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Is the halogen–metal exchange faster than deprotonation in the reaction of *ortho*-carboranyl aryl bromide with butyllithium?

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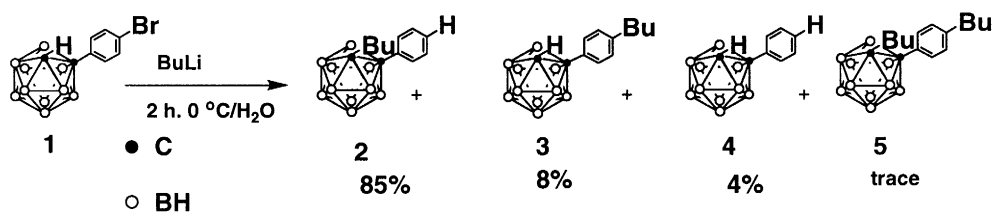
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Abstract

The Br–Li exchange of bromophenyl-*ortho*-carborane **1** is faster than the deprotonation of the acidic C–H hydrogen of the carborane cage. The resulting phenyl anion undergoes rapid proton exchange to give the cluster anion. © 2000 Elsevier Science Ltd. All rights reserved.

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The monolithiation of 1-R-1,2-C₂B₁₀H₁₁ (*ortho*-carborane) at carbon, followed by the use of the resulting monolithiocarborane as a nucleophile,¹ is one of the most valuable synthetic methodologies for the synthesis of disubstituted C₂B₁₀H₁₀ derivatives. For a certain reason, we needed to carry out the methylation of the C–H bond of 1-(4'-Br-C₆H₄)-1,2-C₂B₁₀H₁₁ **1**,² by the traditional monolithiation with *n*-BuLi and subsequent addition of MeI. It seemed to us that this methylation would be very straightforward and proceed smoothly without trouble. However, GC–MS spectra of the crude reaction product showed the formation of only small amounts of the desired methylated product, while the major products showed unexpected high mass peaks. To understand this strange phenomena, we investigated the reaction **1** with *n*-BuLi (Scheme 1).

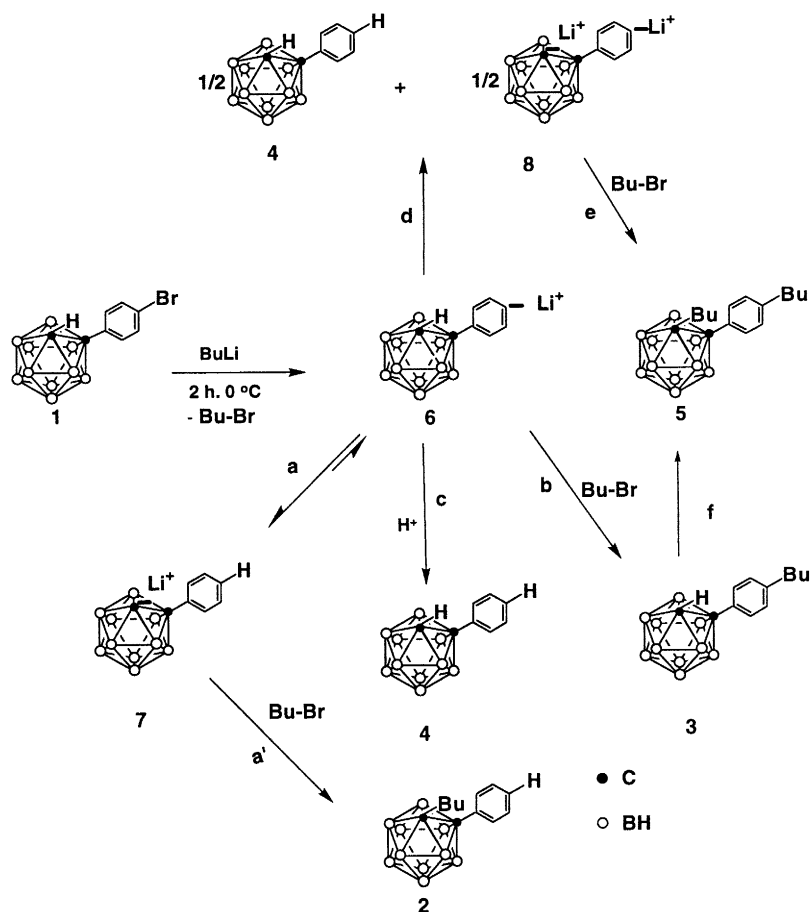


Scheme 1.

n-BuLi (1 mmol, 0.64 ml of *n*-hex/*n*-BuLi 1.57 M hexane solution) was added to a THF (30 ml) solution of **1** (1 mmol, 299 mg) at 0 °C, and the resulting mixture was stirred for 2 h at room temperature.

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The reaction was quenched by addition of water, and the product composition was analyzed by GC–MS. Very interestingly, the butylated product at the carboranyl carbon **2** was obtained as the major product (85%) along with other minor products (**3–5**). The structures of **2–5** were identified unambiguously by comparing their GC–MS spectra to those of authentic compounds synthesized independently.³ A proposed mechanism for the formation of **2–5** is shown in Scheme 2.

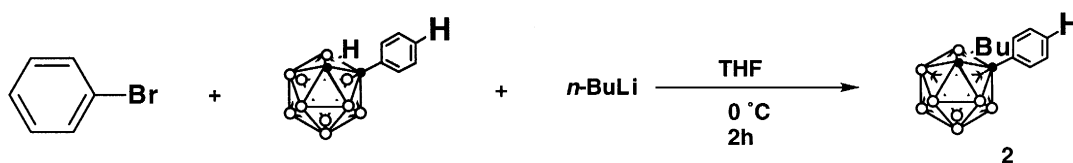


Scheme 2.

The addition of *n*-BuLi to **1** would appear to lead at first to the formation of the phenyl anion **6** via the metal–bromo exchange reaction on the bromophenyl moiety.⁴ BuBr would be produced as a consequence of this exchange reaction. A facile proton exchange (Scheme 2, route **a**) between the CH-carborane cluster and the phenyl anion would produce the lithiated carborane **7**, which would condense with BuBr formed in situ in solution, forming **2** as a major product (route **a'**). A simple electrophilic addition of BuBr or a proton to the phenyl anion carborane cluster **6** would furnish the compound **3** or **4**, respectively (route **b** or **c**), while **6** might undergo disproportionation (route **d**) to give **4** and the dianion **8**, which would afford explicitly the product **5** in the presence of BuBr (route **e**). Of course, there is a possibility that **5** would be formed by deprotonation of **3** followed by the butylation with BuBr (route **f**).

The preferential halogen–metal exchange in the presence of an acidic C–H bond of the carborane was surprising for us, so we examined the intermolecular reaction of bromobenzene (1mmol), phenylorthocarborane (1mmol), and *n*-BuLi (1mmol) under the same reaction conditions as above (Scheme 3). The

reaction was rapid as well, and **2** was obtained essentially in quantitative yield. Accordingly, it is clear that the Li–Br exchange is very rapid and the proton exchange between the resulting phenyl lithium and the carboranyl C–H was also very facile.



Scheme 3.

To confirm this conclusion, we carried out electrochemical studies on **1**. Cyclic voltammetry⁵ of compound **1** in acetonitrile showed one irreversible reduction wave at E_{p_c1} : -2446 mV comparable to the reduction peak potential of bromobenzene -2436 mV and an oxidation peak at E_{p_a1} : -1352.3 mV. This indicates that **1** gave the *ortho*-carboranylphenyl anion **6'** (without Li) by reduction, which underwent proton exchange to give phenyl-substituted *ortho*-carboranyl anion **7'** (without Li). A bulky electrolysis of **1** at -2300 mV led to the reductive cleavage of the bromine–phenyl bond with an electron stoichiometry of 2, forming **4**. Furthermore, no evolution of hydrogen gas occurred during the electrolysis.

In conclusion, the facile cleavage of the bromine–phenyl bond of **1** in the presence of BuLi provides a novel example of a competition between lithium–halogen metal exchange and the deprotonation of an acidic C–H hydrogen of the carboranyl framework. Evidence is thus provided that bonds involving carborane *exo*-cluster aromatic carbon may be cleaved at first forming an aryl anion which in turn promotes a proton transfer at low enough driving forces.

References

- (a) Zakharkin, L. I.; Grebenikov, A. V.; Kazantsev, A. V. *Akad. Nauk SSSR, Ser. Khim.* **1967**, 2077; (b) Gomez, F. A.; Hawthorne, M. F. *J. Org. Chem.* **1992**, *57*, 1384–1390; (c) Grafstein, D.; Bobinski, J.; Dvorak, J.; Smith, H. F.; Schartz, N. N.; Cohen, M. S.; Fein, M. M. *Inorg. Chem.* **1963**, *2*, 1120.
- Compound **1** was synthesized in 63% yield by the standard method of: Coult, R.; Fox, M. A.; Gill, W. R.; Herbertson, P. L.; Macbride, J. A. H.; Wade, K. *J. Organomet. Chem.* **1993**, *462*, 19. ¹H NMR (300 MHz, CD₃COCD₃): δ =3.84 (s, 1H), 7.19–7.42 (2d, 4H); ¹³C NMR (75.45 MHz, CD₃COCD₃): δ =60.10, 129.17, 131.98; Ms m/z (M⁺): found 299.0; calcd 298.80 for B₁₀C₁₂H₁₅Br.
- General procedure for the synthesis of authentic samples **2–5**: a mixture of phenyl-1-hexyne (1.38 g, 8.85 mmol) and decaborane (1.19 g, 9.74 mmol) in toluene (60 ml) and propionitrile (30 ml) was refluxed for 1 night. The solvents were evaporated and silica gel column chromatography of the crude oil (hexane/Et₂O, 9/1) yielded **2** in 55% yield (1.34 g) as a yellowish oil. IR (neat): 2959, 2932, 2872, 2590, 1448 cm⁻¹; ¹H NMR (300 MHz, CD₃COCD₃): δ =0.71 (t, 3H), 1.05–1.41 (m, 4H), 1.87 (q, 2H), 7.49–7.53 (m, 3H), 7.74 (d, 2H); ¹³C NMR (75.45 MHz, CD₃COCD₃): 13.59, 22.54, 32.20, 35.27, 129.94, 131.81; MS m/z : 276 (M⁺); HRMS found 278.2821 calcd 278.2808 for B₁₀C₁₂H₂₄. Compound **3**: Same as for **2** with *para*-butylphenyl acetylene as an alkyne to obtain **3** in 52% yield. IR (neat): 2959, 2931, 2860, 1598, 1514, 1072, 839, 721 cm⁻¹; ¹H NMR (300 MHz, CD₃COCD₃): δ =0.89 (t, 3H), 1.27–1.62 (m, 4H), 2.60 (t, 2H), 5.12 (s, 1H), 7.22 (d, 2H), 7.52 (d, 2H); ¹³C NMR (75.45 MHz, CD₃COCD₃): 14.08, 22.92, 34.04, 35.50, 61.76, 127.21, 129.64, 131.79, 145.87; MS m/z : 276 (M⁺); HRMS Found 278.2833 calcd 278.2808 for B₁₀C₁₂H₂₄. Compound **4**: Authentic sample was purchased from CATCHEM. Compound **5**: The monolithiation of **3** followed by addition of BuLi gave **5** in 80% yield.
- See, for example: *Organometallics in Organic Synthesis*; Negishi, E.-I., Wiley-Interscience, 1980; Vol. 1.
- Cyclic voltammetry of **1** (2.5×10^{-3} M) was carried out in CH₃CN; supporting electrolyte: 0.1 M ⁿBu₄NClO₄; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01N AgNO₃ in acetonitrile with 0.1 M ⁿBu₄ClO₄ ($E_{1/2}$ (ferrocene/ferrocenium)=180 V); scan rate: 100 mVs⁻¹.