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Pentabenzylcyclopentadienides of Lithium

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(Pentabenzylcyclopentadienyl)lithium (Li(η^5-C_5Bz_5)) has been prepared by lithiation of pentabenzylcyclopentadiene with *tert*-butyllithium in toluene or benzene. This compound, which is the nonisolated starting material for most of the known pentabenzylcyclopentadienides, has been characterized by NMR and mass spectroscopy. The molecular structure of the benzene adduct of dimeric Li(η^5-C_5Bz_5) has been determined by X-ray diffraction studies. A triple-decker-like structure, (η^5-C_5Bz_5)Li(η^5-C_5Bz_5)Li(η^2-C_6H_6), results. The reaction of Li(η^5-C_5Bz_5) with Al(η^5-C_5Me_5) leads to Al(η^5-C_5Bz_5) and Li(η^5-C_5Me_5), with [Li(η^5-C_5Bz_5)$_2$][Al(η^5-C_5Me_5)$_2$] as a side product. The molecular structure of the last-named compound consists of the separated sandwich ions [Li(η^5-C_5Bz_5)$_2$]$^-$ and [Al(η^5-C_5Me_5)$_2$]$^+$.

Introduction

The cyclopentadienide anion and its derivatives are some of the most common ligands in main-group and transition-metal chemistry. Replacement of the hydrogen atoms of the C_5H_5 ligand by bulky substituents influences the physical and chemical properties of the corresponding metal complexes.[1] The better shielding of the reactive metal atom by using alkyl, silyl, or aryl groups allows the kinetic stabilization of thermodynamically unstable compounds.[1,2] Furthermore, the increased electron donor ability of the substituted C_5 ring alters the character of the metal−ligand bond toward a higher degree of covalency.[3] By modification of the steric and electronic requirements the properties of the complexes obtained can be tuned; e.g., a much better solubility of *bulky* complexes in nonpolar aprotic solvents is achieved. In addition, the variation of intermolecular interactions caused by different substituents often leads to new and unusual molecular structures.

These influences are reflected in the solid-state structures of indium(I) and thallium(I) cyclopentadienyls. While the C_5H_5 complexes form highly ionic polymeric zigzag chains containing alternating rings and metal atoms,[4] the perbenzylated derivatives (M(η^5-C_5Bz_5)) are mainly covalent molecules arranged in a dimeric fashion with weak metal···metal interactions.[1,5,6] (Figure 1, left). A second modification of Tl(η^5-C_5Bz_5), which is thermodynamically less stable, consists of almost linear chains of monomeric Tl(η^5-C_5Bz_5) molecules[7] (Figure 1, right).

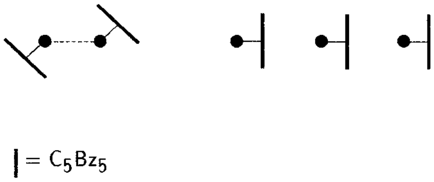

Figure 1. Schematic diagrams: (left) ● = In, Tl; (right) ● = Tl.

The crystal structure of In(η^5-C_5Bz_5) and those of both modifications of Tl(η^5-C_5Bz_5) seem to be mainly caused by packing effects of the bulky ligands.[5−7] Calculations concerning the M(η^5-C_5Bz_5) dimers show that weak metal···metal bonding interactions may be responsible for an additional energy gain, but these interactions are not necessarily structure-determining.[6]

It is of general interest to know what extent other M^I(η^5-C_5Bz_5) structures are influenced by packing effects of the C_5Bz_5 ligands. In this respect the examination of compounds with and without M−M interactions is of interest. Compounds without M−M interactions are expected for alkali metals whereas M−M bonds are predicted to be present in the complexes of B^I, Al^I, and Ga^I in contrast to those shown by their heavier homologues In^I and Tl^I. For the alkali metals [K(η^5-C_5Bz_5)(THF)$_3$] is, as far as we know, the only example whose molecular structure has been reported.[8] However, because of the coordinated THF molecules this complex is not very helpful for a comparison in this field. So far no structural data for C_5Bz_5 compounds are known for B^I, Al^I and Ga^I.

In this paper we describe the properties and the crystal structure of dimeric Li(η^5-C_5Bz_5). In addition the synthesis of Al(η^5-C_5Bz_5) is reported. As a side product, the *double-sandwich* compound [Li(η^5-C_5Bz_5)$_2$][Al(η^5-C_5Me_5)$_2$] can be isolated.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291−393 and references therein.

(2) For example, main-group-metal complexes containing the metal in formally low oxidation states: (a) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164−165. (b) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564−565.

(3) See for example: Jutzi, P.; Leffers, W. *J. Chem. Soc., Chem. Commun.* **1985**, 1735−1736.

(4) Frasson, E.; Menegus, F.; Panattoni, C. *Nature* **1963**, *199*, 1087−1089.

(5) (a) Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243−251. (b) Schumann, H.; Janiak, C.; Pickardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789−790.

(6) Janiak, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924−5946.

(7) Schumann, H.; Janiak, C.; Khan, M. A.; Zuckermann, J. J. *J. Organomet. Chem.* **1988**, *354*, 7−13.

(8) Lorberth, J.; Shin, S.-H.; Wocadlo, S.; Massa, W. *Angew. Chem.., Int. Ed. Engl.* **1989**, *28*, 735−736.

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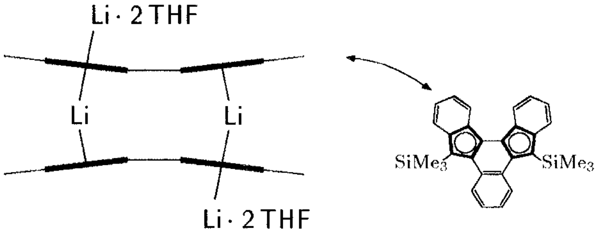

Figure 2. Schematic representation of dimeric $[Li_2\{C_{24}H_{14}(SiMe_3)_2\}]\cdot 2THF$.[9]

Results and Discussion

$[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$. $Li(\eta^5\text{-}C_5Bz_5)$ is easily available by lithiation of pentabenzylcyclopentadiene with *tert*-butyllithium in toluene. Single crystals were obtained by recrystallization of the crude product from benzene or, as presented here, from perdeuteriobenzene.

$[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)](C_6D_6)_2$ crystallizes in the monoclinic space group $P2_1/c$. The X-ray structure determination demonstrates that the asymmetric unit contains the benzene adduct of dimeric $Li(\eta^5\text{-}C_5Bz_5)$ and of two additional benzene molecules, separated by normal van der Waals distances.

As expected for mainly ionic compounds, $Li(\eta^5\text{-}C_5Bz_5)$ dimerizes in a head-to-tail manner, whereas in the above-mentioned dimeric $\eta^5\text{-}C_5Bz_5$ compounds of In^I and Tl^I the metal atoms point towards each other. $Li(\eta^5\text{-}C_5Bz_5)$ exhibits two differently coordinated Li atoms, very similar to the dimeric $[Li_2\{C_{24}H_{14}(SiMe_3)_2\}]\cdot 2THF$, which contains two Li atoms sandwiched between the Cp rings of two polycyclic dianions and two further THF-solvated Li atoms situated on the outside of the sandwich units[9] (Figure 2).

In $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)](C_6D_6)_2$ Li1 is sandwiched between two η^5-bonded C_5Bz_5 ligands (A and B) with two significantly different Li1 to ring centroid distances (1.78 and 2.03 Å; see Figure 3).[10] The first one, which is among the shortest known for cyclopentadienyl complexes of lithium, is very close to the values observed for the adducts of $Li(C_5H_2(SiMe_3)_3)$ with monodentate bases (e.g. 1.79 Å for $Li(C_5H_2(SiMe_3)_3)$−quinuclidine).[11] The longer one is comparable to the corresponding distances of $[Li(C_5R_5)_2]^-$ anions (e.g. 2.01 Å for $[Li(C_5H_5)_2]^-$).[12a]

The "external" Li2 atom is η^5-bonded to ring B with a Li2 to ring centroid distance of 1.90 Å. The coordination sphere of Li2 is completed by a benzene molecule, which encloses an angle of 34.9° with the plane of ring B.

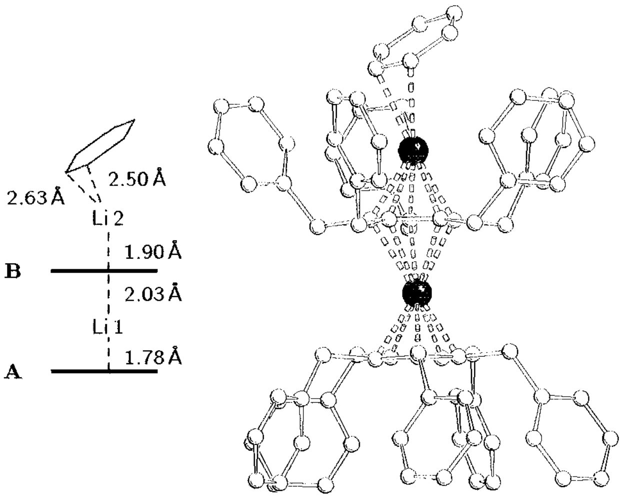

Figure 3. Molecular structure of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ (H and D atoms omitted for clarity). Li to ring centroid distances and the closest Li−benzene distances are given in the schematic representation. Li−C distances (Å): Li1 to ring A, 2.11(2)−2.19(2) (average 2.15); Li1 to ring B, 2.29(2)−2.42(2) (average 2.36); Li2 to ring B, 2.23(2)−2.27(2) (average 2.25).

The closest Li−C distances between Li2 and benzene, 2.50 and 2.63 Å, are in the typical range for weak Li−arene interactions,[13] while the closest Li−phenyl distances are much longer (3.32 Å). In the crystal the $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ units are arranged in columns. Interestingly, very short C···C distances between benzene and phenyl C atoms of the two neighboring $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ units are observed (Figure 4). The values, 3.48, 3.49, and 3.54 Å, are very close to the shortest C···C distances found in a high-pressure form of solid benzene (C···C = 3.50 Å).[14] Therefore, on the one hand it might be possible that closer Li2−benzene contacts are prevented by steric reasons. On the other hand, nearly identical C···C distances to both neighboring $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2]$ units suggest that mainly attractive van der Waals forces between benzene and phenyl rings causes the column structure of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$, with Li−benzene interactions being less important.

It should be mentioned that solid $[Fe(\eta^5\text{-}C_5Bz_5)_2](C_6H_5Me)_2$ forms the same column structure as $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)](C_6D_6)_2$, with the exception that the columns contain no arene molecules between the sandwich molecules.[15] This may support the significance of Li−benzene interactions in $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$. The observed dimeric structure of $Li(\eta^5\text{-}C_5Bz_5)$ may be regarded as a special case of supramolecular chemistry in which one molecule possesses host as well as guest character.[16]

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[9] Malaba, D.; Chen, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1992**, *11*, 1007−1009.

[10] For a comparison of distances of alkali-metal cyclopentadienyl complexes, see for example: Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168−2171.

[11] Jutzi, P.; Schlüter, E.; Pohl, S.; Saak, W. *Chem. Ber.* **1985**, *118*, 1959−1967. Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449−1456.

[12] (a) Harder, S.; Prosenc, S. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744−1745. (b) Wessel, J.; Lork, E.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2376−2377. (c) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Sivik, M. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 6466−6467.

[13] Similar values have been reported previously for intramolecular interactions of Li with ipso carbon atoms of mesityl or phenyl groups in $[LiC(SiMe_2Ph)_3(THF)]$ and $[\{Li(C_6H_3Mes_2)\}_2]$: Earborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1390−1391. Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353−11357.

[14] Piermarini, G. J.; Mighell, A. D.; Weir, C. E.; Block, S. *Science* **1969**, *165*, 1250−1255.

[15] The packing of sandwich molecules and arene molecules between the columns in solid $[Fe(\eta^5\text{-}C_5Bz_5)_2](C_6H_5Me)_2$ is almost exactly identical with that in $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)](C_6D_6)_2$, but the $Fe(\eta^5\text{-}C_5Bz_5)_2$ molecules are stacked in columns without an arene between them. On the basis of this fact and on shorter metal−C distances of $Fe(\eta^5\text{-}C_5Bz_5)_2$ the lattice constant *a* of the Fe compound is smaller, whereas the lattice constants *b* and *c* of the two compounds discussed here are very similar. (Schumann, H.; Janiak, C.; Köhn, R. D.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *365*, 137−150).

[16] E.g.: (a) Cram, J. M. In *Container Molecules and their Guests*; Stoddard, J. F., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1994; Chapter 6, p 107. (b) Cram, D. J.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 7748.

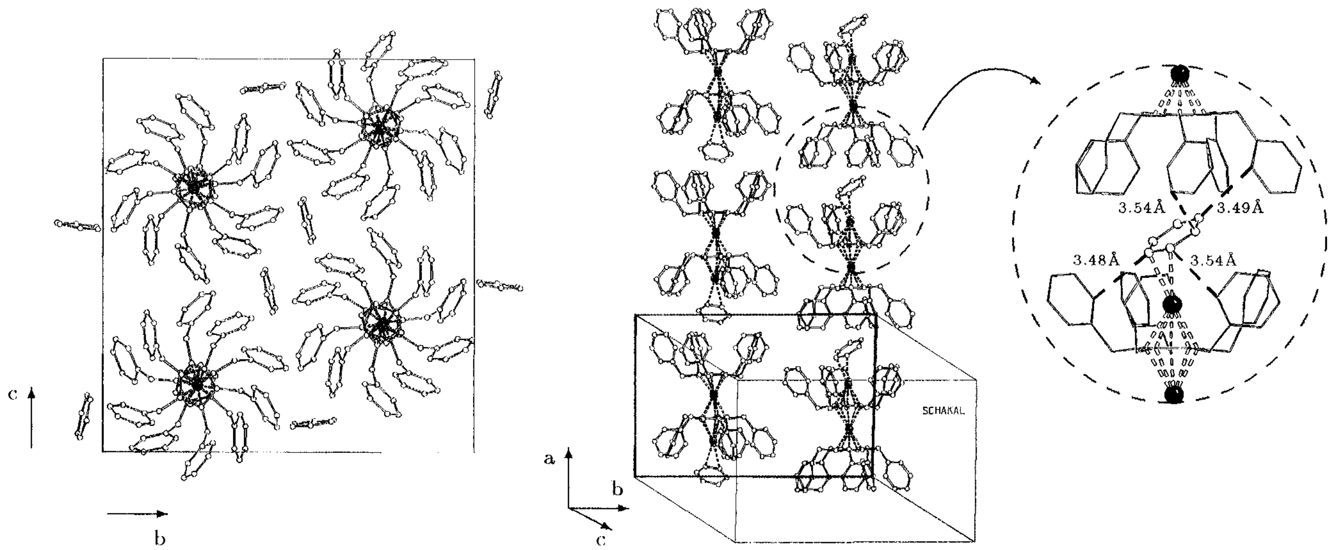
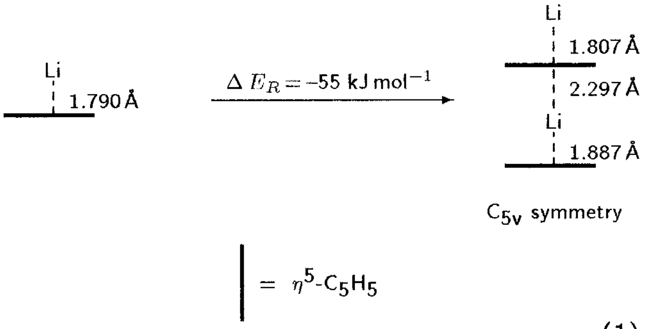


Figure 4. Left: unit cell of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]\cdot C_6D_6$ viewed down the *a* axis. Right: side view of two columns of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ molecules (*a* axis parallel to the plane of the paper); short benzene phenyl C···C distances (see text) are illustrated in the dashed area. Hydrogen atoms are omitted for clarity.

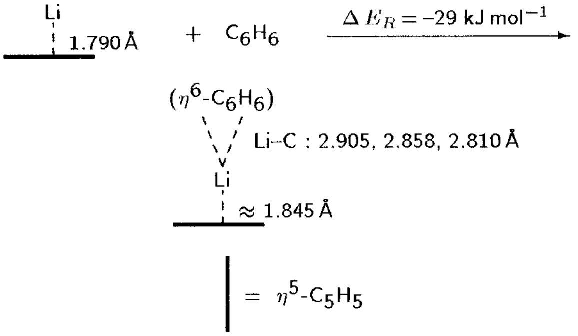
To gain a better insight into the bonding of dimeric $Li(\eta^5\text{-}C_5Bz_5)$ and of the influences of benzene, we have performed ab initio quantum-chemical calculations.[17] The studies were restricted to unsubstituted Cp species, since only trends need to be demonstrated. Dimeric $Li(\eta^5\text{-}C_5H_5)$ with a C_{5v} structure is formed from two $Li(\eta^5\text{-}C_5H_5)$ molecules exothermically, with $\Delta E_R = -55$ kJ mol^{-1} (eq 1).



(1)

To estimate the energetic situation for the addition of a benzene molecule, we have calculated η^6- and η^2-C_6H_6 adducts of $Li(\eta^5\text{-}C_5H_5)$ (eq 2).

The η^6-C_6H_6 adduct of $Li(\eta^5\text{-}C_5H_5)$ is only 1.5 kJ mol^{-1} more stable than an η^2-C_6H_6 adduct, with Li−C distances of 2.59 Å between Li and benzene.



(2)

The calculated $Li-C_{benzene}$ distances (η^2-C_6H_6),[19] which are close to the experimental values of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$, and the calculated formation energy of $(\eta^2\text{-}C_6H_6)Li(\eta^5\text{-}C_5H_5)$ depicts the significance of Li−arene interactions in $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$. However, regarding the dimerization as the first step in polymerization, it seems to be more favorable for $Li(\eta^5\text{-}C_5H_5)$ to form polymeric chains than neutral oligomeric arene adducts.

A structure consisting of (theoretically) infinite chains of stacked lithium cyclopentadienyl dipoles is known for $[Li(\eta^5\text{-}C_5H_4(SiMe_3))]_n$. Each Li is located almost symmetrically between two cyclopentadienyl rings (average Li to ring centroid distance 1.967 Å). Obviously an analogous polymeric structure of $Li(\eta^5\text{-}C_5Bz_5)$ with similar Li to ring centroid distances is not possible for steric reasons. A chainlike structure of $M(\eta^5\text{-}C_5Bz_5)$ as observed for the second modification of $Tl(\eta^5\text{-}C_5Bz_5)$ affords a much larger separation of the cyclopentadienyl rings and is therefore unfavorable for ionic compounds with attractive forces between the $M^{\delta-}(C_5Bz_5)^{\delta-}$ dipoles.

The structure of $Li(\eta^5\text{-}C_5H_5)$ is unknown so far, but due to its low solubility it is very likely that it is polymeric in the solid state and that dimeric or monomeric neutral arene adducts are unfavorable. In contrast, the formation of anionic arene complexes of alkaline cyclopentadienides such as $[Li(C_5H_5)_2]^-$ [12] and $[Cs_2(C_5H_5)_3]^-$ [18] has been demonstrated experimentally. This is in line with our *ab initio* calculations: the formation of $[Li(\eta^5\text{-}C_5H_5)_2]^-$ from the free $[C_5H_5]^-$ anion and $Li(\eta^5\text{-}C_5H_5)$ is highly exothermic ($\Delta E_R = -172$ kJ mol^{-1}; D_{5h} symmetry). Our calculated Li to ring centroid distance for $[Li(\eta^5\text{-}C_5H_5)_2]^-$ is 2.09 Å (d(Li−C) =

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[17] (a) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776−8789. (b) Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 7093−7100. The semiempirical calculations presented in (a) and (b) reveal the same trend as our ab initio calculations.

[18] Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 97−99.

[19] It should be mentioned that in general the calculated Li−C distances are about 2−4% longer than those determined experimentally. Furthermore, the experimentally observed Li−C distances are shorter if substituted cyclopentadienyls are involved. This trend is in accord with quantum-chemical calculations: $[Li(\eta^5\text{-}C_5H_5)_2]^-$, d(Li−C) = 2.406 Å; $[Li(\eta^5\text{-}C_5Me_5)_2]^-$, d(Li−C) = 2.374 Å.

[20] Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3903−3907.

2.41 Å[19]). Especially if proper cations are present, anionic arene complexes should be observed instead of polymers. The formation of small neutral arene adducts of alkaline cyclopentadienides such as $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ seems to be restricted to special conditions in which (i) the substituents of the ligand are bulky enough to avoid the formation of polymers, (ii) no proper cation can be generated (see below), and (iii) no strong donor molecules are present, since they can stabilize monomeric species such as $Li(C_5H_2(SiMe_3)_3){\cdot}THF$[10,11]

In order to investigate the nature of $Li(C_5Bz_5)$ in solution, ^7Li NMR spectra were recorded. When $Li(C_5Bz_5)$ is dissolved in benzene or toluene, only one ^7Li NMR signal at −10.3 ppm is observed, indicating either the presence of monomeric species or a fast equilibrium between monomeric and dimeric species. In view of the structure of solid $Li(\eta^5\text{-}C_5Bz_5)$ higher aggregates seem to be unrealistic. Since the observed shifts depend neither on the temperature (+60 to −70 °C for toluene) nor on the concentration (0.2 M solution, melt) monomeric species are more likely.[21] In OEt_2 (0.2 M solution) again only one ^7Li NMR signal is observed (−7.6 ppm between +25 and −110 °C). The stronger shielding of $Li(\eta^5\text{-}C_5Bz_5)$ in arene solutions might be a result of the ring current of coordinated arene molecules.[17a]

In THF below −10 °C a single resonance at −7.2 ppm is accompanied by two new signals at −0.2 and −12.1 ppm. These results can be interpreted by the presence of an equilibrium of THF-solvated, monomeric $Li(\eta^5\text{-}C_5Bz_5)$ with $Li^+{\cdot}n$THF/$[Li(\eta^5\text{-}C_5Bz_5)_2]^-$. Equilibrium reactions of this type have been extensively studied for $Li(C_5H_5)$ and lithium isodicyclopentadienide.[17] Further cooling of the $Li(\eta^5\text{-}C_5Bz_5)$/THF samples causes two additional signals at −1.5 and −7.9 ppm, indicating a more complex situation perhaps involving dimeric species of $Li(\eta^5\text{-}C_5Bz_5)$.

Reaction of $Li(C_5Bz_5)$ with $Al(C_5Me_5)$. Using the lattice energy of $Li(C_5Me_5)$, which is insoluble in aromatic hydrocarbons, as a driving force, the synthesis of $Al(C_5Bz_5)$ was attempted according to eq 3.

$$Li(C_5Bz_5) + Al(C_5Me_5) \rightarrow Al(C_5Bz_5) + Li(C_5Me_5)\downarrow \tag{3}$$

The products of the reaction were separated by virtue of their differing solubility in toluene, the soluble compounds being $Al(C_5Bz_5)$ and residual $Li(C_5Bz_5)$. Unfortunately, to date it has proved impossible to isolate $Al(C_5Bz_5)$ as a pure compound. However, NMR and mass spectroscopic data give evidence that $Al(C_5Bz_5)$ is monomeric both in solution and in the gas phase.

$Li(\eta^5\text{-}C_5Me_5)$ and the side products $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$ and aluminum metal (maximum 3% of the total Al content) are insoluble in toluene. $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$, presumably formed as shown in eq 4, is obtained as a colorless crystalline compound. The identity of this product was confirmed by X-ray structural studies.[22] $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$ is insoluble in all common solvents.

$$2Li(C_5Bz_5) + 3Al(C_5Me_5) \rightarrow Al^0 + [Al(C_5Me_5)_2]^+ + [Li(C_5Bz_5)_2]^- + Li(C_5Me_5) \tag{4}$$

The crystallographic unit cell of $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$ contains three almost identical entities of $[Al(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Li(\eta^5\text{-}C_5Bz_5)_2]^-$ which are separated by normal van der Waals distances. One of the $[Li(\eta^5\text{-}C_5Bz_5)_2]^-$ species resides on a crystallographic center of inversion.[22] In addition, toluene molecules are present. Since the experimental data are not sufficient to solve the structure properly, we will not present detailed structural data, besides the comments that the structure of the cation $[Al(\eta^5\text{-}C_5Me_5)_2]^+$ is comparable to our former results[23] and that the anion $[Li(\eta^5\text{-}C_5Bz_5)_2]^-$ exhibits a slightly shorter Li to ring center distance (1.90 Å) than was obtained for $[Li(\eta^5\text{-}C_5H_5)_2]^-$ experimentally (2.01 Å).[12] The distance between both C_5Bz_5 rings is in the same range as in $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ (3.80 Å; cf. Figure 3). In contrast to $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$, the benzyl groups of $[Li(\eta^5\text{-}C_5Bz_5)_2]^-$ are not oriented symmetrically.

Experimental Section

General Comments. All operations were carried out under dry nitrogen. Solvents were dried by conventional procedures. NMR spectra were recorded by means of a Bruker AC 250 (^1H, ^{13}C) or a Bruker AMX 300 spectrometer (^7Li, ^{27}Al). Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.15 ppm, ^1H), C_6D_6 (128.0 ppm, ^{13}C), external LiCl/D_2O (1 M, 0 ppm, ^7Li) and external $[Al(H_2O)_6]^{3+}$ (0.5 M, 0 ppm, ^{27}Al). Mass spectra were obtained by electron impact. Melting points are observed in sealed capillaries under vacuum and are uncorrected. *t*-BuLi was obtained from Merck as a 1.6 M hexane solution and used as purchased.

Synthesis of C_5Bz_5H. The compound was synthesized by a modification of the method by Hirsch and Bailey.[24] The solvents diisopropylbenzene and benzene were replaced by isopropylbenzene and toluene, respectively. Originally the final purification was carried out by distillation of the crude product. Instead of this procedure, the resulting viscous orange crude product was suspended with hot methanol and treated with ultrasonic waves to dissolve impurities. After cooling of the suspension to room temperature, the methanol was decanted. This process was repeated several times until removal of the last solvent by vacuum (10^{-3} mbar) left colorless C_5Bz_5H (63% yield). Mp: 72−74 °C. MS (*m/e*, ion, relative intensity): 516, $[M]^+$, 39%; 425, $[M - Bz]^+$, 18%;, 91, $[Bz]^+$, 100%.

Synthesis of $Li(C_5Bz_5)$. C_5Bz_5H was dissolved in toluene to give a 0.2 M solution. An equimolar amount of a hexane solution of *t*-BuLi was added (the reaction flask was connected to a mercury overpressure valve). The slow metalation was

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(21) The degree of aggregation (n) was also measured by cryoscopic and osmometric molecular weight determinations in benzene ($n = 1.04$ for a 0.013 M solution (cryoscopically), $n = 1.12$ for a 0.036 M solution (cryoscopically), and $n = 1.08$ for a 0.04 M solution (osmometrically)). These results confirm monomeric $Li(\eta^5\text{-}C_5Bz_5)$ to be the dominant species over the measured concentration range.

(22) The experimental data obtained are not sufficient to solve the structure properly. Data for the X-ray structural study of $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$: $M_r = 1335.7$, triclinic, space group $P\bar{1}$, $a = 13.712(10)$ Å, $b = 16.443(10)$ Å, $c = 29.86(3)$ Å, $\alpha = 98.46(6)°$, $\beta = 99.63(7)°$, $\gamma = 98.31(6)°$, $Z = 3$, $V = 6466(9)$ Å^3, ρ(calcd) = 1.100 g cm^{-3}, $F(000) = 2298$, $\mu = 0.070$ mm^{-1}, θ range 1.53−22.50°, 15 857 unique reflections, 6436 observed reflections, 1126 parameters, GOF = 1.036, R1 ($I > 2\sigma(I)$) = 0.0951, wR2 = 0.2881, $w = \sigma^{-2}|F|$, largest difference peak 1.068 e Å^{-3}, deepest difference peak −0.611 e Å^{-3}. While one $[Al(\eta^5\text{-}C_5Me_5)_2]^+$ is normal, the second is split over two positions (occupation number 0.25). Whether this is a disorder or an overstructure problem could not be decided because of the low crystal quality.

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completed after 7 days at 25 °C, as determined by ^{1}H NMR spectroscopy. During this period the originally colorless mixture slowly turned red. The solution was concentrated to ca. 30% of the original volume. After addition of a small amount of benzene the product was obtained as a colorless powder (75% yield). Single crystals were obtained by recrystallization from benzene. The crystal used for the collection of the X-ray diffraction data was obtained from a C_6D_6 solution. Mp: 78−79 °C. MS (*m/e*, ion, relative intensity; 80 °C): 84, $[C_6D_6]^+$, 100%. MS (*m/e*, ion, relative intensity; 250 °C): 522, $[Li(C_5Bz_5)]^+$, 70%; 445, $[Li(C_5Bz_5) - Ph]^+$, 22%; 91, $[Bz]^+$, 100%; 84 $[C_6D_6]^+$, 0%. ^{7}Li NMR (0.2 M, C_6D_6): −10.3. ^{1}H NMR (0.2 M, C_6D_6): 3.73 (s, 10H); 7.06 (m, 25H). ^{13}C NMR (0.2 M, C_6D_6): 32.4 (CH_2); 113.9 (C_5); 125.4 (Ph C4); 128.4, 128.8 (Ph C2/3/5/6); 144.7 (Ph C1).

Synthesis of $Al(C_5Bz_5)$ and $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}(C_5Me_5)_2]$. A 100 mg (0.62 mmol) amount of $Al(\eta^5\text{-}C_5Me_5)$[2b] was suspended in 20 mL of toluene. A solution containing 0.62 mmol of $Li(\eta^5\text{-}C_5Bz_5)$ in 8 mL of toluene was added, whereupon slow precipitation of finely divided $Li(\eta^5\text{-}C_5Me_5)$ was observed. Although the solution was heated to 50 °C, the metal exchange is extremely slow (further heating leads to increased formation of aluminum metal as a result of the disproportionation of Al^I species). After 12 days the toluene-insoluble products were removed by filtration. The solid material consists of $Li(\eta^5\text{-}C_5Me_5)$, trace amounts of Al^0, and colorless single crystals of $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$ (ca. 10 mg), which were used for the X-ray diffraction studies.

The toluene-soluble products were isolated by removal of the toluene under vacuum (10^{-3} mbar). Afterward the resulting light yellow oil was dissolved in pentane. Slow concentration of this solution afforded $Al(\eta^5\text{-}C_5Bz_5)$ as an off-white waxy product. Spectroscopic studies of the product revealed small amounts of $Li(\eta^5\text{-}C_5Bz_5)$ as an impurity. MS (*m/e*, ion, relative intensity; 160 °C): 542, $[Al(C_5Bz_5)]^+$, 25%. ^{27}Al NMR: −155 ($w_{1/2} = 1500$ Hz). ^{1}H NMR: 3.70 (s, 10H): 7.04 (m, 25H). ^{13}C NMR: 31.7 (CH_2); 119.9 (C_5); 126.2 (Ph C4); 128.6, 129.2 (Ph C2/3/5/6); 141.2 (Ph C1).

X-ray Data Collection and Solution and Refinement of the Structure. The crystals were selected under nitrogen in polyfluorinated polyethers. The oil-coated crystals were manipulated onto a glass fiber and transferred to the cold nitrogen stream of the Stoe Stadi IV diffractometer. The data were collected at 210 K with Mo Kα radiation (graphite monochromated, $\lambda = 0.710\ 69$ Å) under the conditions given in Table 1. Calculations were carried out with the SHELX program system. Atom form factors, including anomalous scattering, were taken from ref 25. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included in the refinement at calculated positions. In $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]$ all non-hydrogen atoms were refined anisotropically; in $[Li(\eta^5\text{-}C_5Bz_5)_2][Al(\eta^5\text{-}C_5Me_5)_2]$ not all non-hydrogen atoms could be refined anisotropically and the C_5 and C_6 rings were refined as rigid groups.

Table 1. Data for the X-ray Structural Study of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]\cdot 2C_6D_6$

formula	$C_{98}H_{70}D_{18}Li_2$
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
fw	1296.2
a, Å	14.018(9)
b, Å	22.364(11)
c, Å	24.087(14)
α, deg	90
β, deg	101.32(5)
γ, deg	90
Z	4
V, Å^3	7404(7)
ρ(calcd), g cm^{-3}	1.139
cryst dimens, mm	0.5 × 0.3 × 0.3
F(000)	2728
μ, mm^{-1}	0.064
θ range, deg	2.51−20.02
scan width, deg	0.68, ω-scan
max scan time, s	34 (per rfln)
no. of rflns collct	6909
no. of unique rflns	6909
no. of params	901
GOF	0.963
wR2 (all data)	0.1966
R1	0.0606
largest diff peak, e Å^{-3}	+0.194
deepest diff peak, e Å^{-3}	−0.181

Computational Details. *Ab initio* SCF calculations were performed using basis sets of TZP-quality as implemented in the TURBOMOLE[26] program system. In order to save computational time, the calculations were restricted to unsubstituted C_5H_5 systems.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and an additional ORTEP view of $[\{Li(\eta^5\text{-}C_5Bz_5)\}_2(C_6D_6)]\cdot 2C_6D_6$ (13 pages). Ordering information is given on any current masthead page.

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