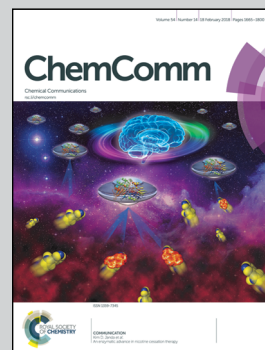


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the synthesis of ditopic ligands for supramolecular frameworks

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Crystal structure of a carborane *endo/exo*-dianion and its use in the synthesis of ditopic ligands for supramolecular frameworks†

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The crystal structure of the deprotonated monocarba-*closo*-dodecaborate [12-CN-CB₁₁H₁₁][−] is reported. This dianion, featuring a delocalized endohedral negative charge and an *exo*-cluster C–[Li] moiety, was used for the synthesis of ditopic ligands with the potential to form novel supramolecular frameworks.

Carboranes based on cages [CB₁₁H₁₂][−] (**1**) and C₂B₁₀H₁₂ (**2a–c**) are icosahedral clusters in which one or two boron vertices are replaced by a carbon unit (Fig. 1a). Their delocalization of electron density represents a three-dimensional extension of the π aromaticity of organic arenes, leading to exceptional chemical and thermal

stability.^{1,2} A large number of applications of carboranes have emerged over the past decade; their utility has become evident in ligand design,³ supramolecular⁴ and medicinal⁵ chemistry, as well as fluorescence/phosphorescence⁶ and materials science.⁷ Weakly coordinating halogenated derivatives of **1** are the anions of choice as counterions for cationic reactive intermediates and of highly active catalysts.⁸ The practical versatility of boron clusters coupled with an incomplete understanding of some of their fundamental properties makes these species an important subject of further study.

The study of the structure, stability and reactivity of carbanions plays a central role in chemistry. On the one hand, this is because they constitute a class of fundamentally important organic intermediates. On the other hand, modern synthesis heavily relies on organolithium reagents as well as various transmetalated species for C–X (X = C, N, O, S, halogen) bond formation.⁹ X-ray crystallography allows for the determination of the exact structure of carbanions in the solid state, providing accurate data about distances, angles and coordination mode of the cation(s) around the formal anionic center. While such information is highly valuable from a fundamental and also a practical perspective, obtaining single crystals of organo-alkaline metal intermediates is challenging due to their exceedingly facile protonation and oxidation. In 1984, Wade and coworkers published the crystal structure of the pentamethyldiethylenetriamine adduct of 1-lithio-2-methyl-1,2-dicarba-*closo*-dodecaborane (**3**) (Fig. 1b).¹⁰ The compound featured a C–Li distance of 2.18(1) Å, with coordination numbers of 6 and 4 for C and Li, respectively. To date, **3** has remained the only X-ray crystal structure of a carboranyl lithium; the authors attributed its monomeric nature to a combination of electronic and steric reasons. In the chemistry of aryllithium compounds, considerable steric protection is required to prevent aggregate formation. Following this strategy, several terphenyllithium etherates **4** have been prepared and found to be monomeric in the solid state, the observed C–Li distances ranging from 2.02 to 2.14 Å.¹¹ In principle, one could imagine the formation of a class of σ/π -dianions by adding an additional negative charge to the π system of aryllithiums. In the simplest case, one-electron reduction of phenyllithium would lead to the hypothetical σ/π -dianion **5**. While such organic aryl-dilithium

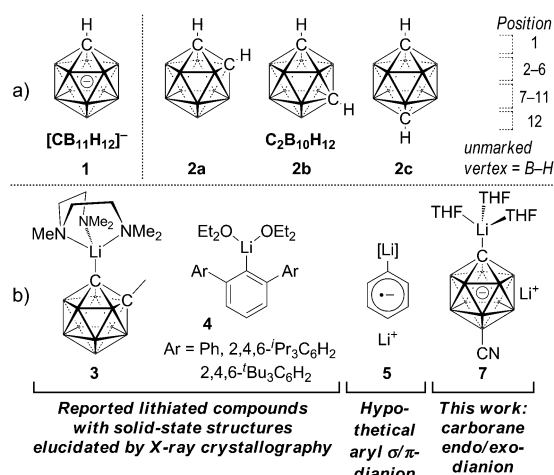


Fig. 1 General framework of icosahedral carboranes (a) and structures of C-lithiated carboranes and arenes (b).

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† Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data. CCDC 1559903–1559909 (**7**, **10a**, **10d**, **10e**, **10f**, **10g** and **11**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc07724f

species are too reactive to be isolated, the three-dimensional distribution of negative charge in **1** allows for the preparation of analogous *endo/exo*-dianions with one delocalized charge and a σ -type C–[Li] moiety.¹² Here we report on cyano-substituted **7**, the first crystal structure of a C1-lithiated derivative of **1**, and coupling reactions affording 1,12-ditopic ligands **10**. Carboranes have attracted much attention due to their unique electronic and structural properties, which set them apart from common organic or inorganic building blocks. Although a number of studies on **2** as building blocks for supramolecular chemistry and MOFs have been published,^{4,7} such utility of donor-substituted **1** has not been investigated. The potential of **10** to form supramolecular frameworks is demonstrated by the preparation and crystal structure of a Cu(I) 1D polymer.

We initially investigated the deprotonation of the anion [12-CN-CB₁₁H₁₁][−] (**6**) (Scheme 1a).¹³ To avoid nucleophilic attack at the cyano carbon atom, sterically encumbered amide bases were tested. Reactions were carried out in THF at 25 °C and followed by ¹¹B NMR spectroscopy. Using a slight excess of lithium 2,2,6,6-tetramethylpiperidide lead to clean conversion to **7**, a result indicating the pK_a-lowering effect of the 12-CN group on the cluster C–H position.¹⁴ Deprotonation caused a downfield shift of the B2–6/7–11 resonances and a shielding of the B12 position (Fig. 2a and b). Solutions of **7** in THF remained inert over several days at room temperature, and in particular no self-attack at the cyano group was observed.

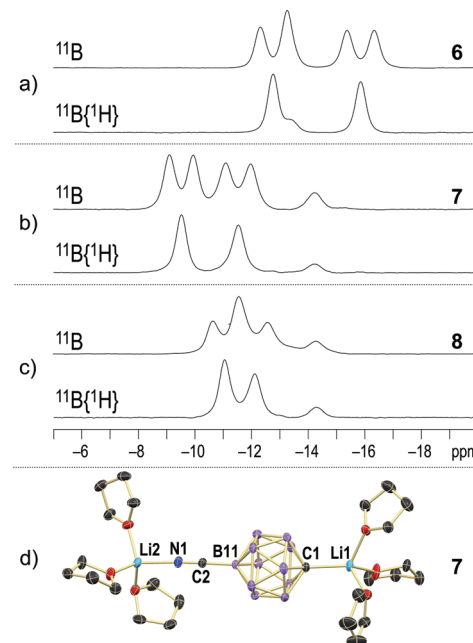
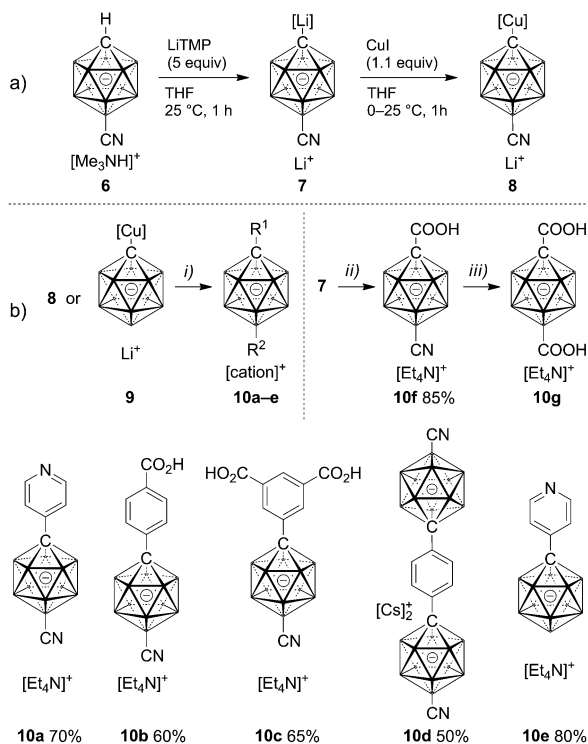


Fig. 2 NMR spectra of **6**, **7** and **8** (a–c, 128 MHz for ¹¹B, THF, 23 °C); X-ray crystal structure of **7** (d) (H atoms omitted for clarity, 25% displacement ellipsoids).



Scheme 1 Preparation of C1-metalated carboranes (a) and synthesis of ligands **10** (b). Conditions: (i) Ar–I, Pd(OAc)₂, P(2-OMe–C₆H₄)₃, THF, 0–25 °C, 16 h; (ii) CO₂ (g), THF, 0–25 °C, 10 h; (iii) conc. aq. HCl, AcOH, 180 °C, 3 h. Yields are isolated yields with respect to **6** or **1**.

Single crystals of **7** suitable for X-ray diffraction were obtained by diffusion of hexane into a THF solution at 25 °C. In the solid state, the dianion is coordinated to two [Li(THF)₃]⁺ fragments at the C1 and N1 positions, respectively (Fig. 2d). The C1–Li1 distance of 2.084(7) Å is similar to those in **3** and **4**; other key distances and angles are B11–C2 1.551(5) Å, C2–N1 1.126(4) Å, 1.987(7) Å and B11–C2–N1 178.3(4)°. Neither any considerable distortion of the carborane cage nor interaction of C1 with a second Li center were observed.

Next, the preparation of a series of cyanocarborane-based ligands with two metal binding sites at opposite termini was examined. The recent report by Uchiyama and coworkers on the C-vertex coupling of **1** led us to probe the cross coupling of **7**.¹⁵ Addition of one equivalent of CuI in THF resulted in the clean formation of cuprate **8**, as concluded from ¹¹B NMR spectra (Scheme 1b and Fig. 2d). With respect to **7**, the B2–6/7–11 resonances experienced a slight shielding to –10.1 and 12.2 ppm, while the shift of the B12 position was practically unaffected. Such solutions remained inert over days.

Palladium-catalyzed cross coupling of **8** with iodoarenes provided access to ligands **10a–d**. Pd(OAc)₂ in combination with tris(2-methoxyphenyl)phosphine provided the products in 50–70% isolated yields with respect to **6** after purification by column chromatography. Coupling in the case of **10b** and **10c** involved the use of the iodoarene carboxylic acid ethyl and dimethyl esters, respectively, followed by hydrolysis to give the free acids. Because **1** is known to coordinate to [Rh(PR₃)₂]⁺ fragments with its B7–H/B12–H vertices *via* agostic-like interactions,¹⁶ product **10e** was synthesized as a ditopic B–H/N donor ligand from **9**. Previously reported^{3l} carboxylic acid **10f** was made and converted to **10g** as a negatively charged analog of terephthalic acid. The latter

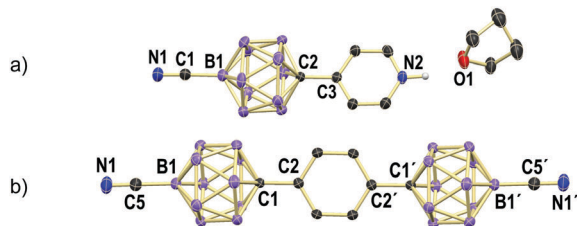
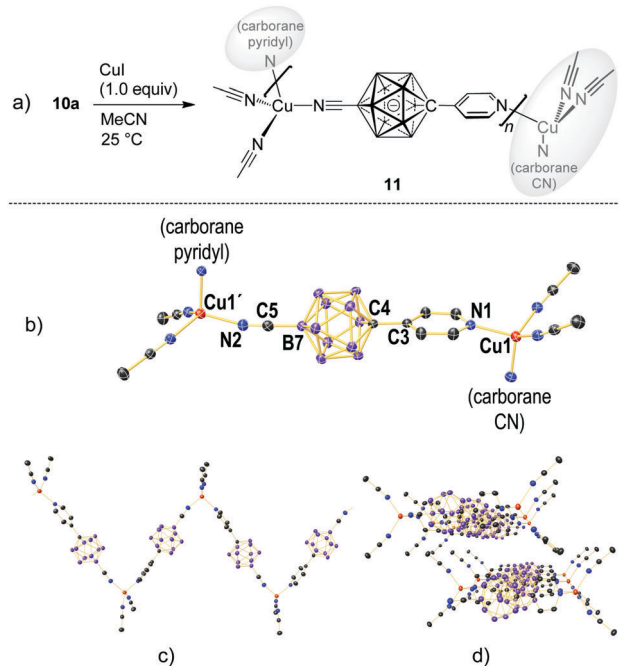


Fig. 3 X-ray crystal structures of **10a**-THF (protonated at N2) (a) and **10d** (b) (H atoms except for N–H and $[\text{Et}_4\text{N}]^+$ cations of **10d** omitted for clarity, 25% displacement ellipsoids; atoms marked with a prime character are at equivalent positions ($-x, 2 - y, 1 - z$)).

transformation required harsh conditions and worked only on a small scale (see the ESI† for details). Products **10** were fully characterized by NMR spectroscopy and mass spectrometry. Furthermore, the solid-state structures of **10a** and **10d–g** were elucidated by X-ray crystallography; two representative structures are shown in Fig. 3. The molecular geometries did not exhibit any unusual features. Uniformly, the distances $\text{C}_{\text{cage}}\text{--C}_{\text{aryl}}$, B--CN and $\text{C}\equiv\text{N}$ were 1.494(4)–1.510(3) Å, 1.542(17)–1.557(5) Å and 1.134(4)–1.139(15) Å, respectively.

Compound **10a** was chosen to probe the ability of the synthesized ligands to form coordination frameworks. Combining **10a** with one equivalent of CuI in MeCN followed by slow evaporation of *ca.* 70% of the solvent afforded colorless crystals of the composition $[(\text{pyridyl-CB}_{11}\text{H}_{10}\text{-CN})\text{-Cu}(\text{MeCN})_2]_n$ in 50% yield (Scheme 2a). X-ray crystallographic analysis of **11** revealed



Scheme 2 Synthesis of 1D-polymer **11**, with the repeating unit shown in black (a); X-ray crystal structure of **11**: repeating unit with two $\text{Cu}(\text{MeCN})_2$ moieties shown (b), single chain formed by repeating units (c), channel formed by single chains (d) (H atoms omitted for clarity; 25% displacement ellipsoids; the prime character of Cu1' indicates that this atom is at an equivalent position ($1/2 + x, 3/2 - y, 3/2 - z$)).

tetrahedral coordination of the Cu center with distances of 1.973(4) Å, 2.051(3) Å and 1.977(3) Å for $\text{Cu1}'\text{--N2}$, Cu1--N1 and Cu1--NCMe , respectively (Scheme 2b). A mirror plane, including $\text{Cu1--NC--B7--C4--C3--N1}$, dissects the pyridyl–carborane–Cu axis, and observed angles are $\text{C5--N2--Cu1}'$ 165.2(4)° and C6--N3--Cu1 165.3(3)°. A zig-zag-like arrangement of the repeating units results in the formation of a 1D-polymer (Scheme 2c). These chains are at a sheet-to-sheet distance of about 6.3 Å, as defined by the distance between the above-mentioned mirror plane of one chain to that of a neighboring chain. The 1D-polymers are assembled to create solvent-free channels without specific interactions between the chains (Scheme 2d, see also Fig. S15–S19, ESI†).

In conclusion, we have described the first crystal structure of a dianion of the $\{\text{CB}_{11}\}$ cage. Lithiate **7** was found to be a monomer with coordination to two $[\text{Li}(\text{THF})_3]^+$ fragments at the CN and the C_{cage} positions. Subsequent Pd-catalyzed coupling with iodoarenes provided access to cluster ligands with donor units at opposite vertices. Finally, one of the products was shown to form a 1D-polymer with Cu(I). These results set the stage for further investigations into the structural characterization and solution behavior of carborane dianions. We are currently exploring the potential of ligands **10** to form supramolecular frameworks with transition metals.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) R. N. Grimes, *Carboranes*, Elsevier, Amsterdam, 2nd edn, 2011; (b) N. S. Hosmane, *Boron Science: New Technologies and Applications*, Taylor & Francis/CRC, Boca Raton, 2011.
- (a) C. Douvris and J. Michl, *Chem. Rev.*, 2013, **113**, PR179–PR233; (b) C. Knapp, Weakly Coordinating Anions: Halogenated Borates and Dodecaborates, *Comprehensive Inorganic Chemistry II*, Elsevier, Amsterdam, 2013, vol. 1, pp. 651–679; (c) R. N. Grimes, *Dalton Trans.*, 2015, **44**, 5939–5956.
- (a) M. Finze, J. A. P. Sprenger and B. B. Schaack, *Dalton Trans.*, 2010, **39**, 2708–2716; (b) A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant and C. A. Mirkin, *Nat. Chem.*, 2011, **3**, 590–596; (c) Z.-J. Yao and G.-X. Jin, *Coord. Chem. Rev.*, 2013, **257**, 2522–2535; (d) A. El-Hellani and V. Lavallo, *Angew. Chem., Int. Ed.*, 2014, **53**, 4489–4493; (e) M. J. Asay, S. P. Fisher, S. E. Lee, F. S. Tham, D. Borchardt and V. Lavallo, *Chem. Commun.*, 2015, **51**, 5359–5362; (f) L. E. Riley, A. P. Y. Chan, J. Taylor, W. Y. Man, D. Ellis, G. M. Rosair, A. J. Welch and I. B. Sivaev, *Dalton Trans.*, 2016, **45**, 1127–1137; (g) J. Estrada, C. A. Lugo, S. G. McArthur and V. Lavallo, *Chem. Commun.*, 2016, **52**, 1824–1826; (h) A. L. Chan, J. Estrada, C. E. Kefalidis and V. Lavallo, *Organometallics*, 2016, **35**, 3257–3260; (i) S. P. Fisher, A. El-Hellani, F. S. Tham and V. Lavallo, *Dalton Trans.*, 2016, **45**, 9762–9765; (j) J. Holmes, C. M. Pask, M. A. Fox and C. E. Willans, *Chem. Commun.*, 2016, **52**, 6443–6446; (k) Y.-P. Zhou, S. Raoufmoghaddam, T. Szilvási and M. Driess, *Angew. Chem., Int. Ed.*, 2016, **55**, 12868–12872; (l) F. Šembera, J. Plutnar, A. Higelin, Z. Janoušek, I. Císařová and J. Michl, *Inorg. Chem.*, 2016, **55**, 3797–3806; (m) P. Coburger, J. Schulz, J. Klose, B. Schwarze, M. B. Sárosi and E. Hey-Hawkins, *Inorg. Chem.*, 2017, **56**, 292–304; (n) C. Selg, W. Neumann, P. Lönnecke, E. Hey-Hawkins and K. Zeitler,

- Chem. – Eur. J.*, 2017, **23**, 7932–7937; (o) J. Estrada and V. Lavallo, *Angew. Chem., Int. Ed.*, 2017, **56**, 9906–9909.
- 4 (a) H. Jude, H. Disteldorf, S. Fischer, T. Wedge, A. M. Hawkrige, A. M. Arif, M. F. Hawthorne, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2005, **127**, 1231–12139; (b) S.-L. Huang, L.-H. Weng and G.-X. Jin, *Dalton Trans.*, 2012, **41**, 11657–11662; (c) L. Kobr, K. Zhao, Y. Shen, R. K. Shoemaker, C. T. Rogers and J. Michl, *Adv. Mater.*, 2013, **25**, 443–448; (d) R. D. Kennedy, V. Krungleviciute, D. J. Clingerman, J. E. Mondloch, Y. Peng, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, J. T. Hupp, T. Yildirim, O. K. Farha and C. A. Mirkin, *Chem. Mater.*, 2013, **25**, 3539–3543; (e) Y.-F. Han and G.-X. Jin, *Acc. Chem. Res.*, 2014, **47**, 3571–3579; (f) C. E. Housecroft, *J. Organomet. Chem.*, 2015, **798**, 218–228; (g) D. J. Clingerman, W. Morris, J. E. Mondloch, R. D. Kennedy, A. A. Sarjeant, C. Stern, J. T. Hupp, O. K. Farha and C. A. Mirkin, *Chem. Commun.*, 2015, **51**, 6521–6523; (h) S. Rodríguez-Hermida, M. Y. Tsang, C. Vignatti, K. C. Stylianou, V. Guillermin, J. Pérez-Carvajal, F. Teixidor, C. Viñas, D. Choquesillo-Lazarte, C. Verdugo-Escamilla, I. Peral, J. Juanhuix, A. Verdaguer, I. Imaz, D. MasPOCH and J. Giner Planas, *Angew. Chem., Int. Ed.*, 2016, **55**, 16049–16053; (i) M. Y. Tsang, S. Rodríguez-Hermida, K. C. Stylianou, F. Tan, D. Negi, F. Teixidor, C. Viñas, D. Choquesillo-Lazarte, C. Verdugo-Escamilla, M. Guerrero, J. Sort, J. Juanhuix, D. MasPOCH and J. Giner Planas, *Cryst. Growth Des.*, 2017, **17**, 846–857.
- 5 (a) I. B. Sivaev and V. V. Bregadze, *Eur. J. Inorg. Chem.*, 2009, 1433–1450; (b) F. Issa, M. Kassiou and L. M. Rendina, *Chem. Rev.*, 2011, **111**, 5701–5722; (c) M. Scholz and E. H-Hawkins, *Chem. Rev.*, 2011, **111**, 7035–7062; (d) Z. J. Leśnikowski, *J. Med. Chem.*, 2016, **59**, 7738–7758.
- 6 (a) Y.-J. Cho, S.-Y. Kim, M. Cho, W.-S. Han, H.-J. Son, D. W. Cho and S. O. Kang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9702–9708; (b) B. H. Choi, J. H. Lee, H. Hwang, K. M. Lee and M. H. Park, *Organometallics*, 2016, **35**, 1771–1777; (c) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire and N. S. Hosmane, *J. Am. Chem. Soc.*, 2016, **138**, 6578–6587; (d) S. Mukherjee and P. Thilagar, *Chem. Commun.*, 2016, **52**, 1070–1093; (e) J. C. Axtell, K. O. Kirlakoval, P. I. Djurovich, D. Jung, V. T. Nguyen, B. Munekiyo, A. T. Royappa, A. L. Rheingold and A. M. Spokoiny, *J. Am. Chem. Soc.*, 2016, **138**, 15758–15765; (f) R. Núñez, M. Tarrés, A. Ferrer-Ugalde, F. F. de Biani and F. Teixidor, *Chem. Rev.*, 2016, **116**, 14307–14378; (g) H. Naito, K. Nishino, Y. Morisaki, K. Tanaka and Y. Chujo, *Angew. Chem., Int. Ed.*, 2017, **56**, 254–259; (h) A. Ferrer-Ugalde, J. Cabrera-González, E. J. Juárez-Pérez, F. Teixidor, E. Pérez-Inestrosa, J. M. Montenegro, R. Sillanpää, M. Haukka and R. Núñez, *Dalton Trans.*, 2017, **46**, 2091–2104; (i) N. V. Nghia, J. Oh, J. Jung and M. H. Lee, *Organometallics*, 2017, **36**, 2573–2580; (j) N. Shin, S. Yu, J. H. Lee, H. Hwang and K. M. Lee, *Organometallics*, 2017, **36**, 1522–1529; (k) M. Hailmann, N. Wolf, R. Renner, B. Hupp, A. Steffen and M. Finze, *Chem. – Eur. J.*, 2017, **23**, 11684–11693.
- 7 (a) K. Tanaka and Y. Chujo, *Macromol. Rapid Commun.*, 2012, **33**, 1235–1255; (b) E. G. Cansu-Ergun and A. Cihaner, *Mater. Chem. Phys.*, 2013, **143**, 387–392; (c) J. Pecyna, D. Pocięcha and P. Kaszyński, *J. Mater. Chem. C*, 2014, **2**, 1585–1591; (d) T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizunl, R. Zhang, S. Shirai and J. W. Kampf, *Angew. Chem., Int. Ed.*, 2014, **53**, 3173–3177; (e) S. G. McArthur, L. Geng, J. Guo and V. Lavallo, *Inorg. Chem. Front.*, 2015, **2**, 1101–1104; (f) J. Pecyna, P. Kaszyński, B. Ringstrand, D. Pocięcha, S. Pakhomov, A. G. Douglass and V. G. Young, Jr., *Inorg. Chem.*, 2016, **55**, 4016–4025; (g) R. Núñez, I. Romero, F. Teixidor and C. Viñas, *Chem. Soc. Rev.*, 2016, **45**, 5147–5173; (h) R. Furue, T. Nishimoto, I. S. Park, J. Lee and T. Yasuda, *Angew. Chem., Int. Ed.*, 2016, **55**, 7171–7175; (i) S. G. McArthur, R. Jay, L. Geng, J. Guo and V. Lavallo, *Chem. Commun.*, 2017, **53**, 4453–4456; (j) Y. Zhu and N. S. Hosmane, *J. Organomet. Chem.*, 2017, **849**–850, 286–292.
- 8 (a) K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin and J. B. Lambert, *Science*, 2002, **297**, 825–827; (b) T. Kato and C. A. Reed, *Angew. Chem., Int. Ed.*, 2004, **43**, 2908–2911; (c) C. Douvris and O. V. Ozerov, *Science*, 2008, **31**, 1188–1190; (d) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldrige and J. S. Siegel, *Science*, 2011, **332**, 574–577; (e) C. A. Reed, *Acc. Chem. Res.*, 2010, **43**, 121–128; (f) Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama and T. Fukushima, *Nat. Chem.*, 2014, **6**, 498–503; (g) B. Shao, A. L. Bagdasarian, S. Popov and H. M. Nelson, *Science*, 2017, **355**, 1403–1407.
- 9 (a) E. Bunzel and T. Dust, *Comprehensive Carbanion Chemistry. Part A. Structure and Reactivity*, Elsevier, Amsterdam, 1980; (b) E. Bunzel and T. Dust, *Carbanion Chemistry. Structures and Mechanisms*, Oxford University Press, New York, 2003; (c) Z. Rappoport and I. Marek, *The Chemistry of Organolithium Compounds*, John Wiley & Sons, Chichester, 2006; (d) H. J. Reich, W. S. Goldenberg, A. W. Sanders, K. L. Jantzi and C. C. Tzschucke, *J. Am. Chem. Soc.*, 2003, **125**, 3509–3521; (e) H. J. Reich, *Chem. Rev.*, 2013, **113**, 7130–7178.
- 10 W. Clegg, D. A. Brown, S. J. Bryan and K. Wade, *Polyhedron*, 1984, **3**, 307–311.
- 11 For 4 and other crystallized aryllithiums, see: (a) B. Schiemenz and P. P. Power, *Organometallics*, 1996, **15**, 958–964; (b) R. C. Crittendon, B. C. Beck, J. Su, X.-W. Li and G. H. Robinson, *Organometallics*, 1999, **18**, 156–160; (c) K. V. Bukhryakov, R. R. Schrock, A. H. Hoveyda and P. Müller, *Org. Lett.*, 2017, **19**, 2607–2609; (d) T. Maetke and D. Seebach, *Helv. Chim. Acta*, 1989, **72**, 624–630; (e) M. M. Olmstead and P. P. Power, *J. Organomet. Chem.*, 1991, **408**, 1–6; (f) G. S. Girolami, M. E. Riehl, K. S. Suslick and S. R. Wilson, *Organometallics*, 1992, **11**, 3907–3910; (g) G. W. Rabe, R. D. Sommer and A. L. Rheingold, *Organometallics*, 2000, **19**, 5537–5540.
- 12 For selected examples of C-lithiation of {CB11} cages and reaction with electrophiles, see: (a) B. T. King, S. Körbe, P. J. Schreiber, J. Clayton, A. Nemcová, Z. Havlas, K. Vyakaranam, M. G. Gete, I. Zharov, J. Ceremuga and J. Michl, *J. Am. Chem. Soc.*, 2007, **129**, 12960–12980; (b) M. J. Nava and C. A. Reed, *Inorg. Chem.*, 2010, **49**, 4726–4728; (c) A. Himmelsbach, J. A. P. Sprenger, J. Warneke, M. Zähres and M. Finze, *Organometallics*, 2012, **31**, 1566–1577; (d) A. Himmelsbach, J. Warneke, M. Schäfer, M. Hailmann and M. Finze, *Organometallics*, 2015, **34**, 462–469; see also ref. 2a, 3a and l.
- 13 A. J. Rosenbaum, D. H. Juers and M. A. Juhasz, *Inorg. Chem.*, 2013, **52**, 10171–10719.
- 14 See the ESI† for more details. For substituent effects in derivatives of 1, see: M. Otsuka, R. Takita, J. Kanazawa, K. Miyamoto, A. Muranaka and M. Uchiyama, *J. Am. Chem. Soc.*, 2015, **137**, 15082–15085. Unsubstituted 1 requires alkylolithium bases for deprotonation, while 2a has a substantially lower pK_a of ca. 23 (ref. 1a and 2a).
- 15 (a) J. Kanazawa, R. Takita, A. Jankowiak, S. Fujii, H. Kagechika, D. Hashizume, K. Shudo, P. Kaszyński and M. Uchiyama, *Angew. Chem., Int. Ed.*, 2013, **52**, 8017–8021; for a structurally characterized cuprate of a highly fluorinated carborane, see: (b) S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev and S. H. Strauss, *J. Am. Chem. Soc.*, 1998, **120**, 4224–4225.
- 16 A. Rifat, N. J. Patmore, M. F. Mahon and A. S. Weller, *Organometallics*, 2002, **21**, 2856–2865.