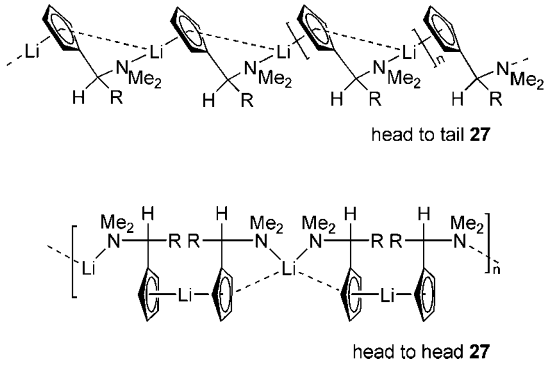


Figure 11. Molecular structure of compound **28b**.

Scheme 15



is a possibility of forming two different types of oligomeric chain structures either by head-to-tail or by head-to-head arrangement of the respective monomers. Examples of both structural types were observed experimentally.[28] For a schematic view see Scheme 15.

Compound **27d** (R = *p*-tolyl, see Scheme 8) represents a typical example of a polymeric head-to-tail structured arrangement. The lithium atom is η^5-coordinated to the Cp ring of one monomeric unit [Li−C(Cp) range: 2.164(5) to 2.220(4) Å], and it is connected to the adjacent monomer by strong coordination to the nitrogen atom of the $-CHAr-NMe_2$ substituent (Li−N2*: 2.032(5) Å). Li coordination to the adjacent Cp unit in this case is only very weak (Li1−C21*: 3.154 Å, Li1−C22*: 2.995 Å). In the similarly head-to-tail structured compound **27b** (R = *n*-butyl) Li1 is coordinated to nitrogen as well (Li−N1: 2.106(4) Å, Li2−N11: 2.095(4) Å), but in addition features some supporting Li−C(Cp) interaction [Li1−C22: 2.486(4) Å, Li1−C21: 2.710(3) Å; Li2−C122: 2.461(4) Å, Li2−C121: 2.694(3) Å]. Consequently, the Li−η^5-C(Cp) interaction in **27b** [2.242(4)−2.300(4) Å] seems to be slightly weaker than in compound **27d** (see above). The chain structure of $[(Cp\text{-}CMe_2NMe_2)Li]_n$ that is depicted on the cover of this issue of the journal is of a similar type.[27j]

The alternative oligomeric head-to-head chain structure (see Scheme 15) was found in crystalline **27e** (R = Ph).[28] The chain is constructed of individual −RCp−Li−CpR− lithiocene units that are connected by bridging bis(amino)Li structural units. The Li1−C(Cp) bonds inside the lithiocene subunit are in a narrow range (2.27(2) to 2.37(2) Å). The corresponding lithium−nitrogen bonds were found at 2.20(2) Å (Li2−N2) and 2.62(2) Å (Li2−N1), respectively. In addition, Li2 is η^2-coordinated to the outside of the adjacent lithiocene Cp ring (Li2−C28: 2.32(2) Å, Li2−C32: 2.49(2) Å) (see Figure 13).

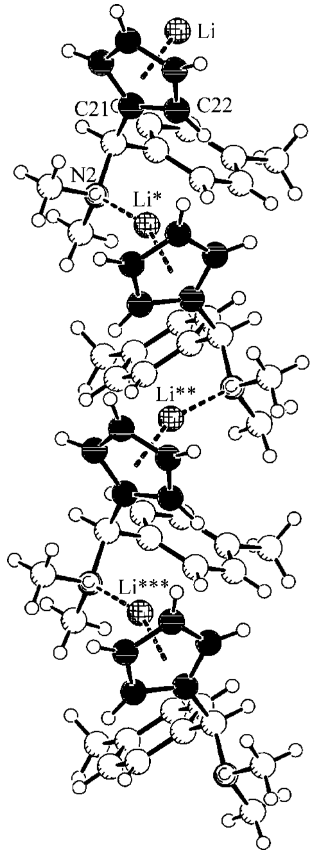


Figure 12. View of oligomeric "head-to-tail" structure of compound **27d**.

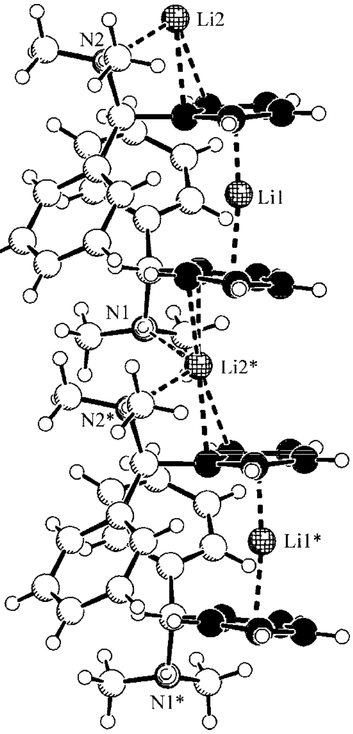


Figure 13. Molecular structure of compound **27e**.

The dilithium C_1-bridged "constrained geometry" Cp/amido systems (**36**, **37**, see Scheme 12) feature a similar dichotomy of head-to-tail and head-to-head polymeric chain structures in the solid state.[51] Compound **37a** (Ar = *p*-anisyl) features an oligomeric head-to-tail structural arrangement in the crystal. It

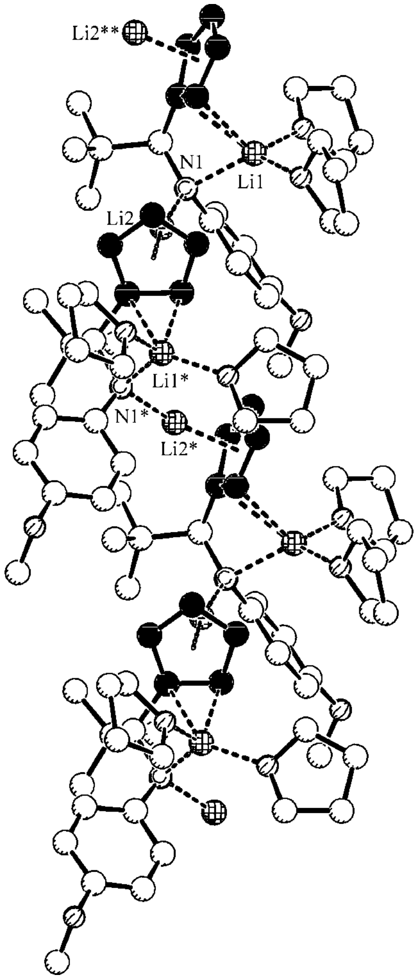


Figure 14. Molecular chain structure of **37a**·2THF.

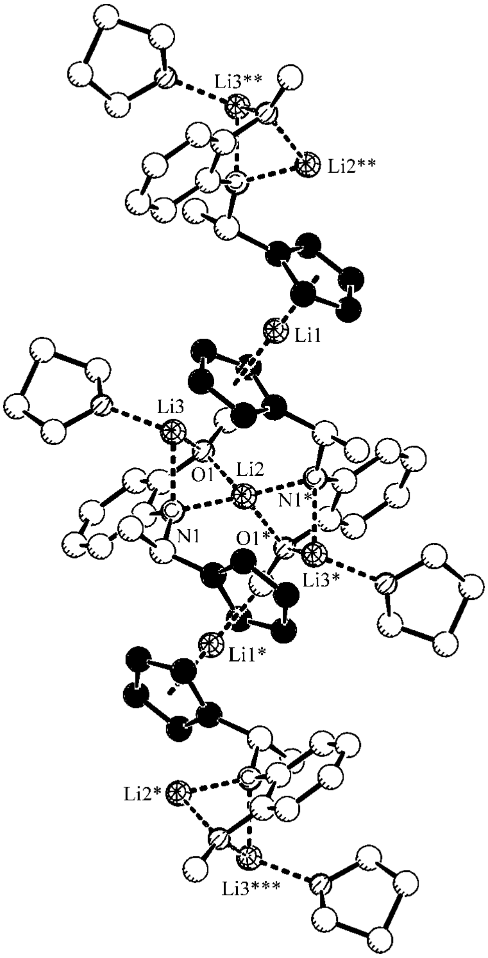


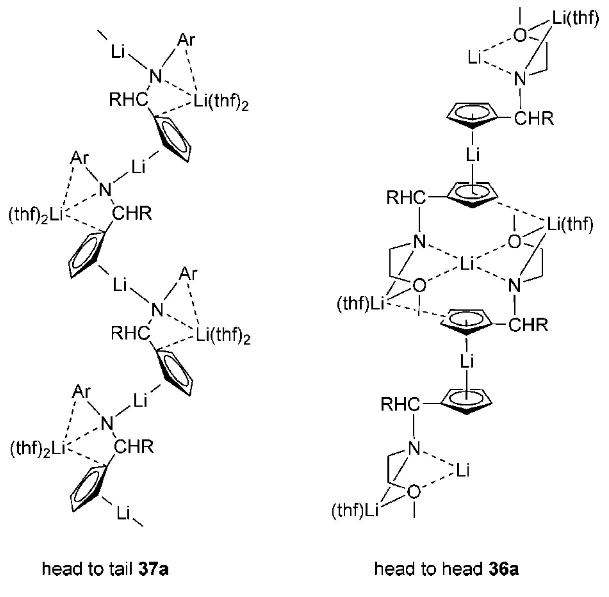
Figure 15. View of the molecular chain structure of compound **36a**·THF.

contains two lithium atoms per monomeric unit that are both in markedly different coordination geometries. One of the lithium atoms connects the monomeric units. It is η^5-coordinated to a Cp ring [Li2−C(Cp) bond range 2.207(4) to 2.401(4) Å] and bonded to the amide nitrogen atom of the next "dianionic" ligand [Li2−N1: 1.998(4) Å]. The other lithium atom is exclusively coordinated to a single ligand monomer, namely, through the amide nitrogen center [Li1−N1: 2.088(4) Å], two Li−C(Cp) contacts [Li1−C5: 2.353(4) Å, Li1−C1: 2.499(4) Å], and a weak contact to the arene ring at nitrogen [Li1−C8: 2.570(4) Å]. In addition, Li1 has a pair of THF ligands bonded to it [Li1−O3: 1.961(4) Å, Li1−O2: 1.971(4) Å, angle O3−Li1−O2: 101.2(2)°] (see Figure 14 and Scheme 16).

Compound **36a** (see Scheme 12, Ar = *o*-anisyl) features a head-to-head arrangement of the monomeric "dianionic" units (see Figure 15). This leads to the formation of lithiocene anion substructures, as usual. Inside the −RCp−Li−CpR moieties of **36a** the lithium atom (Li1) is rather uniformly η^5-coordinated to the pair of Cp ligands [Li−C(Cp) range: 2.278(2)−2.323(2) Å]. These units are connected by a pseudotetrahedrally coordinated lithium atom [Li2−N1: 1.948(2) Å, Li2−O1: 2.030(3) Å]. Both their lithium atoms inside the polymeric main chain have occupancy one-half; that is, they both are shared between two monomeric units. There is a third lithium with occupancy one, which is bonded to the periphery of each of the monomeric units, again in a pseudotetrahedral geometry, which includes coordination of a THF ligand [Li3−O1: 2.544(3) Å, Li3−N1: 2.084(3) Å, Li3−O2(thf): 2.012(3) Å].

(c) Dynamic Features and Reactions. In solution the [formimidoyl-Cp]Li systems (**30**, see Schemes 9 and 17) exhibit slightly more complicated features as compared to the solid state. A typical example is compound **30b**, which shows a pair of isomers in d_8-THF solution [typical imino-CH=N ^{1}H NMR

Scheme 16



head to tail **37a** head to head **36a**

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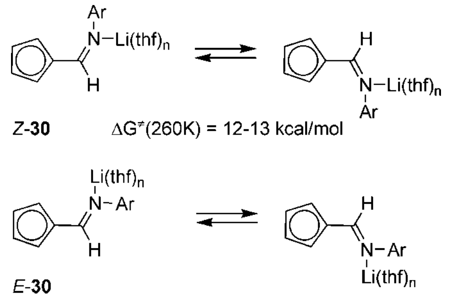
(51) Kotov, V. V.; Wang, C.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2007**, *26*, 6258–6262.

Scheme 17



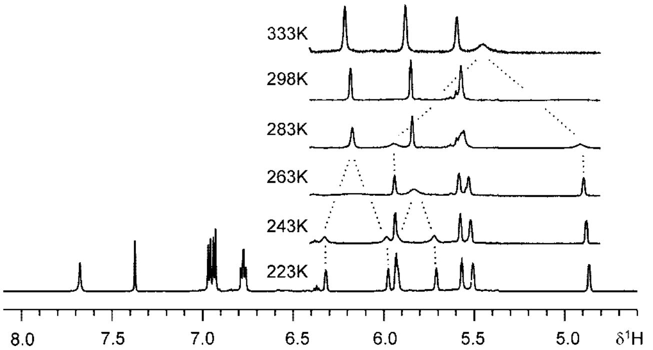
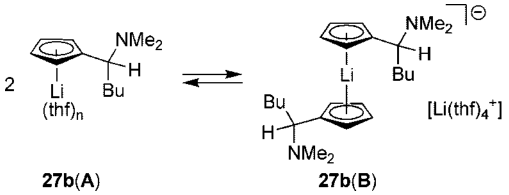


Figure 16. Dynamic ^{1}H NMR spectra (600 MHz, d_8-THF) of *E*-/*Z*-**30b**.

Scheme 18



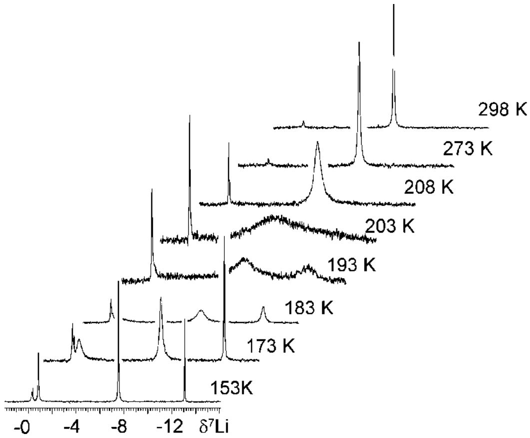


Figure 17. Temperature-dependent ^{7}Li NMR spectra of **27b** (194 MHz, 1:1 THF/THF-d_8).

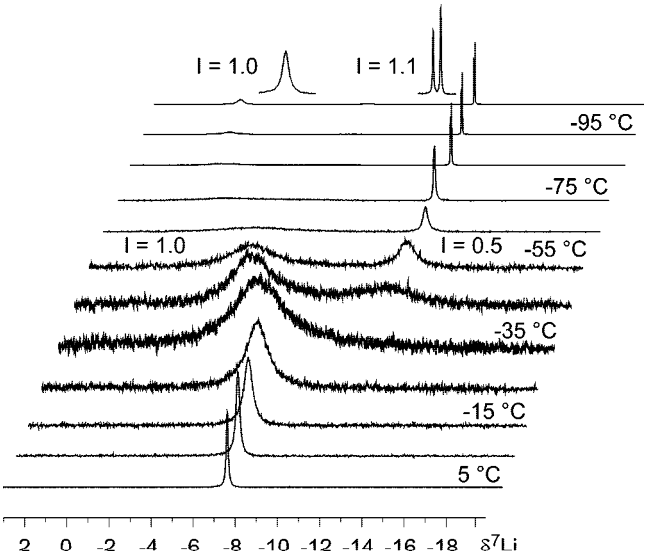


Figure 18. Temperature-dependent ^{7}Li NMR spectra of the 2 **15e**(**A**) ⇄ **15e**(**B**) equilibrium.

resonances at δ 7.66/7.42 (^{13}C: δ 162.3/157.1].[30] We assign them to the structures of the *E*- and *Z*-formimidoyl isomers (E-**30b**, *Z*-**30b**). At >330 K we observed a pair of C_5H_4-(Cp) ^{1}H NMR resonances for each of them. Lowering the temperature to 223 K led to decoalescence to eventually two sets of four ^{1}H NMR resonances of the monofunctionalized Cp ring (δ 6.34, 5.98/5.94, 5.72; δ 5.94, 4.88/5.58, 5.51, see Figure 16). This indicates hindered rotation of the Li-formimidoyl substituent around the C1−C6 bond in each of the isomers [$\Delta G^{\ddagger}_1$(260 K) = 11.7 ± 0.2 kcal/mol; $\Delta G^{\ddagger}_2$(265 K) = 12.7 ± 0.2 kcal/mol] and thus a marked electronic conjugation between the Cp ring and its attached unsaturated −CH=NAr(Li) substituent (see Scheme 17).

In solution the [dimethylaminomethyl-Cp]Li compounds (**27**, see Scheme 8) undergo transfer of the substituted Cp ligand, leading to rapid equilibration of the [mono-Cp-CHRNMe$_2$]Li(THF)$_n$ species (**27A**) with the lithiocene anion structure (**27B**, see Scheme 18).[28] This equilibration can readily be analyzed by temperature-dependent dynamic ^{7}Li NMR spectroscopy.[52] At 298 K the typical example **27b** (R = *n*-butyl) features a sharp ^{7}Li NMR resonance at ~δ −8.0 in d_8-THF solution that broadens upon lowering the monitoring temperature to eventually split into a typical resonance of the "monomer" **27b**(**A**) (δ −7.8) and a pair of resonances of the [(Cp-CHBuNMe$_2$)$_2$Li]$^-$[Li(THF)$_4$]$^+$ salt [**27b**(**B**)] at δ −0.8 and −13.0 (at 153 K; intensity 1:1) (see Figure 17), respectively. The latter value is typical of lithiocene anion structures.[52]

The ligand system **27b** contains a chirality center. Therefore, the lithiocene anion [**27b**(**B**)] formation should have involved the occurrence of diastereomeric meso- and rac-isomers, which was not observed (or spectroscopically resolved) in this case.[28] However, formation of the respective diastereomeric lithiocene anions was detected in the case of the planarly chiral 3-alkyl-substituted lithium (1-methylethenyl)cyclopentadienides (**15**, see Scheme 5).[43] Cooling a sample of the *tert*-butyl-substituted system **15e** in d_8-THF from room temperature to −95 °C (see Figure 18) resulted in the decoalescence of the single ^{7}Li NMR resonance at ~δ −7.5 to eventually give a broad [Li(THF)$_4^+$] singlet (δ −1.1) and a ca. 1:1 intensity pair of the respective lithiocene anion resonances (δ −12.2/−12.3 at 168 K). A close inspection of the NMR line shape at the intermediate temperatures indicated a rapid and strongly temperature-dependent equilibration of the "monomeric" **15e(A)** structure with the **15e(B)** lithiocene salt (see Scheme 19). For some of the additional examples in the **15a**−**e** series the **15(A)** component was even detected in the low-temperature decoalesced ^{7}Li NMR spectra by their typical resonance at ca. δ −6 to −8.[53]

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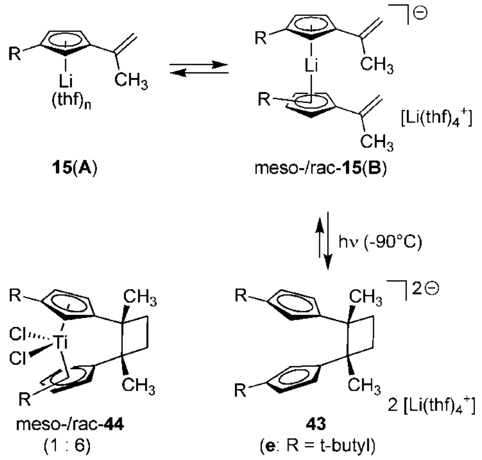
Scheme 19



The favored occurrence of the **15(B)** lithiocene structure in this equilibrium system was utilized to carry out a remarkable carbon–carbon coupling reaction at the active organolithium stage. Photolysis of **15e** in THF using quartz-filtered UV light at −90 °C resulted in an efficient intramolecular [2+2] cycloaddition reaction to yield the cyclobutylene-bridged ansa-lithiocene system **43e** (95%). It was used for transmetalation to yield the respective ansa-titanocene complex **44e**, which was characterized by X-ray diffraction. A variety of substituted analogues (**15a–d**) also undergo this photochemical [2+2] cycloaddition at the lithiocene anion stage, although only the examples bearing bulky substituents have led to high conversion to the ansa-lithiocenes under photostationary conditions.[43]

Some Conclusions

The examples presented and discussed in this article have shown that functional substituents at the cyclopentadienide framework can in principle be divided into two major groups. Various directly bonded "soft" functionalities appear to only marginally disturb the typical structural alkali metal cyclopentadienide pattern. Amino-Cp or even enamino-Cp lithium systems were shown to exhibit variants of the ubiquitous oligomeric supersandwich structures. Other functionalities such as acyl- or iminoacyl-type substituents behave as "hard" functional groups that want to directly interact with the metal cations. Therefore, such functionalized CpLi systems seem to favor structures with a pronounced participation of the respective heteroatoms. That applies also for the nitrogen centers of substituted aminomethyl-Cp systems. Here the participation of the heteroatom has become structurally determining, leading to the formation of either head-to-tail or head-to-head oligomeric chains. It is remarkable that the analogous structural motifs reappear in the respective "dianionic" series of the C$_1$-bridged dilithium Cp/amido systems.

Functional groups at the cyclopentadienide moiety may lead to interesting new reactions. We have described first examples where a typical organic functional group chemistry can be carried out at the stage of the active Cp-anion reagent, leading to carbon–carbon coupled derivatives, provided suitable reaction conditions are chosen. Overall, functionalized cyclopentadienide chemistry seems to be expanding and becoming ever more useful for providing selectively tailored ligands for use in organometallic chemistry and catalysis.

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