JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Rubidium-Mediated Birch-Type Reduction of 1,2-Diphenylbenzene in Tetrahydrofuran

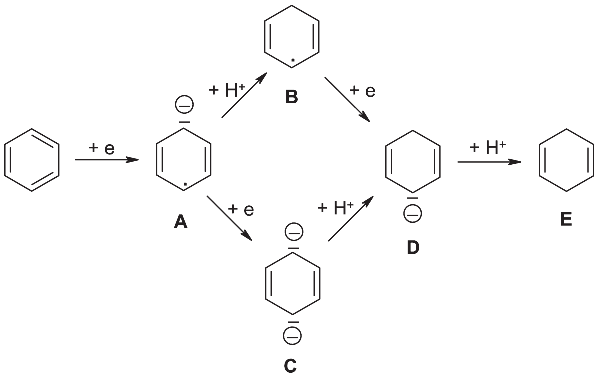
Sven Krieck,[†] Robert Kretschmer,[‡] Helmar Görls,[§] and Matthias Westerhausen*,[§]

[†]Institut für Chemie/Bereich Anorganische Chemie, Karl-Franzens-Universität Graz, Schubertstrasse 1, A-8010 Graz, Austria
[‡]Institut für Chemie, Fachgruppe Organische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany
[§]Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldtstrasse 8, D-07743 Jena, Germany,

Supporting Information

ABSTRACT: The reaction of 1,2-diphenylbenzene with rubidium metal in THF yields extremely sensitive and pyrophoric [η^5-{1,2-diphenyl-2,5-cyclohexadienyl}rubidium]$_\infty$ (**1**). Compound **1** characterizes a possible intermediate in a Birch-type reaction and represents a very rare example of a fully characterized organorubidium complex as well as an open main-group metal pentadienide as part of a six-membered ring. In the solid state the rubidium atoms interact with the cyclohexadienyl moiety, whereas the coordination sphere of the soft cation is additionally stabilized exclusively by several metal π-arene interactions despite the presence of strongly coordinating donors. The bonding situation was elucidated by MP2/def2-TZVPP calculations including population analysis.

Scheme 1. Possible Intermediates of the Birch-Type Reduction of Benzene via a Neutral (B) or a Di-anionic Intermediate (C)

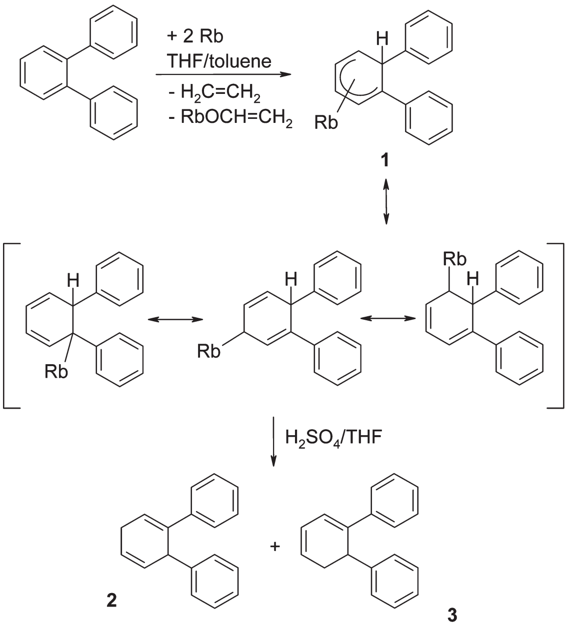


The chemistry of radical anions and dianions of aromatic hydrocarbons represents a broad, intensely investigated, and long-pursued research field.[1] These paramagnetic species have interesting properties, and Birch reduction of them offers a mild reduction procedure for the synthesis of 1,4-cyclohexadienes. On the basis of the work of Wooster and Godfrey,[2] who reduced toluene with sodium and water in liquid ammonia, Birch developed the first preparative protocols.[3] Now, the so-called Birch reduction is a well-established procedure with a wide variety of applications, making this method one of the most powerful reductions in synthetic organic chemistry, e.g., for the reduction of arenes in order to prepare 1,4-hexadienes. The generally accepted mechanism involves an electron transfer from an electropositive metal (sodium or potassium) to the arene (formation of a radical anion **A**) which is protonated by a Brønsted acid (such as ammonia, alcohol, or water), yielding radical **B**. Subsequent reduction (formation of a cyclohexadienide anion **D**) and protonation steps yield the desired 1,4-hexadienes **E** according to Scheme 1. The pentadienyl radical[4] (**B**) and pentadienide anions[5] (**D**) represent possible intermediates on this preparative route. The electron-withdrawing and -donating properties of substituents determine their position in relation to the double bonds of the resulting cyclohexadiene. Another type of this reaction cascade also seems to be feasible: two-fold electron transfer leads to the formation of an arene dianion **C**, which then can be protonated twice. In either case, the cyclohexadienide **D** represents an intermediate in the sequence of electron-transfer and protonation steps leading to partially reduced arenes or heteroarenes. The Birch reduction of 1,2-diphenylbenzene was performed with lithium and ammonium chloride (or water) in liquid ammonia, yielding mainly 2,3-diphenyl-1,4-cyclohexadiene.[6] Bock and co-workers[7] reduced 1,2-diphenylbenzene with potassium in bis(methoxyethyl)ether (diglyme) and isolated the coordination polymer $[\{(\text{diglyme})\text{K}^{+}\}_2\{\text{Ph}_2\text{C}_6\text{H}_4^{2-}\}]_\infty$. 1,3,5-Triphenylbenzene (tpb) can also be reduced twice with alkali metals (AM), leading to a disproportionation equilibrium between $\{(\text{AM}^+)_2(\text{tpb}^{2-})\}$ on the one hand and $\{(\text{AM}^+)(\text{tpb}^-) + \text{AM}\}$ on the other.[8,9] The nature of the metal (ionization potential, size, hardness) and the arene (availability of the LUMO π^* orbital) as well as of the proton source (pK_a value, Lewis basicity of the remaining anion) play key roles; therefore, we investigated a Birch-type reduction with 1,2-diphenylbenzene employing rubidium in tetrahydrofuran (THF) without additional proton sources. The tendency toward α-deprotonation is expressed much more for THF than for acyclic ethers.[9]

Rubidium metal ($E^0 = -2.99$ V)[10] was suspended in a mixture of toluene and THF, and 1,2-diphenylbenzene ($E^0_{(1)} = -2.62$ V, $E^0_{(2)} = -2.72$ V)[11] was added in small portions at −40 °C (Scheme 2). The solution turned dark violet, and 2 equiv of the metal dissolved during this exothermic reaction. Crystallization afforded black opalescent and pyrophoric cube-shaped single crystals of 1,2-diphenylcyclohexadienyl rubidium **1**. This compound is extremely air and moisture sensitive and decomposes above 59 °C.

Received: March 8, 2011
Published: April 19, 2011

Scheme 2. Reduction of 1,2-Diphenylbenzene with Rubidium followed by a Protolytic Workup Yielding Cyclohexadienes; Middle Row Shows the Resonance Forms of the Anion



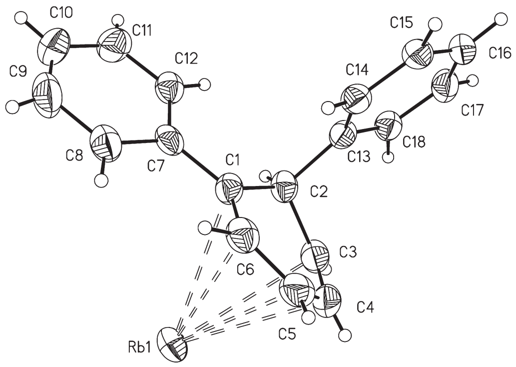


Figure 1. Asymmetric unit and numbering scheme of [η^5-{1,2-diphenyl-2,5-cyclohexadienyl}rubidium] (**1**). The ellipsoids represent a probability of 40%. H atoms are shown with arbitrary radii. Selected bond lengths (pm): Rb1−C1 332.1(5), Rb1−C3 329.0(5), Rb1−C4 316.0(5), Rb1−C5 324.0(6), Rb1−C6 319.8(5), C1−C2 152.3(7), C1−C6 138.7(8), C1−C7 145.3(7), C2−C3 151.5(7), C2−C13 154.7(7), C3−C4 134.8(9), C4−C5 141.3(10), C5−C6 138.7(8).

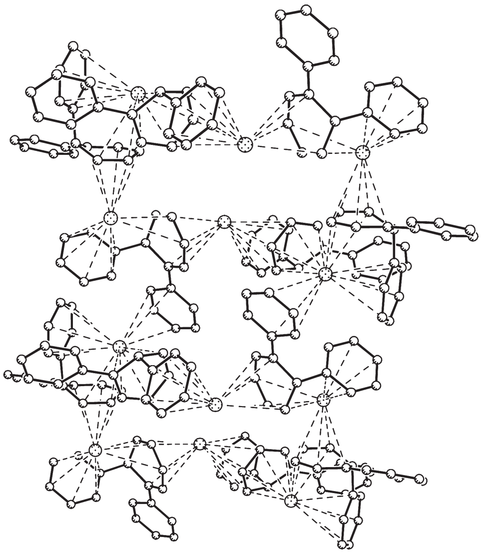


Figure 2. Coordination environment of the hydrocarbon anion of **1** and presentation of the aggregation pattern. The atoms are drawn with arbitrary radii, and H atoms are omitted for clarity. Rb atoms are represented as dotted circles and C atoms as shaded ones. Broken lines represent short contacts between Rb and the carbon atoms.

Because this solution showed the same color as reported for the 1,2-diphenylbenzene dianion, we assume the formation of this dianion as the first reaction step, in accordance with NMR studies of the reduction with lithium in THF-d_8 yielding the dilithium adduct.[12] Thereafter, THF molecules serve as proton sources, leading to ether degradation via α-deprotonation, which is a common reactivity of THF in the presence of strong reducing reagents[13,14] and was also observed earlier for arene anions.[1] Recent investigations show the deprotonation side reactions of arenes with strong electropositive s-block organometallics as dominant reaction pathways.[14a,15] It is remarkable that, even in the presence of strong chelating donors such as dimethoxyethane (dme), 1,3,5-trimethyl-1,3,5-triazinane (tmta), or 1,2-bis(methoxyethoxy)ethane (triglyme), the cosolvent-free complex [η^5-{1,2-diphenyl-2,5-cyclohexadienyl}rubidium]$_\infty$ (**1**) crystallized. Consistent with alkylation reactions,[5c,6,16] protolysis of **1** yielded a mixture of 2,3-diphenyl-1,4-cyclohexadiene (**2**) and 2,3-diphenyl-1,5-cyclohexadiene (**3**), as shown in Scheme 2.

The asymmetric unit and numbering scheme of **1** are displayed in Figure 1.[17] The hydrocarbon anion binds to three rubidium cations as shown in Figure 2, which leads to the formation of a three-dimensional coordination polymer. The cyclohexadienide anion is bound to two rubidium atoms on opposite sides, which are also surrounded by three additional side-on-coordinated phenyl groups. The Rb−C distances to the anionic moiety vary between 316.0(5) (Rb1−C4) and 332.1(5) pm (Rb1−C1), whereas the Rb1−C distances to the phenyl groups adopt slightly larger values, >326 pm. Due to charge delocalization, the contribution of additional electrostatic attraction is rather small. Therefore, the distances of the Rb1 atom to the aromatic planes also vary within a rather narrow range ([Rb1 and plane of C1,C3−C6, 302.1(5) pm; Rb1 and plane of C7−C12, 331.2(5) pm; Rb1 and plane of C13−C18, 312.0(5) pm].

The protonated carbon atom C2 expectedly shows a tetrahedral environment and lies 49.3 pm above the plane of the pentadienide unit (C1,C3−C6). This leads to an envelope-shaped inner six-membered ring. The C2−C bond lengths are characteristic for single bonds to sp^3-hybridized carbon atoms. Charge delocalization leads to similar C−C bond lengths within the pentadienide fragment (average 138.4 pm). Comparable values were observed for a calcium complex of U-shaped 2,4-di(*tert*-butyl)pentadienide (average C−C bond length 140 pm).[18] The C1−C7 bond length of 145.3(7) pm excludes strong charge delocalization into the phenyl substituent, even though the twisting angle between the planes of C7−C12 and C1,C3−C6 shows only a value of 26.1°.

To elucidate the bonding situation in **1**, we performed MP2/def2-TZVPP calculations including population analysis. The MP2-optimized structure reproduces the experimental structure in a satisfying manner, as shown in Figure 3. According to the

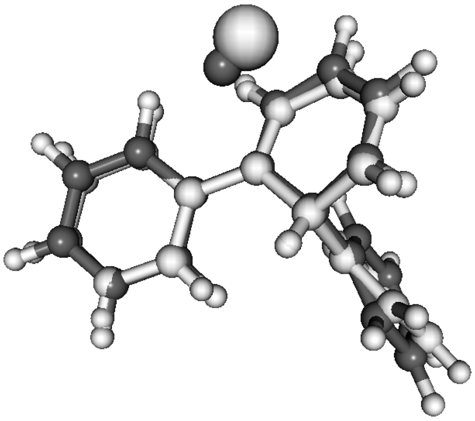


Figure 3. Alignment of calculated geometry (dark gray) and the X-ray structure-based molecular presentation (light gray).

Table 1. Calculated, Multicenter-Corrected Atomic Charges and Two-Center Shared Electron Numbers (σ) for Selected Atoms of 1 at RIMP2/def2-TZVPP Level of Theory

atom	charge	σ	atom	charge	σ
C1	−0.2356	0.0576	C6	−0.0263	0.0955
C2	0.0492	0.0958	C8	−0.1924	0.0348
C3	−0.2289	0.2082	C9	−0.0121	–
C4	−0.0152	0.0551			
C5	−0.2686	0.1212	Rb	0.7646	–

charge distribution given in Table 1, the negative charge is mainly localized at the carbon atoms C1, C3, and C5 of the central ring, indicating the presence of a conjugated pentadienide moiety. Interestingly, the elongation of the C4−C5 bond is attended by a pronounced negative charge at C5. The stronger bonding of Rb1 to C3 and C5 in comparison to the other carbon atoms of the center ring is also reflected in the high value for the shared-electron numbers, which can represent the bond strength of a covalent bond in a comparative way.[19,20] Otherwise, theoretical studies of acyclic pentadienyl rubidium complexes[21] and allyl rubidium complexes[22] (pentadienyl systems can be regarded as vinylogous allyl compounds) predict bonding situations similar to that found in **1**.

The Birch-type reduction of 1,2-diphenylbenzene with rubidium in THF allows the isolation of 1,2-diphenylcyclohexadienyl rubidium (**1**). This complex represents a very rare example of a main-group metal pentadienide complex. THF molecules are able to selectively protonate the 1,2-diphenylbenzene dianion, but the monoanion of **1** is stable in THF solutions. In this reduction process, THF is consumed as a stoichiometric component. In addition, 1,2-diphenylbenzene reacts much faster than toluene under these reaction conditions at −40 °C. In contrast to rather hard ethers and amines, the soft rubidium cation prefers a coordination environment with soft side-on-bound arene ligands. Protolysis of **1** yields a mixture of 2,3-diphenyl-1,4-cyclohexadiene (**2**) and 2,3-diphenyl-1,5-cyclohexadiene (**3**).

Heavier alkali organometallics are exceedingly sensitive toward moisture and air and often pyrophoric, and they show thermal decomposition at ambient temperatures. Due to the highly polarized metal−carbon interactions, such compounds are sparingly soluble in hydrocarbons, whereas in polar media side reactions (solvent deprotonation and cleavage) occur.[23] For these reasons, structurally characterized heavier alkali organometallics are still a rarity.[24] Sufficient description of the bonding situation in these complexes in terms of traditional coordination chemistry is challenging due to the number of multi-hapto interactions.[25] Large (soft) metal ions interact with large anions with at least partially delocalized charge, leading to powerful nucleophiles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental and calculation details; crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

m.we@uni-jena.de

■ ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft (DFG, Bonn/Germany) for generous financial support of this research initiative. We also acknowledge the financial support of the Fonds der Chemischen Industrie (VCI/FCI). S.K. and R.K. are very grateful to the Stiftung Stipendienfonds im Verband der Chemischen Industrie for a Ph.D. grant.

■ REFERENCES

(1) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243–277.

(2) Wooster, C. B.; Godfrey, K. L. *J. Am. Chem. Soc.* **1937**, *59*, 596–597.

(3) (a) Birch, A. J. *J. Chem Soc.* **1944**, 430–436. (b) Birch, A. J. *J. Chem. Soc.* **1945**, 809–813. (c) Birch, A. J. *J. Chem. Soc.* **1946**, 593–597.

(4) Sustmann, R.; Schmidt, H. *Chem. Ber.* **1979**, *112*, 1440–1447.

(5) (a) Yasuda, H.; Yamauchi, M.; Ohnuma, Y.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1481–1491. (b) Pratt, L. M.; Streitwieser, A. *J. Org. Chem.* **2000**, *65*, 290–294. (c) Melero, C.; Herrera, R. P.; Guijarro, A.; Yus, M. *Chem. Eur. J.* **2007**, *13*, 10096–10107. (d) Cerpa, E.; Tenorio, F. J.; Contreras, M.; Villanueva, M.; Beltrán, H. I.; Heine, T.; Donald, K. J.; Merino, G. *Organometallics* **2008**, *27*, 827–833.

(6) Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *J. Am. Chem. Soc.* **1972**, *94*, 5412–5420.

(7) Bock, H.; Havlas, Z.; Gharagozloo-Hubmann, K.; Holl, S.; Sievert, M. *Angew. Chem.* **2003**, *115*, 4521–4525; *Angew. Chem. Int. Ed.* **2003**, *42*, 4385–4389.

(8) Lühder, K. *Z. Chem.* **1969**, *9*, 459–460.

(9) Krieck, S.; Görls, H.; Westerhausen, M. *Organometallics* **2010**, *29*, 6790–6800.

(10) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1999.

(11) (a) Reiser, O.; König, B.; Meerholz, K.; Heinze, J.; Wellauer, T.; Gerson, F.; Frim, R.; Rabinovitz, M.; de Meijere, A. *J. Am. Chem. Soc.* **1993**, *115*, 3511–3518. (b) Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839–1854.

(12) Huber, W.; May, A.; Müllen, K. *Chem. Ber.* **1981**, *114*, 1318–1336.

(13) Maercker, A. *Angew. Chem.* **1987**, *99*, 1002–1019; *Angew. Chem. Int. Ed.* **1987**, *26*, 972–989.

(14) (a) Krieck, S.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *J. Am. Chem. Soc.* **2010**, *132*, 12492–12501. (b) Krieck, S.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2009**, *694*, 2204–2209. (c) Langer, J.; Krieck, S.; Fischer, R.; Görls, H.; Walther, D.; Westerhausen, M. *Organometallics* **2009**, *28*, 5814–5820. (d) Kennedy, A. R.; Klett, J.;

Mulvey, R. E.; Wright, D. S. *Science* **2009**, *326*, 706–708. (e) Gärtner, M.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2008**, *693*, 221–227.

(15) Orzechowski, L.; Jansen, G.; Harder, S. *Angew. Chem.* **2009**, *121*, 3883–3887; *Angew. Chem. Int. Ed.* **2009**, *48*, 3825–3829.

(16) (a) Vitorelli, P.; Peter-Katalinić, J.; Mukherjee-Müller, G.; Hansen, H. J.; Schmied, H. *Helv. Chim. Acta* **1975**, *58*, 1379–1425.

(17) Crystallographic data for **1** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC-803788. 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].

(18) Overby, J. S.; Hanusa, T. P. *Angew. Chem.* **1994**, *106*, 2300–2302; *Angew. Chem. Int. Ed.* **1994**, *33*, 2191–2193.

(19) (a) Davidson, E. R. J. *J. Chem. Phys.* **1967**, *46*, 3320–3324. (b) Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231–245.

(20) Reiher, M. *Found. Chem.* **2003**, *5*, 147–163.

(21) Cerpa, E.; Tenorio, F. J.; Contreras, M.; Villanueva, M.; Beltrán, H. I.; Heine, T.; Donald, K. J.; Morino, G. *Organometallics* **2008**, *27*, 827–833.

(22) van Eikema Hommes, N. J. R.; Bühl, M.; von Ragué Schleyer, P. *J. Organomet. Chem.* **1991**, *409*, 307–320.

(23) Wardell, L. . In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 1.

(24) (a) von Ragué Schleyer, P.; Schade, C. *Adv. Organomet. Chem.* **1987**, *27*, 169–278; (b) Weiss, E. *Angew. Chem. Int. Ed.* **1993**, *32*, 1501–1523; (c) von Ragué Schleyer, P.; Schade, C. *Angew. Chem.* **1994**, *106*, 1187–1199; *Angew. Chem. Int. Ed.* **1994**, *33*, 1129–1140. (d) Smith, J. D. *Adv. Organomet. Chem.* **1999**, *43*, 267–343.

(25) Smith, J. D. *Angew. Chem.* **2009**, *121*, 6721–6723; *Angew. Chem. Int. Ed.* **2009**, *48*, 6597–6599.

(26) *TURBOMOLE*, V6.1, 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989—2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

(27) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(28) (a) Weigend, F.; Häser, M.; Patzeltand, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143–152. (b) Hellweg, A.; Hättig, C.; Höfenerand, S.; Klopper, W. *Theor. Chem. Acc.* **2007**, *117*, 587–597.

(29) Varetto, U. *Molekel 5.4.0.8*; Swiss National Supercomputing Centre: Manno, Switzerland.

(30) *COLLECT*, Data Collection Software; Nonius B.V.: Delft, The Netherlands, 1998.

(31) Otwinowski, Z.; Minor, W. . In *Macromolecular Crystallography*, Part A; Methods in Enzymology 276; Carter, C. W., Sweet, R. M., Eds.; Academic Press: San Diego, CA, 1997; pp 307—326.

(32) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A46*, 112–122.