Alkali Metal-Stabilized 1,3,5-Triphenylbenzene Monoanions: Synthesis and Characterization of the Lithium, Sodium, and Potassium Complexes[†]

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Received October 5, 2010

Alkali metal stabilized monoanions of 1,3.5-triphenylbenzene can be obtained by various reactions starting from the alkali metal. Reduction of the Grignard compound $[\{(2,4,6-Ph_3-C_6H_2)Mg_3-K_6H_2)Mg_3-K_6H_2\}$ $(dme)Br_{2}(\mu-O,O'-dme)$ (3) in DME (1,2-dimethoxyethane) with alkali metals yields solventseparated ions $[(dme)_3A]^+[C_6H_2-2,4,6-Ph_3]^-$ (A = Li, Na (4)) with a localized 2,4,6-triphenylphenyl carbanion via metal-metal exchange. Contrarily to this observation, radical monoanions of 1,3,5triphenylbenzene are generated via transmetalation of the Grignard reagent [$\{2,4,6-Ph_3-C_6H_2\}$ Mg-(thf)₂Br] (2) with alkali metals in THF (including ether cleavage as the dominant reaction step). Reduction of 2 with lithium yields the solvent-separated ion pair $[(tmta)_4Li_7Br_4O]^+[C_6H_3-2,4,6 Ph_3$ ⁽⁶⁾ (tmta = 1,3,5-trimethyl-1,3,5-triazinane) with an oxygen-centered lithium cage as complex cation. However, reactions of 2 with sodium as well as potassium lead to formation of halogen-free contact ion pairs $[(thf)_3Na(u-\eta^6-C_6H_3-2.4,6-Ph_3)]$ (7) and $[(thf)_4K(u-\eta^6-C_6H_3-Ph_3)]$ (8), respectively. Treatment of 1,3,5-triphenylbenzene in THF with lithium leads to fragmentation of the inner arene core, whereas usage of the corresponding heavier alkali metals sodium and potassium, respectively, also generates 7 or 8. Depending on the metal counterion, reduction of the propeller-shaped 1,3,5triphenylbenzene system leads to partial planarization in combination with bond elongations of the inner arene. Derivatives 7 and 8 consist of a 3,3'-di(phenyl)biphenyl moiety with phenyl substituents twisted by 11° in the same direction (7) or contrary to each other (8). The same high symmetry was found in the solid state as well as in solution, which was verified by X-ray structure determinations and EPR measurements including simulation studies. In the solid state, the alkali metal stabilized 1,3,5-triphenylbenzene radical-monoanions (6, 7, and 8) are pyrophoric and strong black-opalescent, whereas solutions show solvato- and thermochromic behavior.

Introduction

Organometallic compounds can be divided into two major classes, namely, derivatives with discrete metal-carbon σ -bonds on one hand and those with multihapto coordination modes of π -systems to the metals on the other hand. The latter class contains cyclic aromatic ligands with different ring sizes, which are able to stabilize low-valent metal ions and even metal(0) fragments, with the most important examples being (i) cyclopentadienides (Cp⁻, e.g. metallocenes),

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(ii) arenes (e.g., benzene adducts), and (iii) cyclooctatetraenediides (Cot^{2–}). Metallocenes are generated by deprotonation via metalation under formation of an aromatic ring, which is the reason for their stability, leading to an enormous variety of metallocenes,¹ varying from ionic alkali metal derivatives to covalently bound metallocenes of late d- and p-block metals. In general, the generation of metal π -complexes of arenes and arene anions involves metalation (e.g., Cp[–]) or electron transfer reactions (e.g., Cot^{2–}) with strongly electropositive metals (such as alkali metals A or alkaline earth metals Ae). These compounds can function as group transfer reagents in a salt metathesis reaction in order to prepare π complexes of less electropositive metals (such as late transition metals and p-block metals).

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The π -system can be extended not only by ring expansion but also by linkage and annulation of aromatic rings. Alkali metal π -complexes with several polycyclic unsaturated hydrocarbons were intensively investigated by Bock and coworkers, and quite a few unusual molecular structures were observed.² In preparative chemistry these alkali metal π -complexes are used as strong reducing reagents, as catalysts in polymerization reactions, in the synthesis of low-valent transition metal organometallics, or as redox

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Scheme 1. Conversion of the Grignard Reagent [{2,4,6-Ph₃-C₆H₂}Mg(thf)₂Br] (2) into Its dme Analogue 3 as Well as Solvent Dependency of Their Reduction with the Lighter Alkali Metals Lithium and Sodium



mediators working in homogeneous phase with an exactly defined stoichiometry in contrast to the solid metals themselves. Despite a wide range of applications, structurally characterized compounds are rare due to their high reactivity and sensitivity toward moisture and air. Recently Zhou et al. have investigated the solid-state structure of potassium naphthalenide [(thf)K₂(C₁₀H₈)] (C₁₀H₈ = naphthalene).³ Whereas alkali metal π -complexes of anthracene (C₁₄H₁₀) are soluble in common organic solvents, complexes of the alkaline earth metals [(thf)_nAe(anthracene)] (Ae *n*: Mg 3, Ca 4, Sr 2, Ba 1)⁴ are less soluble and thermolabile. For this reason dismutation reactions regenerate the original metals as finely dispersed powders, so-called activated metals (M*) according to Bogdanović's activation procedure.^{4,5} Completely different properties were achieved by reduction of anthracene with the β -diketiminate-stabilized homodinuclear magnesium(I) complex [(mesnacnac)Mg]₂, yielding thermally stable and soluble [{(mesnacnac)Mg]₂(anthracene)], very recently shown by Jones and co-workers.⁶

In the presence of Brønsted acids the metal π -complexes undergo subsequent reactions that can be used in synthetic chemistry, e.g., Birch-type reduction of organic substrates.⁷ With an excess of metal a cascade of several electron transfer (reduction) and protonation steps occurs, as shown by the synthesis of the stable organocalcium(I) inverse sandwich [(thf)₃Ca(μ - η^6 , η^6 -C₆H₃-1,3,5-Ph₃)Ca(thf)₃] (1) consisting of a strictly planar bridging arene ligand between two (thf)₃Ca^I moieties that are located on opposite sides of a C₃ axis.^{8,9} The reaction sequence involves ether degradation of THF via α -deprotonation reactions by the post-Grignard reagent arylcalcium halide (yielding 1,3,5-triphenylbenzene, tpb) and reduction finally yielding the 1,3,5-triphenylbenzene dianion.⁹

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the key intermediate of the formation reaction consists of a solvent-separated ion pair of the constitution [(thf)₃Ca- $(\mu - C_6H_2 - C_6H_4 - Ph_2)(\mu - O - CH = CH_2)Ca(thf)_3 ||C_6H_3 - Ph_3|^{10}$ Alkali metals (A) and alkaline earth metal monocations $(Ae^+, ns^1, open-shell systems)$ are isoelectronic, whereas alkali metal ions (A⁺) are isoelectronic to the divalent alkaline earth metal ions $(Ae^{2+}, ns^0, closed-shell systems)$. Hence, the replacement of Ca^+ in derivative 1 by K yields an isoelectronic complex anion that should exhibit functional relationships to 1 with a similar reducing power. Substitution of Ca^+ by K^+ leads to the formation of a neutral complex with a reduced reduction power because solely the 1,3,5triphenylbenzene anion acts as electron donor. Early investigations on the reduction of 1,3,5-triphenylbenzene with, for example, potassium showed that in contrast to calcium this alkali metal is able to reduce this arene once or twice, yielding radical anions of tpb.

Results and Discussion

The reaction of bromo-2,4,6-triphenylbenzene (tpb Br) with Rieke magnesium in THF yielded the expected Grignard reagent [{2,4,6-Ph₃-C₆H₂}Mg(thf)₂Br] (**2**).⁸ A similar reaction at low temperatures with activated calcium powder led to formation of the highly reactive heavy post-Grignard reagent [{2,4,6-Ph₃-C₆H₂}Ca(thf)₃Br], which degrades promptly under formation of 1,3,5-triphenylbenzene via ether cleavage of THF.¹⁰ Ether cleavage reactions are common in the organometallic chemistry of strongly electropositive metals, particularly s-block metals, and in some cases this type of degradation dominates the synthesis.¹¹ Only in THF did an excess of calcium powder lead to formation of the inverse sandwich complex [(thf)₃Ca(μ - η^6 , η^6 -C₆H₃-1,3,5-Ph₃)Ca(thf)₃] (1) via subsequent reduction steps, yielding the planar 1,3,5-triphenylbenzene dianion.

In order to investigate the influence of the solvent on the degradation reaction, the Grignard compounds [$\{2,4,6-Ph_3-C_6H_2\}Mg(thf)_2Br$] (2)⁸ and [$\{(2,4,6-Ph_3-C_6H_2)Mg(dme)Br\}_2-(\mu-O,O'-dme)$] (3) were reacted with alkali metals, resulting in a different reactivity pattern (Scheme 1). The latter compound 3 was prepared from 2 via repeated crystallization from 1,2-dimethoxyethane (DME).

The molecular structure and numbering scheme of $[\{(2,4,6-Ph_3-C_6H_2)Mg(dme)Br\}_2(\mu-O,O'-dme)]$ (3) (Figure 1) contains a pentacoordinate magnesium atom with a bridging dme molecule. The environment of Mg consists of a distorted trigonal bipyramid with the axial atoms being O1 and Br1 (O1-Mg1-Br1 165.7(1)°). Distortions are caused by the small bite (O1···O2 distance) of the bidentate dme ligand and the bulkiness of the 2,4,6-triphenylphenyl group. Due to the larger coordination number, the Mg-C bond length of 2.178(4) Å is slightly elongated compared to 2 (Mg-C 2.148(3) Å).⁸ This effect is even more pronounced for the



Figure 1. Molecular structure and numbering scheme of $[\{(2,4,6-Ph_3-C_6H_2)Mg(dme)Br\}_2(\mu-O,O'-dme)]$ (3). The H atoms are omitted for clarity reasons. The ellipsoids represent a probability of 40%. Selected bond lengths [Å] and angles [deg]: Mg1-C1 2.178(4), Mg1-Br1 2.5973(14), Mg1-O1 2.209(3), Mg1-O2 2.132(3), Mg1-O3 2.087(3); O2-Mg1-C1 139.77(13), O3-Mg1-C1 121.50(14), O3-Mg1-O2 92.05(12), O1-Mg1-Br1 165.68(11), C1-Mg1-Br1 105.68(11).

Mg–Br distances (2: 2.4683(9) Å, 3: 2.597(1) Å) and the Mg–O bond lengths (average values, 2: 2.037 Å, 3: 2.143 Å) and is in agreement with comparable magnesium *m*-terphenyl-based compounds.¹² As is common for aryl groups bound to very electropositive metals, a rather narrow endocyclic C2–C1–C6 angle of 114.0(4)° is observed. A rather similar structure was observed for the *m*-terphenylcalcium iodide [{2,4,6-Ph₃-C₆H₂}Ca(thf)₃I].¹⁰

Reaction of 3 with lithium and sodium sand, respectively, in DME (Scheme 1) led to metal-metal exchange by precipitation of magnesium metal, yielding solvent-separated ion pairs $[(dme)_3A]^+[C_6H_2-2,4,6-Ph_3]^-$ (A = Li, Na (4)). Alkali metals reduce Mg(II) to Mg(0), in agreement with the activation methods according to Rieke¹³ and Bogdanović,^{4,5} and the strong chelating effect of the bidentate Lewis base DME leads to a separation of the generated organyl alkali metal into solvent-separated ions. The presence of a localized phenyl anion instead of a radical anion of 1,3,5-triphenylbenzene is clearly demonstrated by NMR experiments $(\delta(^{13}C) C_i 183.1 \text{ ppm})$ as well as by the absence of an EPR resonance. Furthermore, 4 reacted with iodine in THF solution nearly quantitatively to form iodo-2,4,6-triphenyl-benzene (5).¹⁴ On one hand, these findings support the assumption that 1,2-dimethoxyethane exhibits a larger kinetic stability toward ether degradation reactions. On the other hand binding interaction versus solvation effects are in direct competition with each other. Metal-halogen exchange of iodo-2,6-di(mesityl)benzene and n-BuLi in hexane yields the dimeric, aryl-bridged lithium derivative [$\{Li(\mu-C_6H_3 Mes_2$ }, $\frac{15}{2}$ and metathesis reactions give the corresponding organyl sodium complex [{ $Na(\mu-C_6H_3-Mes_2)$ }].¹⁶

Reactions in THF follow different pathways: Treatment of one equivalent of lithium sand with a solution of [$\{2,4,6-$ Ph₃-C₆H₂ $\}$ Mg(thf)₂Br] (**2**) in THF led to precipitation of magnesium metal and to a slightly green coloration of the solution during a short time. Addition of further lithium equivalents led to a deeply colored (+2 equiv: green; +3 equiv: violet)

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and extremely air- and moisture-sensitive solutions. Surprisingly, however, by addition of further excess of lithium the metal dissolves completely during several hours, forming "black" solutions. Biphenyl displays a similar behavior by treatment with excess lithium metal.¹⁷ Hydrolysis of a reaction mixture containing 2 and 10 equivalents of lithium in THF after 24 h reaction time and analyses via HPLC and GC/MS techniques underly the various reactions by several fragments of the triphenylbenzene system, e.g., terphenyls, biphenyls, phenyls, styrene, and oligomers (via polymerization of fragments). Due to its Pearson hardness, lithium preferably interacts with centers of large charge densities (σ -bond skeleton), with an excess of reduction equivalents leading to σ -bond cleavage reactions. In contrast, treatment of bromo-2,4,6-triphenylbenzene with excess of *n*-BuLi in ether yields only the expected product of metalhalogen exchange reactions, namely, [{2,4,6-Ph₃-C₆H₂}Li- $(Et_2O)_2].^{18}$

Reaction of $[\{2,4,6-Ph_3-C_6H_2\}Mg(thf)_2Br]$ (2) with four equivalents of lithium in THF at -60 °C, interruption of the reaction by filtration (separation of excess of reducing agents) after 2 h, followed by several recrystallization steps after addition of small amounts of 1,3,5-trimethyl-1,3,5triazinane (tmta) yield black, opalescent, pyrophoric, and toluene-soluble $[(tmta)_4Li_7Br_4O]^+[C_6H_3-2,4,6-Ph_3]^-$ (6) as an ion pair complex (Scheme 1) with a yield of 83% (based on bromine content). The mother liquor contains a similar pattern of arene fragments to that described above.

The structural motif (represented in Figure 2) of 6 shows once again the unwillingness of lithium π -coordination of the soft arenes in the presence of harder Lewis bases, but prefers aggregation and cage formation with various geometries.¹⁹ In general, cages are formed containing triangular lithium faces, which build platonic bodies.²⁰ In compound **6** the cationic lithium cage [(tmta)₄Li₇Br₄O]⁺ contains an inner oxygen-centered lithium octahedron with nearly ideal octahedral geometry due to anionic (O^{2-}) compensation of the electrostatic Li...Li repulsion forces. Three lithium atoms of the octahedron form a face-sharing tetrahedron with a further lithium atom with bridging bromide μ_3 -Br on each face, similar to the octahedral face in trans position to this Li₄ tetrahedron. The coordination sphere is completed by three tridentate ligands tmta (1,3,5-trimethyl-1,3,5-triazinane). Contrary to derivative 4, in complex 6 the anion $[C_6H_3$ -2,4,6-Ph₃]⁻ is a π -radical monoanion of 1,3,5-triphenylbenzene, characterized by EPR and susceptibility measurements $(\mu_{\rm eff} = 1.31 \,\mu_{\rm B})$. The recorded EPR spectrum of a solution of crystalline 6 in toluene and a simulated spectrum are compared



Figure 2. Representation of the proposed structural motif of $[(tmta)_4Li_7Br_4O]^+[C_6H_3-2,4,6-Ph_3]^-$ (6), based on a rather poor diffractometer data set.



Figure 3. Simulated and measured EPR spectrum (X band) of a solution of crystalline $[(tmta)_4Li_7Br_4O]^+[C_6H_3-2,4,6-Ph_3]^-$ (6) in toluene at room temperature (g = 2.0023).

in Figure 3. In accordance with the molecular structure of the 1,3,5-triphenylbenzene monoanion in **6** (Figure 2) the simulation suggests two chemically equivalent phenyl substituents as in the case of a planar *m*-terphenyl system with a twisting phenyl group in the 5 position. The presence of the 1,3,5-triphenylbenzene anion and the oxygen-centered lithium cage indicates ether cleavage reactions (Wittig rearrangement, particularly in the case of lithium organyls)^{11e} in a stoichiometric ratio during the reaction of lithium metal with organyl magnesium [{2,4,6-Ph₃-C₆H₂}Mg(thf)₂Br] (**2**).

Completely different reactivity was observed for sodium and potassium, because this system remains stable also after addition of an excess of these softer metals in comparison to harder lithium. After reaction times of several days, the excess reducing agent was removed and no kind of ligand fragmentation was found. In THF, ether cleavage was the dominant reaction by treatment of **2** with the corresponding alkali metal, and the time-delayed formation of an initially deep green and finally deep violet solution in combination with magnesium metal precipitation was observed. Extraction with mixtures of toluene/THF and cooling of these solutions led to the crystallization of halide-free [(thf)₃Na-(μ - η^6 -C₆H₃-2,4,6-Ph₃)] (7) and [(thf)₄K(μ - η^6 -C₆H₃-Ph₃)] (8),

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Scheme 2. Reactivity Pattern of Sodium- and Potassium-Stabilized 1,3,5-Triphenylbenzene Monoanions



respectively, which are extremely sensitive toward moisture and air as well as pyrophoric in the solid state. These compounds were also accessible via the direct reduction of 1,3,5triphenylbenzene with the corresponding metal in THF (Scheme 2). Treatment of bromo-2,4,6-triphenylbenzene with potassium sand in THF yields 8, also. These findings underlie the instability of the in situ generated alkali metal organyls (via transmetalation reaction) in the presence of further reducing equivalents. Ether degradation yields the 1,3,5-triphenylbenzene system. An excess of sodium or potassium gave deep violet solutions of the respective dinuclear complexes $\{A_2(C_6H_3-1,3,5-Ph_3)\}$ (A = Na, K), which showed a disproportionation equilibrium with 7 and 8, respectively, and the elemental alkali metals. Heating of a deep violet THF solution of 1,3,5-triphenylbenzene containing two equivalents of sodium metal led to a color change to green under metal separation, whereas cooling completely dissolved the metal in combination with re-formation of the initial violet color. Addition of 1,3,5-triphenylbenzene to a solution of the dianion led to a green solution of the corresponding singly reduced arene system. This behavior was already noticed earlier by Lühder,²¹ and this fact is also described for multiply reduced perphenyl-substituted benzenes.²² The colors are strongly influenced by the concentration, the temperature (thermochromism), and the solvents (solvatochromism). Reduction of 1,2,4,5-tetraphenylbenzene with lithium and sodium, respectively, displays similar phenomena.²² Due to the extremely large extinction coefficients and the above-mentioned equilibrium, the color of the solution is not an unequivocal indicator for the presence of singly or doubly reduced systems. Interpretation and additional studies of color effects were impeded by the extraordinarily large extinction coefficients in combination with the high sensitivity of 7 and 8, respectively, in solution. Bock specified the knowledge of these systems as "tip of the iceberg of equilibria networks in solution".2e

All attempts to isolate dinuclear alkali metal complexes of 1,3,5-triphenylbenzene failed, whereas calcium stabilizes the dianion in the case of the inverse sandwich Ca(I) complex

 $[(thf)_{3}Ca(\mu - \eta^{6}, \eta^{6} - C_{6}H_{3} - 1, 3, 5 - Ph_{3})Ca(thf)_{3}]$ (1). Susceptibility measurements gave 1.62 $\mu_{\rm B}$ for 7 and 1.73 $\mu_{\rm B}$ for 8, respectively, and represents a singly reduced triphenylbenzene anion with one unpaired electron, whereas in 1 (2.33 $\mu_{\rm B}$) the dianion was found to correlate to a triplet ground state (S = 1).⁸ Aromatic hydrocarbons containing a 3- or 6-fold axis of rotation (e.g., benzene, triphenylene, 1,3,5-triphenylbenzene) possess 2-fold degenerate highest bonding and lowest antibonding π -orbitals, resulting in a triplet ground state after reduction.²³ 1,3,5-Triphenylbenzene can be reduced reversibly only once or twice according to previous investigations.²⁴ Addition of a larger amount of cold *n*-pentane to a solution of 7 in THF led to discoloration and separation of a black, pyrophoric solid with variable compositions containing traces of elemental sodium (1.83-2.06 $\mu_{\rm B}$, mixture of several compounds).

The molecular structure of 1 showed a strictly planar 1,3,5triphenylbenzene anion (D_{3h} symmetry), whereas the neutral tpb molecule exhibits a propeller-like arrangement of the phenyl substituents (C_3 symmetry) with a twisting angle of 38°.25 The C-C distances of the neutral arene show an average value of 1.387 Å, and the inter-ring distance lies at 1.487 Å, which is a characteristic value for a single bond between two sp²-hybridized C atoms. In 1 the average C-Cbond (1.464 Å) within the inner arene ring is elongated, and between the rings a smaller value of 1.435 Å is observed in accordance with an effective charge delocalization. From the equilibrium of sodium with 1,3,5-triphenylbenzene crystals of black $[(thf)_3Na(\mu-\eta^6-C_6H_3-2,4,6-Ph_3)]$ (7) were obtained. The molecule of 7 contains a mirror plane, and its structure is shown in Figure 4. The sodium atom is located in a distorted tetrahedral environment of four ligands with the arene binding in a η^6 -fashion (average Na-O 2.292 Å, Na-C 2.887 Å). In this compound the triphenylbenzene fragment is nearly planar (the biphenyl unit is strictly planar and the

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Figure 4. Molecular structure and numbering scheme of $[(thf)_3-Na(\mu-\eta^6-C_6H_3-2,4,6-Ph_3)]$ (7). The H atoms are neglected and the η^6 -Na-benzene interactions are drawn as a stick to the centroid of the inner arene for clarity reasons. The ellipsoids represent a probability of 40%. Selected bond lengths [Å] and angles [deg]: Na-O1 2.2908(14), Na-O2 2.293(2), Na-C1 2.864(3), Na-C2 2.893(2), Na-C3 2.908(2), Na-C4 2.857(3), C1-C2 1.416(2), C2-C3 1.447(2), C3-C4 1.435(2); O1-Na-O1A 108.24(8), O1-Na-O2 103.02(6).

phenyl groups in the 3/3' positions (at C2/C2A, see Figure 4) are twisted by the same angle of 11° of the plane with a mirror plane orthogonal to the 4,4'-plane of biphenyl) with average C-C bonds of 1.433 Å (arene) and 1.465 Å (ring-ring bond), adopting rather similar values.

The molecular structure of $[(thf)_4 K(\mu - \eta^6 - C_6 H_3 - Ph_3)]$ (8) is represented in Figure 5. The potassium atom occupies the center of a distorted square pyramid binding to four THF molecules (average K-O 2.727 Å) and in a η^6 -fashion (average K-C 3.250 Å) to the nearly planar arene. The 1,3,5-triphenylbenzene monoanion consists of a planar biphenyl moiety with two twisted phenyl groups in 3/3' position (at C2 and C6, Figure 5) against each other (twisting angle 11°). The C-C bonds in the central ring are elongated (average C-C 1.433 Å), as also observed for 7.

An important issue in the context of the alkali metalarene adducts is given by the comparatively high symmetry of the reduced 1,3,5-triphenylbenzene ligand resulting from crystal-packing effects in the solid state or mainly by extensive metal π -arene interactions. The EPR spectrum of a solution of crystalline [(thf)₃Na(μ - η^6 -C₆H₃-2,4,6-Ph₃)] (7) in THF (Figure 6) is well resolved and shows a highly symmetric resonance, typical for organic π -radicals with the g value of 2.0023 (g value of the "free" electron), in accordance to 1 and earlier studies,²⁴ of organic compounds with delocalized electrons. Furthermore, the EPR spectra are nearly independent of the kind of solvent (THF, toluene), as well as of temperature effects; raising the temperature causes a slight decrease in spectral intensity without markedly altering the hyperfine structure. For comparison reasons, simulated spectra of a strictly planar 1,3,5-triphenylbenzene system with three principal mirror planes (D_{3h}) : four different types of protons in the ratio 3:3:6:6) and 3:3'di(phenyl)biphenyl with a lower symmetry of a vertical mirror plane (C_s : 8 or 10 different types of protons in the



Figure 5. Molecular structure and numbering scheme of $[(thf)_4K(\mu-\eta^6-C_6H_3-2,4,6-Ph_3)]$ (8). The H atoms are neglected and the η^6 -K-benzene interactions are drawn as a stick to the centroid of the inner arene for clarity reasons. The ellipsoids represent a probability of 40%. Selected bond lengths [Å] and angles [deg]: K-O1 2.7347(19), K-O2 2.728(2), K-O3 2.7313(19), K-O4 2.712(2), K-C1 3.243(3), K-C2 3.305(2), K-C3 3.295(3), K-C4 3.251(2), K-C5 3.209(3), K-C6 3.196(3), C1-C2 1.430(3), C2-C3 1.429(3), C3-C4 1.420(3), C4-C5 1.449(3), C5-C6 1.448(3); O1-K-O2 91.59(6), O1-K-O3 143.14(7).



Figure 6. Simulated and measured EPR spectra (X band) of a solution of crystalline [(thf)₃Na(μ - η ⁶-C₆H₃-2,4,6-Ph₃)] (7) in THF at room temperature (g = 2.0023).

ratio 1:1:2:2:2:2:4:4 or 1:1:2:2:2:2:2:2:2, depending on the rotational position of the outer aryl moieties) or a bisecting C_2 axis are included in Scheme 3. The resulting C_s/C_2 symmetry of the solid-state structure of 7 was verified by EPR experiments in solution. Solutions of crystalline [(thf)₄K(μ - η ⁶-C₆H₃-Ph₃)] (8)

Scheme 3. Different Kinds of Protons Depending on the Symmetry of the 1,3,5-Triphenylbenzene Monoanion



 $C_{\rm s}(7)$

D_{3h} (**1**)

Scheme 4. Observed Equilibrium of Mono- and Dianionic 1,3,5-Triphenylbenzene Sodium Adducts in THF Solution



in THF also display a complicated EPR spectrum caused by decreased symmetry.

As a consequence of several disproportionation equilibria, attempts to isolate solid (crystalline) di(sodium) adducts of 1,3,5-triphenylbenzene failed (Scheme 4). Figure 7 represents an EPR spectrum at low temperatures received by measuring a frozen solution of crystalline $[(thf)_3Na(\mu-\eta^6-C_6H_3-2,4,6-$ Ph₃)] (7) in THF in a tube containing a sodium mirror. The EPR spectrum is well resolved and almost identical to the spectrum of the dianionic arene in the calcium(I) complex $[(thf)_3Ca(\mu-\eta^6,\eta^6-C_6H_3-1,3,5-Ph_3)Ca(thf)_3]$ (1).⁸ Simulation experiments verified this assumption, finding four different types of protons in the ratio 3:3:6:6, verifying the strictly planar structure of the 1,3,5-triphenylbenzene unit (D_{3h}) symmetry), whereby the coupling constants are multiples of each other. Two coupling constants are found $[n = 2 \times 3H]$ $(A = 0.85 \text{ G}), 2 \times 6 \text{H} (A = 1.70 \text{ G})$, identical to 1. Hence, a 2-fold reduction of the arene leads to increased symmetry as a consequence of complete planarization. These findings suggest for the di(sodium) adduct of 1,3,5-triphenylbenzene a similar structural motif to that in 1 with bifacial coordination of the metal ions on opposite sides of the arene plane (Scheme 4), in contrast to the di(lithio) hexakis(trimethylsilyl)benzenediide [(thf)₂Li]₂[C₆(SiMe₃)₆], showing syn-facial location of the lithium atoms of the benzene dianion with a boat conformation.26

The reduction of the propeller-shaped 1,3,5-triphenylbenzene ligand leads to enhancement of the symmetry by complete planarization (dianion, 1) or partial planarization (monoanion, 6, 7, and 8). During planarization considerable strain (caused



Figure 7. Simulated and experimental EPR spectra (X band) at 77 K of a frozen solution of crystalline [(thf)₃Na(μ - η^6 -C₆H₃-2,4,6-Ph₃)] (7) in THF measured in a tube containing a sodium mirror (g = 2.0023).

by repulsion between the ortho hydrogen atoms and the H atoms of the inner arene ring) has to be overcompensated by an effective delocalization of the anionic charge.²⁷ The limitation of rotation of the phenyl substituents around the $C-C \sigma$ -bonds rises with the degree of reduction, suggesting an increase of the π -bond order by extended charge delocalization, whereas the C-C bonds of the inner arene ring show values nearly characteristic for single bonds between sp²hybridized carbon atoms.²² The stabilization of the carbanion is additionally influenced by the association between the metal counterion and the 1,3,5-triphenylbenzene radical anion.²⁸ In general, increasing charge delocalization within the carbanion weakens the electrostatic anion-cation interactions.²⁹ Investigations of alkali metal trityl adducts $(trityl = triphenylmethyl anion, Ph_3C^-)$ gave similar results; due to multihapto coordination modes, heavier alkali metals are able to increasingly planarize the ligand.²⁹

As mentioned above, the symmetry of the arene system influences its bonding situation (Table 1). In neutral,

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Table 1. Comparison of Selected Bond Lengths [Å] of 1, 7, and 8

parameter	1	7	8	
C1-C2	1.478(7)	1.416(2)	1.430(3)	
C2-C3	1.449(7)	1.447(2)	1.429(3)	
C3-C4	b	1.435(2)	1.420(3)	
C4-C5		b	1.449(3)	
C5-C6			1.448(3)	
C6-C1			1.424(3)	
av C–C	1.464	1.433	1.433	
av $C_i - C_o$	1.435	1.464	1.463	
M-C1	2.598(3)	2.864(3)	3.243(3)	
M-C2	2.586(3)	2.893(2)	3.305(2)	
M-C3	b	2.908(2)	3.295(3)	
M-C4		2.857(3)	3.251(2)	
M-C5			3.209(3)	
M-C6			3.196(3)	
av M–C	2.592	2.836	3.250	
$M-C_{centr}^{a}$	2.139	2.477	2.917	
M-L	2.405(3)	2.2908(14)	2.728(2)	
		2.293(2)	2.7347(19)	
			2.7313(19)	
			2,712(2)	

^a Arithmetical averaged M-C distance. ^b Presence of mirror planes.

propeller-shaped 1,3,5-triphenylbenzene the C–C equilibrium distance in the central benzene is determined to be 1.387 Å.²⁵ Monoreduction led to elongation of about 0.046 Å to a value of 1.433 Å (**6**, **7**, and **8**), and 2-fold reduction led to further elongation by approximately 0.031 Å (**1**, in sum 0.077 Å). Due to charge delocalization, the exocyclic phenyl substituents are shortened (**6**–**8** 0.027 Å, **1** 0.052 Å). These trends are independent of the interactions via contact-ion- (**1**, **7**, **8**) or solvent-separated ion couples (**6**).

Similar properties are observed for the reduction of tetraphenylethylene (Ph₂C=CPh₂) with sodium in diethyl ether, yielding polymeric [(Et₂O)₂Na(μ_2 - η^6 -Ph₂C=CPh₂)]_{∞} with an elongated olefinic double bond (1.49 Å).^{2a,30} Reaction of 1,2diphenylbenzene (C₆H₄-1,2-Ph₂) with potassium in diglyme [diglyme = di(2-methoxyethyl) ether] generates the arene dianion [{(diglyme)K}₂(C_6H_4 -1,2-Ph₂)] with elongation of the C-C bonds in the central arene (0.04–0.11 Å) and shortening of the exocyclic C-C bonds to the phenyl substituents (0.07 Å).³⁰ However, in sterically more encumbered arenes these effects are much more pronounced: Reduction of 1,2,3triphenylbenzene (C_6H_3 -1,2,3-Ph₃) with sodium in diglyme yields solvent-separated [(diglyme)Na)]⁺[(diglyme)Na-µ- $(\eta^{6}-C_{6}H_{3}-1,2,3-Ph_{3})$ with both elongated C-C bonds in the central arene and a shortening of the exocyclic C-C bonds to the phenyl substituents of approximately 0.10 Å.³⁰

The elongation of the C–C equilibrium distance in the central arene core could not be verified by theoretical investigations regarding metal π -arene interactions with alkali metal ions,³¹ but with alkaline earth metal ions.³²

The cation radius of potassium (1.49 Å) is at least 27% larger than that of sodium (1.17 Å), whereas the metal centroid distance increases by only about 17% (Na–C_{centr} 2.501 Å, K–C_{cent} 2.917 Å).³³ The average multihapto metal

Table 2. Comparison of Calculated versus Experimental Structural Data of Sodium and Potassium Arene Adducts (average values in Å)

system	method	parameter	Na	K
$M(\eta^3 - C_3 H_3)^{37}$	MP2/6-31G**	М-С	2.425-2.491	2.791-2.811
$M(\eta^6 - C_6 H_6)^{38}$	MP2/6-31G**	M-C	2.804	3.217
	,	M-C _{centr}	2.426	2.894
$M(\eta^{6}-C_{6}H_{6})^{39}$	MP2/6-311G**	M-C	2.803	3.137
	,	M-C _{centr}	2.425	2.805
$M(\eta^n - CPh_3)^{35}$		M-C _{centr}		2.870
7,8		M-C	2.881	3.250
		M-C _{centr}	2.501	2.917

carbon contacts in $[(thf)_3Na(\mu-\eta^6-C_6H_3-2,4,6-Ph_3)]$ (7) are comparable to those in $[(Et_2O)_2Na(\mu_2-\eta^6-Ph_2C=CPh_2)]_{\infty}$ (av Na-C 2.70-2.82 Å, Na-O 2.32 Å).³⁰ Neutral benzene ligation leads to slight elongation, e.g., in the weak coordinating, icosahedral carboranate [CB11Me12] stabilized di-(benzene)sodium(I) sandwich (Na-C_{centr} 2.69 Å).³⁴ The $(thf)_4 K^+$ fragments in 8 bind via a η^6 -coordination mode to the arene radical-monoanion (av K-C 3.250 Å, K-C_{centr} 2.917 Å, K–O 2.727 Å). Comparable data are found for trityl potassium compounds [(thf)(pmdta)K(η^6 -CPh₃)] (av $K-C 3.204 \text{ Å}, K-C_{centr} 2.781 \text{ Å}, K-O 2.721 \text{ Å}; pmdta = N,$ N, N', N'', N''-pentamethyldiethylenetriamine),³⁵ for the reduction product of 1, 1, 4, 4-tetraphenylbutadiene (C₂₈H₂₂) with potassium forming [{(dme)K}₂(μ - η^{6} -C₂₈H₂₂)](K-C 3.02-3.12 Å),^{2e} and for benzyl potassium derivatives [(pmdta)K(μ - η^3 -CH₂Ph)·(CH₃Ph)]_{\$\sigma\$} (K-C 3.171(2)-3.297(2) Å) and $[(\text{pmdta})\text{K}(\mu - \eta^6 - \text{CH}_2\text{Ph})]_{\infty}$ (K-C 3.150(2)-3.288(2) Å).

In Table 2 a comparison of calculated and experimentally obtained data is given for selected complexes. The differences of the Na–C and K–C distances reflect the sodium and potassium radii. In general, the calculated distances are slightly smaller than those found in single-crystal structure determinations. Furthermore, the nature and diversity of interactions (such as electrostatic, dipole–dipole, quadrupole, polarization, solvation effects) proved to be challenging for theoretical methods.^{8,40}

Conclusions

The reactivity of the Grignard complexes [{2,4,6-Ph₃- $C_{6}H_{2}Mg(thf)_{2}Br](2)$ and $[\{(2,4,6-Ph_{3}-C_{6}H_{2})Mg(dme)Br\}_{2} (\mu - O, O' - dme)$] (3) toward alkali metals strongly depends on the solvent. On one hand, in DME a metal-metal exchange is observed leading to any metal derivatives $[(dme)_3A]^+[C_6H_2-$ 2,4,6-Ph₃]⁻ (A = Li, Na (4)), which are solvent-separated due to the effective chelating behavior toward the alkali metal cations. On the other hand, a transmetalation reaction in THF is accompanied by prominent ether attack and arene radical monoanions are formed. Hard lithium ions prefer harder coordination environments, yielding an oxygen-centered lithium cage in solvent-separated $[(tmta)_4Li_7Br_4O]^+[C_6H_3-2,4,6-Ph_3]^-$ (6). The heavier cations of sodium and potassium are markedly softer Lewis acids, resulting in contact ions pairs with the soft arene anion in $[(thf)_3Na(\mu-\eta^6-C_6H_3-2,4,6-Ph_3)]$ (7) and $[(thf)_4-\eta^6-C_6H_3-2,4,6-Ph_3)]$ $K(\mu - \eta^6 - C_6 H_3 - Ph_3)$] (8), respectively.

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The colors of the solutions of these anions clearly show the degree of reduction, solutions of monoanions being green and of dianions being deep violet, whereas dependencies on the metal, on the temperature (thermochromism), and on the solvent (solvatochromism) were also observed. The negative charges lead to an alignment of the inner arene ring with bond elongations and increasing planarity of the arene moiety. It was shown that reduction of the phenyl-substituted arene restricted the free rotation of the phenyl substituents around the C–C σ -bond both in the solid state and in solution. Phenyl as well as silyl substituents²⁶ are able to stabilize the anionic state of the benzene core.

The peculiar redox properties of 1,3,5-triphenylbenzene lead to an equilibrium of { $A_2(C_6H_3-1,3,5-Ph_3)$ } with { $A_2(C_6H_3-1,3,5-Ph_3)$ } + A, with the monoanion being favored in the crystallization process. The corresponding dianion in the case of the di(sodium) 1,3,5-triphenylbenzene adduct was verified via EPR measurements, being an isostructural fragment of the inverse organocalcium(I) sandwich [(thf)_3Ca(μ - $\eta^6, \eta^6-C_6H_3-1,3,5-Ph_3$)Ca(thf)_3] (1). The first ionization energies of Na (IE_{Na} = 5.14 eV)^{41} and K (IE_K = 4.34 eV)^{41} are comparable to the first IE of calcium (IE_{Ca1} = 6.11 eV), ⁴¹ but the second IE_{Ca2} of 11.87 eV⁴¹ is significantly larger. This fact and the possibility of calcium to employ d-type orbitals⁴² with the arene π -system⁸ seem to stabilize the unusual inverse sandwich complex [(thf)_3Ca(μ - $\eta^6, \eta^6-C_6H_3-1,3,5-Ph_3$)Ca-(thf)_3] (1).

Experimental Section

Manipulation and handling of all compounds were performed in an argon atmosphere using standard Schlenk techniques. Solvents were dried thoroughly and distilled under argon. 1,3,5-Triphenylbenzene was purchased from Aldrich, and bromo-2,4,6-triphenylbenzene was prepared from 1,3,5-triphenylbenzene and bromine in tetrachloromethane.⁴³ The Grignard reagent [{2,4,6-Ph₃-C₆H₂}Mg(thf)₂Br] (2) was prepared according to a literature procedure.⁸ Calcium (granules) was used for the activation process⁴⁴ as purchased from Aldrich without further purification. Rieke magnesium was prepared according to a literature procedure,⁴⁵ washed several times with hot acetone, and dried under vacuum at 80 °C. The necessity to maintain a THF-saturated atmosphere in order to prevent aging of the crystals and the extreme sensitivity toward moisture and air, especially the highly pyrophoric nature of some compounds, made the analytical characterization difficult. The bromide content was determined via argentometric titration with potentiometric indication of the end-point.

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For the NMR assignments, atoms in the central ring are unprimed, atoms in the *ortho*-phenyl groups are primed, and atoms in the *para*-phenyl group are doubly primed. EPR spectra were measured on a Bruker ESP 300 E X-band spectrometer with a modulation amplitude of 0.104 G. EPR spectrum simulations were carried out with the Easyspin software package.⁴⁶

Synthesis of $[\{(2,4,6-Ph_3-C_6H_2)Mg(dme)Br\}_2(\mu-O,O'-dme)]$ (3). Solid $[\{2,4,6-Ph_3-C_6H_2\}Mg(thf)_2Br]$ (2) (1.11 g, 2.00 mmol) was dissolved in DME (20 mL) at 80 °C and stirred for additional 2 h. The resulting solution was filtered off, and storage at -20 °C led to crystallization of 3 as large colorless cubes. Separation and gently drying under vacuum gave 0.96 g (0.9 mmol, 90%) of 2.

Physical Data of 3. Melting point: 168 °C. Anal. Calcd for $C_{60}H_{64}Br_2Mg_2O_6$ (1089.56 g mol⁻¹): Mg, 4.39 Found: Mg, 4.21. ¹H NMR (400.25 MHz, 25 °C, [D8]THF): δ 3.27 (18H, s, CH_3 , dme), 3.43 (12H, s, CH_2 , dme), 7.27 (6H, m, ${}^3J_{H-H} = 7.6$ Hz, p'/p''-CH), 7.37 (4H, t, ${}^3J_{H-H} = 7.6$ Hz, m''-CH), 7.43 (8H, t, ${}^3J_{H-H} = 8.0$ Hz, m'-CH), 7.60 (4H, s, m-CH), 7.76 (8H, d, ${}^3J_{H-H} = 8.0$ Hz, n'-CH), 7.91 (4H, d, ${}^3J_{H-H} = 7.6$ Hz, o''-CH). ¹³C{¹H} NMR (100.65 MHz, 25 °C, [D8]THF): δ 58.8 (6C, CH₃, dme), 72.7 (8C, CH₂, dme), 124.4 (4C, m-CH), 125.5 (4C, o''-CH), 128.1 (4C, m'-CH), 129.5 (8C, o'-CH), 139.5 (2C, i''-C), 143.3 (2C, p-C), 150.6 (4C, i'-C), 154.2 (4C, o-CH), 164.1 (2C, i-C). IR (Nujol, KBr, cm⁻¹) v: 2922, vs(br); 2727, m; 2347, m; 2312, m; 1949, w; 1889, w; 1823, w; 1774, w; 1595, m; 1576, m; 1518, m; 1491, m; 1456, s; 1411, m; 1378, s; 1291, m; 1246, m; 1221, w; 1190, m; 1156, m; 1102, s; 1054, s; 1028, s; 988, m; 912, m; 884, m; 871, m; 827, w; 752, s; 732, m; 697, s; 634, m; 623, m; 611, m.

Synthesis of $[(dme)_3Na]^+[C_6H_2-2,4,6-Ph_3]^-$ (4). Sodium sand (0.06 g, 2.61 mmol) was melted, resulting in a metal mirror, and a solution of $[(\{2,4,6-Ph_3-C_6H_2\}Mg(dme)Br)_2(\mu-O,O'-dme)]$ (3) (0.40 g, 0.37 mmol) in DME (15 mL) was placed in the flask. Stirring for 3 days at room temperature led to formation of a light green solution combined with magnesium metal precipitation. After filtration, the solution was stored at -20 °C, which led to precipitation of light green blocks of **6**. Separation and gently drying under vacuum gave 0.29 g (0.48 mmol, 65%) of **4**.

Physical Data of 4. Dec: 105 °C. Anal. Calcd for C₃₆H₄₇NaO₆ (598.74 g mol⁻¹): C, 72.22; H, 7.91. Found: C, 71.93; H, 7.72. ¹H NMR (400.25 MHz, 25 °C, [D₆]benzene): δ 3.24 (18H, s, CH₃, dme), 3.39 (12H, s, CH₂, dme), 7.25 (3H, m, ${}^{3}J_{H-H} = 7.6$ Hz, p'/p''-CH), 7.36 (2H, t, ${}^{3}J_{H-H} = 7.6$ Hz, m''-CH), 7.41 (4H, t, ${}^{3}J_{H-H} = 8.0$ Hz, m'-CH), 7.61 (2H, s, m-CH), 7.74 (4H, d, ${}^{3}J_{H-H} = 8.0$ Hz, m'-CH), 7.92 (2H, d, ${}^{3}J_{H-H} = 7.6$ Hz, σ'' -CH). ${}^{13}C{}^{1}H{}$ NMR (100.65 MHz, 25 °C, [D₆]benzene): δ 58.6 (6C, CH₃, dme), 72.7 (8C, CH₂, dme), 124.2 (2C, m-CH), 125.3 (2C, σ' -CH), 126.5 (1C, p''-CH), 127.4 (4C, σ' -CH), 139.4 (1C, t'-C), 143.5 (1C, p-C), 150.4 (2C, t'-C), 154.3 (2C, σ -CH), 183.1 (1C, *i*-C).

Synthesis of $[(\text{tmta})_4\text{Li}_7\text{Br}_4\text{O}]^+[\text{C}_6\text{H}_3\text{-}2,4,6\text{-}\text{Ph}_3]^-$ (6). Small portions of lithium sand (0.07 g, 10.09 mmol) were added during one hour to a solution of $[\{2,4,6\text{-}\text{Ph}_3\text{-}\text{C}_6\text{H}_2\}\text{Mg}(\text{thf})_2\text{Br}]$ (2) (1.49 g, 2.69 mmol) in toluene (20 mL)/THF (10 mL) at -60 °C. An exothermic reaction took place under magnesium metal separation, and after half an hour the mixture turned green. After additional stirring for 1.5 h at -20 °C the reaction was aborted by filtration (separation of the metal excess) of the deep redviolet mixture, and 1,3,5-trimethyl-1,3,5-triazinane (1 mL, tmta) was added. The volume of the solution was reduced to half, and filtration and storage at -40 °C led to formation of black scales. Fivefold recrystallization steps (toluene/THF/tmta: 20:20:1, 10 °C) led to crystallization of black opalescent cubes of 6.2(PhMe) (crystalline yield: 0.78 g, 0.56 mmol, 83%, based on Br).

Physical data of 6.2(PhMe). Dec: >46 °C. Anal. Calcd for $C_{62}H_{94}Br_4Li_7N_{12}O$ (1391.69 g mol⁻¹): C, 53.51; H, 6.8; N,

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Table 3. Crystal Data and Refinement Details for the X-ray Structure Determinations of the Compounds 3, 6, 7, and 8

	3	6	7	8
formula	$C_{60}H_{64}Br_2Mg_2O_6, 0.4 \cdot C_4H_{10}O_2$	C ₂₄ H ₅₈ Br ₄ Li ₇ N ₁₂ O, C ₂₄ H ₁₈ , 1.5(C ₇ H ₈)	C ₃₆ H ₄₂ NaO ₃	C ₁₆ H ₃₂ KO ₄ , C ₂₄ H ₁₈
fw $(g \cdot mol^{-1})$	1143.60	1343.63	545.69	633.90
$T(^{\circ}C)$	-90(2)	-140(2)	-90(2)	-140(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\overline{1}$	$P2_1/n$	$P2_1/m$	$P2_1/n$
a (Å)	7.5104(3)	15.3259(5)	7.7567(4)	10.7269(3)
$b(\mathbf{A})$	10.7441(5)	25.4392(8)	18.6392(7)	16.5121(7)
c(A)	19.2715(9)	18.1212(6)	10.7397(5)	19.7339(6)
a (deg)	87.816(3)	90	90	90
β (deg)	79.614(3)	94.099(2)	100.621(2)	93.107(2)
γ (deg)	76.216(3)	90	90	90
$V/\text{\AA}^3$	1485.52(11)	7047.0(4)	1526.13(12)	3490.2(2)
Z	1	4	2	4
$\rho (g \cdot cm^{-3})$	1.278	1.266	1.187	1.206
$\mu (\mathrm{mm}^{-1})$	14.36	23.28	0.86	1.92
measd data	10104	41 504	10719	24 570
data with $I > 2\sigma(I)$	4446	6981	2012	4770
unique data (R_{int})	6602/0.0362	15 578/0.1373	3569/0.0600	7984/0.0747
wR_2 (all data, on F^2) ^{<i>a</i>}	0.1753		0.1651	0.1733
$R_1 (I > 2\sigma(I))^a$	0.0624		0.0555	0.0644
S^b	1.034		1.021	1.023
res dens (e·Å ⁻ 3)	1.288 / -0.600		0.259 / -0.260	0.381/-0.391
absorpt method	none	none	none	none
CCDC no.	745337	motif	745338	782317

^{*a*} Definition of the *R* indices: $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ with $w^{-1} = \sigma^2 (F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + Max(F_o^2]/3$. $bs = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$.

12.08; Br, 22.97. Found: C, 51.24; H, 6.32; N, 11.81; Br, 30.21. EPR (THF solution, rt): g = 2.0023; various hyperfine coupling pattern. Susceptibility measurements (Gouy magnetic balance, 294 K): $\chi_v = 4.182 \times 10^{-7}$, $\chi_g = 1.020 \times 10^{-6}$ cm³ g⁻¹, $\chi_m = 1.420 \times 10^{-3}$ cm³ mol⁻¹, $\mu_{eff} = 1.31 \mu_B$. ⁷Li{¹H} NMR (155.55 MHz, 25 °C, [D₆]benzene): δ 1.48 m(br). IR (Nujol, KBr, cm⁻¹) ν : 2922, vs(br); 2726, m; 2662, m; 1594, w; 1566, w; 1456, vs; 1377, vs; 1308, m; 1267, s; 1233, m; 1158, m; 1116, m; 1004, w; 978, w; 942, m; 914, m; 752, m; 725, s; 697, m.

Synthesis of [(thf)₃Na(μ - η^6 -C₆H₃-2,4,6-Ph₃)] (7). Method A. Small portions of sodium sand (0.86 g, 37.40 mmol) were added during one hour to a solution of 1,3,5-triphenylbenzene (2.86 g, 9.33 mmol) in THF (20 mL) and stirred for 18 h at room temperature. The resulting dark green solution was filtered, all volatiles were distilled off, and the black residue was extracted with a mixture of toluene (10 mL) and THF (10 mL) at room temperature. The extract was filtered once more, and storage at -20 °C led to separation of a black solid. Several steps of recrystallization initiated precipitation of black opalescent and pyrophoric cubes of 7 at -20 °C (crystalline yield: 2.13 g, 3.9 mmol, 42%).

Method B. Small portions of sodium sand (0.25 g, 10.87 mmol) were added during 30 min in a solution of [$\{2,4,6-Ph_3-C_6H_2\}$ Mg-(thf)₂Br] (2) (1.00 g, 1.81 mmol) in THF (15 mL) and stirred for 12 h at room temperature. Magnesium metal precipitated, and a dark green-brown solution was formed. After filtration all volatiles were distilled off and the black residue was extracted with a mixture of toluene (15 mL) and THF (5 mL) at room temperature. The extract was filtered once more, and storage at -20 °C led to separation of an opalescent solid. Several steps of recrystallization generated by storage at -20 °C black opalescent and pyrophoric cubes of 7 (crystalline yield: 0.81 g, 1.48 mmol, 82%).

Physical Data of 7. Dec: >40 °C. Anal. Calcd for $C_{36}H_{42}$ -NaO₃ (545.71 g mol⁻¹): C, 79.23; H, 7.76. Found: C, 79.84; H, 7.91. Susceptibility measurements (Gouy magnetic balance, 294 K): $\chi_v = 1.381 \times 10^{-6}$, $\chi_g = 2.527 \times 10^{-6}$ cm³ g⁻¹, $\chi_m = 1.379 \times 10^{-3}$ cm³ mol⁻¹, $\mu_{eff} = 1.62 \, \mu_B$.

Synthesis of $[(thf)_4 K(\mu - \eta^6 - C_6 H_3 - Ph_3)]$ (8). Method 1. Small portions of potassium sand (0.32 g, 8.18 mmol) were added during one hour in a solution of 1,3,5-triphenylbenzene (1.43 g, 4.67 mmol) in THF (20 mL) and stirred for 18 h at room

temperature. After a second color change from initial green to deep violet the solution was filtered.

Method 2. Small portions of potassium sand (0.36 g, 9.21 mmol) were added during one hour in a solution of [$\{2,4,6-Ph_3-C_6H_2\}Mg(thf)_2Br$] (2) (1.23 g, 2.23 mmol) in THF (25 mL) and stirred for 28 h at room temperature. After separation of magnesium metal the mixture was filtered, resulting in a deep violet solution.

Method 3. Small portions of potassium sand (0.43 g, 11.00 mmol) were added during one hour in a solution of 2,4,6-triphenylbromobenzene (1.72 g, 4.46 mmol) in THF (10 mL). After stirring for 14 h at room temperature the mixture was filtered.

General Procedure. All volatiles were distilled off, and the black residue was extracted with a mixture of toluene (10 mL) and THF (10 mL) at room temperature. The extract was filtered once more, and storage at -20 °C led to precipitation of a black solid. Twofold recrystallization led to formation of black opalescent and pyrophoric prisms of 8 at -20 °C (method 1, crystalline yield: 1.32 g, 2.08 mmol, 45%; method 2, crystalline yield: 0.85 g, 1.34 mmol, 60%; method 3, crystalline yield: 1.53 g, 2.41 mmol, 54%).

Physical Data of 8. Dec: > 34 °C. Anal. Calcd for $C_{40}H_{50}KO_4$ (633.92 g mol⁻¹): C, 75.79; H, 7.95. Found: C, 76.19; H, 8.23. 8: EPR (THF solution, rt): g = 2.0024; various hyperfine coupling pattern in accordance to a tpb-monoanion. Susceptibility measurements (Gouy magnetic balance, 294 K): $\chi_v = 1.276 \times 10^{-6}$, $\chi_g = 2.493 \times 10^{-6}$ cm³ g⁻¹, $\chi_m = 1.580 \times 10^{-3}$ cm³ mol⁻¹, $\mu_{eff} = 1.73 \mu_B$.

EPR Measurements. EPR spectra were measured on a Bruker ESP 300 E X-band spectrometer with a modulation amplitude of 0.104 G. EPR spectrum simulations were carried out with the Easyspin software package using a genetic algorithm and results after 16 h of iteration (40 000 generations).⁴⁶

6: EPR (toluene solution, rt): g = 2.0023; various hyperfine coupling patterns. Simulation (two equivalent phenyl groups, $\Delta H_{\rm pp} = 0.0413$ G, g = 2.0023, Lorentz form, eight different kinds of protons): n = 1H (A = 0.3436 G), 1H (A = 6.2838 G), 2H (A = 6.0279 G), 2H (A = 2.6683 G), 2H (A = 6.1949 G), 2H (A = 0.5170 G), 4H (A = 7.3986 G), 4H (A = 2.8422 G).

7: EPR (THF solution, rt): g = 2.0023; various hyperfine coupling patterns. Simulation (C_s symmetry, $\Delta H_{pp} = 0.19535$ G,

g = 2.0023, Lorentz form, eight different kinds of protons): n = 1H (A = 1.5795 G), 1H (A = 10.3807 G), 2H (A = -6.7406 G), 2H (A = -4.0131 G), 2H (A = -2.0089 G), 2H (A = -1.2012 G), 4H (A = 2.4895 G), 4H (A = 4.8224 G).

7+Na (THF solution, 77 K): g = 2.0023. Simulation (D_{3h} symmetry, $\Delta H_{pp} = 0.85$ G, g = 2.0023, Lorentz form, four different kinds of protons): $n = 2 \times 3$ H (A = 0.8574 G), 2×6 H (A = 1.7068 G).

Crystal Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.^{47,48}

The structures were solved by direct methods (SHELXS⁴⁹) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97⁴⁹). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered, non-hydrogen atoms were refined anisotropically.⁴⁹ The

crystals of **6** were extremely thin and of low quality, resulting in a substandard data set; however, the structure is sufficient to show connectivity and geometry despite the high final R value. We will be publishing only the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG, Bonn/Germany) for generous financial support of this research initiative. We are grateful to Dr. Manfred Friedrich, University of Jena, for EPR measurements and simulation experiments.

Supporting Information Available: Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-745120 for **3**, CCDC-745122 for **7**, and CCDC-782317 for **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk]. This material is available free of charge via the Internet at http://pubs.acs.org.

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