Chemical
Science

ROYAL SOCIETY
OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Sci.*, 2021, **12**, 5616

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 28th December 2020
Accepted 19th February 2021

DOI: 10.1039/d0sc07047e

rsc.li/chemical-science

Tandem [4 + 2]/[2 + 2] cycloaddition of *o*-carboryne with enynes: facile construction of carborane-fused tricyclics†

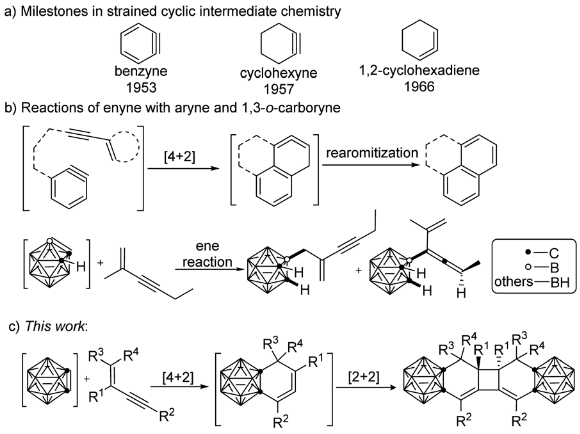
Jie Zhang and Zuowei Xie *

o-Carboryne (1,2-dehydro-*o*-carborane) is a very useful synthon for the synthesis of a variety of carborane-functionalized molecules. With 1-Li-2-OTf-*o*-$C_2B_{10}H_{10}$ as the precursor, *o*-carboryne undergoes an efficient [4 + 2] cycloaddition with various conjugated enynes, followed by a subsequent [2 + 2] cycloaddition at room temperature, generating a series of carborane-fused tricyclo[6.4.0.0^{2,7}]dodeca-2,12-dienes in moderate to high isolated yields. This reaction is compatible with many functional groups and has a broad substrate scope. A reactive carborane-fused 1,2-cyclohexadiene intermediate is involved, which is supported by experimental results and DFT calculations. This protocol offers a convenient strategy for the construction of complex carborane-functionalized tricyclics.

Introduction

Strained cyclic organic molecules, such as arynes, cyclic alkynes and cyclic allenes, have intrigued chemists for more than a century with their unusual structures and high chemical reactivity (Scheme 1a).[1] The considerable ring strain (30–50 kilocalories per mole)[2,3] that characterizes these transient intermediates imparts high reactivity in many reactions, including cycloadditions and nucleophilic trappings, often generating structurally complex products.[4] Cyclic allenes are a relatively less studied class of highly strained intermediate as compared with benzynes and cyclic alkynes. The generation and reactivity of 6-membered cyclic allenes such as the parent 1,2-cyclohexadiene have attracted much research interest in recent years.[5] Strained six-membered-ring allenes are also found as common intermediates in the [4 + 2] cycloaddition of conjugated enynes with unsaturated molecules, including alkenes and alkynes.[6,7] Aryne, a very reactive archetypal two-electron component in [4 + 2] cycloadditions, can react with conjugated enynes to generate isoaromatic cyclic allenes, which undergo isoaromatization to afford the polycyclic aromatics (Scheme 1b).[8]

On the other hand, carborane (*o*-$C_2B_{10}H_{12}$), a three-dimensional relative of benzene, is a molecular boron–carbon cluster.[9] Owing to their unique properties, functionalized carboranes are now finding a broad range of applications encompassing organic synthesis, drug design, polymers, cancer therapy, catalysis, metal–organic frameworks, electronic devices, and more.[9–11] Similarly, 1,2-dehydro-*o*-carborane (*o*-carboryne) can be viewed as a three-dimensional relative of benzene, which has been widely employed as a useful synthon for generating a wide range of functional carboranes over the past two decades.[12] It can undergo cycloadditions,[13–15] the ene reaction[16] and the C–H bond insertion reaction,[17] with a variety of organic molecules to afford a large class of functionalized carboranes. Cycloadditions involving an *o*-carboryne intermediate have been developed to enable the synthesis of various carbocyclic carborane derivatives.[12] In our recently reported work, the ene reaction was observed between 1,3-dehydro-*o*-carboryne and a conjugated enyne due probably to the polarized



Scheme 1 Reactions involving the enynes, aryne and carboryne: (a) strained cyclic intermediates. (b) Reactions of enyne with aryne and 1,3-*o*-carboryne. (c) This work.

Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, China. E-mail: zxie@cuhk.edu.hk

† Electronic supplementary information (ESI) available. CCDC [2052100–2052112]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc07047e

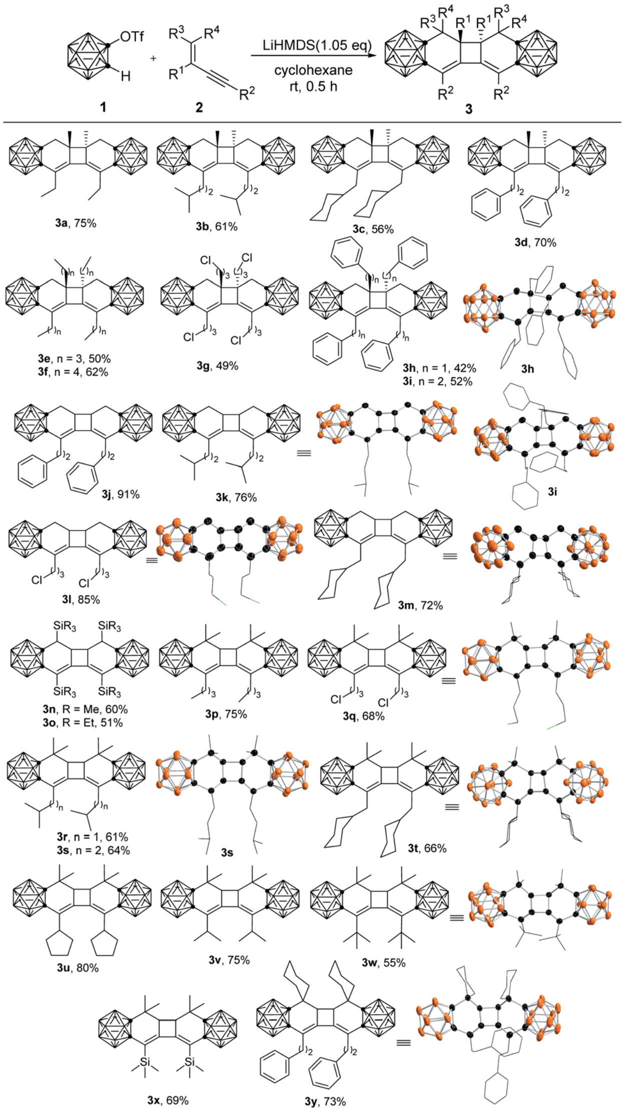
"C═B" multiple bond (Scheme 1b).[18] Surprisingly, 1,2-dehydro-*o*-carboryne (*o*-carboryne) reacted with conjugated enynes in an unprecedented tandem [4 + 2]/[2 + 2] cycloaddition manner, generating a new class of rigid carborane-fused tricyclo[6.4.0.0^{2,7}]dodeca-2,12-dienes (Scheme 1c). Herein, we reported a general method for the construction of such carborane-fused tricyclics.

Results and discussion

In our initial study, the reaction of *o*-carboryne, generated *in situ* by treatment of 1-OTf-*o*-$C_2B_{10}H_{11}$ (**1**) with LiHMDS (lithium bis(trimethylsilyl)amide), with 1.2 equiv. of 2-methyl-1-hexen-3-yne (**2a**) in cyclohexane at room temperature afforded carborane-fused tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene **3a** in 84% GC yield (Table 1, entry 1). Several common bases, such as organic lithium reagents and Grignard reagents, were screened (Table 1, entries 2–5), and the results suggested that LiHMDS was the best choice (Table 1, entry 1).

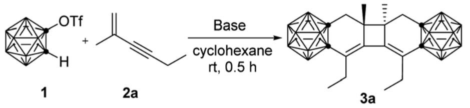
With the optimal reaction conditions in hand, the scope of this tandem [4 + 2]/[2 + 2] cycloaddition of *o*-carboryne with a series of conjugated enynes was examined and the desired carborane-fused tricyclic compounds were obtained in moderate to high yields (Table 2). Various substituents, including linear, branched and cyclic alkyl groups, silyl groups, and distal chloro and phenyl groups, were compatible with this reaction. It was noted that the reaction of the ornamented conjugated enynes directly with the phenyl group led to very complicated results due to the side reactions of the styrene[14i,l] or phenylacetylene[15b] moiety with *o*-carboryne. It was found that the steric hindrance of the substituents may play a role in the reaction, especially for the ones (R^1) attached to the internal alkenyl carbon atom (**3a**–**3i** *vs.* **3j**–**3m**). For instance, the reaction of **2j** or **2l** proceeded smoothly to generate cycloadducts **3j** and **3l** in >85% yields, whereas **3d**, **3g** and **3i** were isolated in <70% yields. When the two terminal alkenyl C–H groups were replaced by methyl groups, the yield of the desired products decreased slightly (**3q** *vs.* **3l**, **3s** *vs.* **3k**, **3t** *vs.* **3m**, and **3y** *vs.* **3j**). Moreover, the substituents (R^2) at the terminal alkynyl carbon atom showed no obvious effect on the yields of **3**.

Table 2 [4 + 2]/[2 + 2] Cycloadditions of *o*-carboryne with enynes[a,b]



[a] Reactions conditions: **1** (0.1 mmol), **2** (0.12 mmol), LiHMDS (0.105 mmol) in cyclohexane (2 mL), rt, 0.5 h. [b] Isolated yields.

Table 1 Optimization of reaction conditions[a]

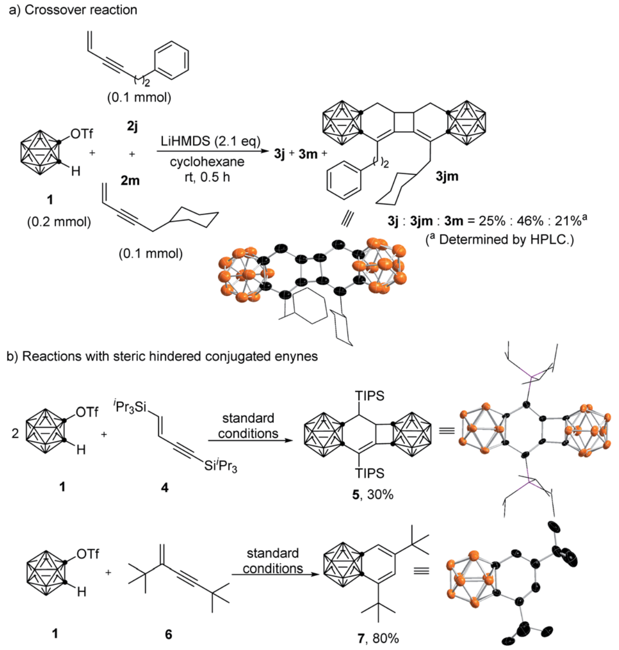


Entry	Base	Yield[b] (**3a**, %)
1	LiHMDS	84 (75)[c]
2	^{n}BuLi	48
3	^{t}BuOLi	33
4	^{i}PrMgCl	35
5	CH_3MgBr	21

[a] Reactions conditions: **1** (0.1 mmol), **2a** (0.12 mmol), base (0.105 mmol) in cyclohexane (2 mL), rt, 0.5 h. [b] Determined by GC. [c] Isolated yield.

Compounds **3** were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as well as by HRMS. The ^{11}B{^{1}H} NMR spectra exhibited a 4 : 2 : 12 : 2 pattern for **3a** and **3d**, a 6 : 14 pattern for **3c**, 3**e**–**j**, 3**n**, and 3**o**, and a 4 : 16 pattern for **3p**–**u** and 3**y**, spanning the range $\delta = -2$ to -14 ppm. The molecular structures of **3h**–**3i**, **3k**–**3m**, **3q**, **3s**–**3t**, **3w** and **3y** were further confirmed by single-crystal X-ray analyses.[19]

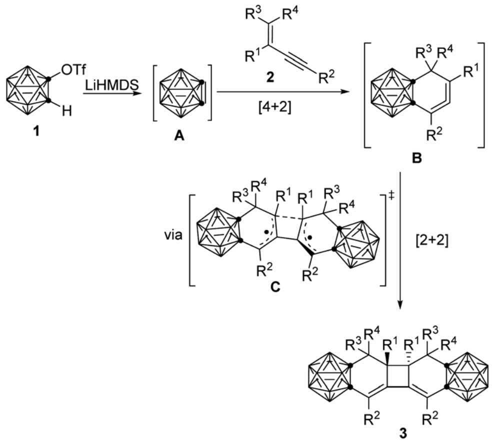
To gain some insight into the reaction mechanism, several control experiments were conducted (Scheme 2). Under standard reaction conditions, *o*-carboryne was treated with a mixture (1 : 1 molar ratio) of **2j** and **2m**, yielding three products **3j**, **3jm**, and **3m** in a molar ratio of around 1 : 2 : 1. The isolation of the crossover product **3jm** suggested that this is a stepwise process and the [2 + 2] cycloaddition step is an intermolecular reaction (Scheme 2a). On the other hand, 1,4-



Scheme 2 Control experiments: (a) crossover reaction. (b) Reactions with sterically hindered enynes.

bis(triisopropylsilyl)-1-buten-3-yne **4**, providing two highly sterically demanding silyl groups at the terminals of 1-buten-3-yne, reacted smoothly with *o*-carboryne to afford **5** in 30% yield (Scheme 2b). In this reaction, the *in situ* generated carborane-fused 1,2-cyclohexadiene intermediate was trapped preferentially by less hindered *o*-carboryne, which can be ascribed to the fact that the resultant sterically demanding cyclic allene intermediate prevents its dimerization.

Furthermore, the treatment of 2,4-bis(*tert*-butyl)-1-buten-3-yne **6** with *o*-carboryne gave benzo-*o*-carborane **7** in 80% yield, which might result from the 1,3-H-migration of the extremely sterically demanding carborane-fused 1,3-di(*tert*-butyl)-1,2-cyclohexadiene intermediate (Scheme 2b). These results further supported that this reaction proceeded *via* a carborane-fused 1,2-cyclohexadiene intermediate. The molecular structures of **3jm**, **5** and **7** were further confirmed by single-crystal X-ray analyses.[19]



Scheme 3 Proposed reaction mechanism.

Based on the above experimental results, a plausible reaction mechanism is proposed in Scheme 3. At first, *in situ* generated *o*-carboryne **A** by reaction of **1** with LiHMDS, reacts with conjugated enyne **2** to form highly reactive carborane-fused 1,2-cyclohexadiene **B** *via* [4 + 2] cycloaddition.[20] Two molecules of cyclic allenes **B** undergo a stepwise [2 + 2] cycloaddition *via* a singlet bis-allyl diradical **C** intermediate,[21] affording the desired carborane-fused tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene **3**. This proposed mechanism is supported by DFT calculations (see ESI† for details).

Conclusions

Using 1-OTf-*o*-$C_2B_{10}H_{10}$ (**1**) as an *o*-carboryne precursor, an unprecedented tandem [4 + 2]/[2 + 2] cycloaddition reaction of *o*-carboryne with conjugated enynes was developed with a broad substrate scope, affording a series of carborane-fused tricyclo[6.4.0.0^{2,7}]dodeca-2,12-dienes in moderate to high yields. In this reaction, a reactive carborane-fused 1,2-cyclohexadiene intermediate was formed, followed by a stepwise [2 + 2] cycloaddition *via* a diallyl diradical to give the final product. This protocol provided a feasible strategy for the synthesis of complex carborane-fused tricyclic compounds in a single process, which is otherwise inaccessible by other means.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by grants from the Research Grants Council of HKSAR (Project No. 14306519) and NSFC/RGC Joint Research Scheme (Project No. N_CUHK402/18), as well as by the CUHK Impact Postdoctoral Fellowship Scheme (IPDFS to Z.J.).

Notes and references

1 H. H. Wenk, M. Winkler and W. Sander, *Angew. Chem., Int. Ed.*, 2003, **42**, 502–528.

2 J. F. Liebman and A. A. Greenberg, *Chem. Rev.*, 1976, **76**, 311–365.

3 R. O. Angus, M. W. Schmidt Jr and R. P. Johnson, *J. Am. Chem. Soc.*, 1985, **107**, 532–537.

4 H. Pellissier and M. Santelli, *Tetrahedron*, 2003, **59**, 701–730.

5 (*a*) I. Quintana, D. Peña, D. Pérez and E. Guitián, *Eur. J. Org. Chem.*, 2009, **2009**, 5519–5524; (*b*) J. S. Barber, E. D. Styduhar, H. V. Pham, T. C. McMahon, K. N. Houk and N. K. Garg, *J. Am. Chem. Soc.*, 2016, **138**, 2512–2515; (*c*) V. A. Lofstrand and F. G. West, *Chem.–Eur. J.*, 2016, **22**, 10763–10767; (*d*) J. S. Barber, M. M. Yamano, M. Ramirez, E. R. Darzi, R. R. Knapp, F. Liu, K. N. Houk and N. K. Garg, *Nat. Chem.*, 2018, **10**, 953–960; (*e*) V. A. Lofstrand, K. C. McIntosh, Y. A. Almehmadi and F. G. West, *Org. Lett.*,

2019, **21**, 6231–6234; (*f*) M. Yamano, R. Knapp, A. Ngamnithiporn, M. Ramirez, K. Houk, B. Stoltz and N. K. Garg, *Angew. Chem., Int. Ed.*, 2019, **58**, 5653–5657; (*g*) Y. A. Almehmadi and F. G. West, *Org. Lett.*, 2020, **22**, 6091–6095; (*h*) M. M. Yamano, A. V. Kelleghan, Q. Shao, M. Giroud, B. J. Simmons, B. Li, S. Chen, K. N. Houk and N. K. Garg, *Nature*, 2020, **586**, 242–247.

6 (*a*) P. Wessig and G. Muller, *Chem. Rev.*, 2008, **108**, 2051–2063; (*b*) V. Gevorgyan and O. V. Zatolochnaya, [4 + 2] Benzannulation of enynes with alkynes, in *Transition-Metal-Mediated Aromatic Ring Construction*, ed. K. Tanaka, 2013, pp. 355–377.

7 (*a*) R. L. Danheiser, R. G. Brisbois, J. J. Kowalczyk and R. F. Miller, *J. Am. Chem. Soc.*, 1990, **112**, 3093–3100; (*b*) J. R. Dunetz and R. L. Danheiser, *J. Am. Chem. Soc.*, 2005, **127**, 5776–5777; (*c*) S. Saito, M. M. Salter, V. Gevorgyan, N. Tsuboya, K. Tando and Y. Yamamoto, *J. Am. Chem. Soc.*, 1996, **118**, 3970–3971; (*d*) V. Gevorgyan, A. Takeda and Y. Yamamoto, *J. Am. Chem. Soc.*, 1997, **119**, 11313–11314; (*e*) V. Gevorgyan, A. Takeda, M. Homma, N. Sadayori, U. Radhakrishnan and Y. Yamamoto, *J. Am. Chem. Soc.*, 1999, **121**, 6391–6402; (*f*) M. Rubina, M. Conley and V. Gevorgyan, *J. Am. Chem. Soc.*, 2006, **128**, 5818–5827; (*g*) Y. Nakao, Y. Hirata, S. Ishihara, S. Oda, T. Yukawa, E. Shirakawa and T. Hiyama, *J. Am. Chem. Soc.*, 2004, **126**, 15650–15651; (*h*) F. Punner and G. Hilt, *Chem. Commun.*, 2012, **48**, 3617–3619.

8 (*a*) M. E. Hayes, H. Shinokubo and R. L. Danheiser, *Org. Lett.*, 2005, **7**, 3917–3920; (*b*) S. Yoshida, K. Shimizu, K. Uchida, Y. Hazama, K. Igawa, K. Tomooka and T. Hosoya, *Chem.–Eur. J.*, 2017, **23**, 15332–15335.

9 (*a*) R. N. Grimes, *Carboranes*, Academic Press, Amsterdam, 3rd edn, 2016; (*b*) N. S. Hosmane, *Boron Science: New Technologies and Applications*, CRC Press, Boca Raton, FL, 2011; (*c*) Z. Xie and G. X. Jin, Carborane Themed Issue, *Dalton Trans.*, 2014, **43**, 4911–5232; (*d*) V. I. Bregadze and Z. Xie, Boron Chemistry Themed Issue, *Eur. J. Inorg. Chem.*, 2017, 4344–4692.

10 For reviews, see:(*a*) R. Núñez, M. Tarrés, A. Ferrer-Ugalde, F. F de Biani and F. Teixidor, *Chem. Rev.*, 2016, **116**, 14307–14378; (*b*) S. Mukherjee and P. Thilagar, *Chem. Commun.*, 2016, **52**, 1070–1093; (*c*) X. Li, H. Yan and Q. Zhao, *Chem.–Eur. J.*, 2016, **22**, 1888–1898; (*d*) Z. Xie, *Acc. Chem. Res.*, 2003, **36**, 66–77; (*e*) W.-B. Yu, P.-F. Cui, W.-X. Gao and G.-X. Jin, *Coord. Chem. Rev.*, 2017, **350**, 300–319; (*f*) Z. Qiu, S. Ren and Z. Xie, *Acc. Chem. Res.*, 2011, **44**, 299–309; (*g*) S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson and V. Lavallo, *Chem. Rev.*, 2019, **119**, 8262–8290; (*h*) J. Zhang and Z. Xie, *Acc. Chem. Res.*, 2014, **47**, 1623–1633; (*i*) M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 950–984; (*j*) M. F. Hawthorne and A. Maderna, *Chem. Rev.*, 1999, **99**, 3421–3434; (*k*) A. F. Armstrong and J. F. Valliant, *Dalton Trans.*, 2007, 4240–4251; (*l*) F. Issa, M. Kassiou and L. M. Rendina, *Chem. Rev.*, 2011, **111**, 5701–5722; (*m*) M. Scholz and E. Hey-Hawkins, *Chem. Rev.*, 2011, **111**, 7035–7062; (*n*) R. Núñez, I. Romero, F. Teixidor and C. Viñas, *Chem. Soc. Rev.*, 2016, **45**, 5147–5173; (*o*) Y. Quan and Z. Xie, *Chem. Soc. Rev.*, 2019, **48**, 3660–3673; (*p*) Y. K. Au and Z. Xie, *Bull. Chem. Soc. Jpn.*, 2021, DOI: 10.1246/bcsj.20200366R; (*q*) N. Grimes, *Dalton Trans.*, 2015, **44**, 5939–5956; (*r*) P. Stockmann, M. Gozzi, R. Kuhnert, M. B. Sárosi and E. Hey-Hawkins, *Chem. Soc. Rev.*, 2019, **48**, 3497–3512.

11 For selected examples, see:(*a*) H. Jude, H. Disteldorf, S. Fischer, T. Wedge, A. M. Hawkridge, A. M. Arif, M. F. Hawthorne, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2005, **127**, 12131–12139; (*b*) B. H. Northrop, H.-B. Yang and P. J. Stang, *Chem. Commun.*, 2008, 5896–5908; (*c*) J. M. Ludlow III, M. Tominaga, Y. Chujo, A. Schultz, X. Lu, T. Xie, K. Guo, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Dalton Trans.*, 2014, **43**, 9604–9611; (*d*) D. Jung, L. M. A. Saleh, Z. J. Berkson, M. F. El-Kady, J. Y. Hwang, N. Mohamed, A. I. Wixtrom, E. Titarenko, Y. Shao, K. McCarthy, J. Guo, I. B. Martini, S. Kraemer, E. C. Wegener, P. Saint-Cricq, B. Ruehle, R. R. Langeslay, M. Delferro, J. L. Brosmer, C. H. Hendon, M. Gallagher-Jones, J. Rodriguez, K. W. Chapman, J. T. Miller, X. Duan, R. B. Kaner, J. I. Zink, B. F. Chmelka and A. M. Spokoyny, *Nat. Mater.*, 2018, **17**, 341–348; (*e*) J. Guo, D. Liu, J. Zhang, J. Zhang, Q. Miao and Z. Xie, *Chem. Commun.*, 2015, **51**, 12004–12007; (*f*) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire and N. S. Hosmane, *J. Am. Chem. Soc.*, 2010, **132**, 6578–6587; (*g*) M. Koshino, T. Tanaka, N. Solin, K. Suenaga, H. Isobe and E. Nakamura, *Science*, 2007, **316**, 853; (*h*) D. Brusselle, P. Bauduin, L. Girard, A. Zaulet, C. Viñas, F. Teixidor, I. Ly and O. Diat, *Angew. Chem., Int. Ed.*, 2013, **52**, 12114–12118; (*i*) O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 12680–12681; (*j*) J. J. Schwartz, A. M. Mendoza, N. Wattanatorn, Y. Zhao, V. T. Nguyen, A. M. Spokoyny, C. A. Mirkin, T. Baše and P. S. Weiss, *J. Am. Chem. Soc.*, 2016, **138**, 5957–5967; (*k*) S. G. McArthur, L. Geng, J. Guo and V. Lavallo, *Inorg. Chem. Front.*, 2015, **2**, 1101–1104; (*l*) 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; (*m*) 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; (*n*) C. A. Lugo, C. E. Moore, A. L. Rheingold and V. Lavallo, *Inorg. Chem.*, 2015, **54**, 2094–2096; (*o*) L. M. A. Saleh, R. M. Dziedzic, S. I. Khan and A. M. Spokoyny, *Chem.–Eur. J.*, 2016, **22**, 8466–8470; (*p*) X. Wei, M.-J. Zhu, Z. Cheng, M. Lee, H. Yan, C. Lu and J.-J. Xu, *Angew. Chem., Int. Ed.*, 2019, **58**, 3162–3166.

12 For reviews on carboryne chemistry, see:(*a*) Z. Qiu and Z. Xie, *Dalton Trans.*, 2014, **43**, 4925–4934; (*b*) D. Zhao and Z. Xie, *Coord. Chem. Rev.*, 2016, **314**, 14–33.

13 Example for [5 + 2]/[3 + 2] cycloaddition of *o*-carboryne: D. Zhao, J. Zhang and Z. Xie, *J. Am. Chem. Soc.*, 2015, **137**, 13938–13942.

14 Select examples for [4 + 2] cycloaddition of *o*-carboryne:(*a*) H. L. Gingrich, T. Ghosh, Q. Huang and M. Jones Jr, *J. Am. Chem. Soc.*, 1990, **112**, 4082–4083; (*b*) J. Jeon, T. Kitamura, B.-W. Yoo, S. O. Kang and J. Ko, *Chem. Commun.*, 2001, 2110–2111; (*c*) T. Ghosh, H. L. Gingrich, C. K. Kam, E. C. M. Mobraaten and M. Jones Jr, *J. Am. Chem. Soc.*, 1991, **113**, 1313–1318; (*d*) L. Barnett-Thamattoor, G.-X. Zheng, D. M. Ho, M. Jones Jr and J. E. Jackson, *Inorg. Chem.*, 1996, **35**, 7311–7315; (*e*) J. H. Atkins, D. M. Ho and M. Jones Jr, *Tetrahedron Lett.*, 1996, **37**, 7217–7220; (*f*) S. R. Wang and Z. Xie, *Organometallics*, 2012, **31**, 3316–3323; (*g*) J. U. Kahlert, A. Rawal, J. M. Hook, L. M. Rendina and M. Choucair, *Chem. Commun.*, 2014, **50**, 11332–11334; (*h*) J. Zhang, Z. Qiu, P.-F. Xu and Z. Xie, *ChemPlusChem*, 2014, **79**, 1044–1052; (*i*) S. R. Wang and Z. Xie, *Tetrahedron*, 2012, **68**, 5269–5278; (*j*) J. Zhang, Z. Qiu and Z. Xie, *Organometallics*, 2017, **36**, 3806–3811; (*k*) D. Zhao, J. Zhang and Z. Xie, *Angew. Chem., Int. Ed.*, 2014, **53**, 8488–8491; (*l*) J. Zhang and Z. Xie, *Chin. J. Chem.*, 2018, **36**, 1041–1046.

15 Select examples for [2 + 2] cycloaddition of *o*-carboryne:(*a*) T. Lee, J. Jeon, K. H. Song, I. Jung, C. Baik, K.-M. Park, S. S. Lee, S. O. Kang and J. Ko, *Dalton Trans.*, 2004, 933–937; (*b*) R. J. Cunningham, N. Bian and M. Jones Jr, *Inorg. Chem.*, 1994, **33**, 4811–4812; (*c*) D. M. Ho, R. J. Cunningham, J. A. Brewer, N. Bian and M. Jones Jr, *Inorg. Chem.*, 1995, **34**, 5274–5278; (*d*) S. R. Wang, Z. Qiu and Z. Xie, *J. Am. Chem. Soc.*, 2010, **132**, 9988–9989; (*e*) D. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 9423–9428; (*f*) J. Zhang and Z. Xie, *Organometallics*, 2020, **39**, 4214–4220.

16 Select examples for ene reactions of *o*-carboryne:(*a*) Q. Huang, H. L. Gingrich and M. Jones Jr, *Inorg. Chem.*, 1991, **30**, 3254–3257; (*b*) H. L. Gingrich, Q. Huang, A. L. Morales and M. Jones Jr, *J. Org. Chem.*, 1992, **57**, 3803–3806; (*c*) D. Zhao, J. Zhang and Z. Xie, *Chem.–Eur. J.*, 2015, **21**, 10334–10337.

17 Select examples for C–H insertion reactions of *o*-carboryne:(*a*) S. R. Wang, Z. Qiu and Z. Xie, *J. Am. Chem. Soc.*, 2011, **133**, 5760–5763; (*b*) D. Zhao, J. Zhang and Z. Xie, *Angew. Chem., Int. Ed.*, 2014, **53**, 12902–12906; (*c*) S. R. Wang and Z. Xie, *Organometallics*, 2012, **31**, 4544–4550; (*d*) R. Cheng, J. Zhang, J. Zhang, Z. Qiu and Z. Xie, *Angew. Chem., Int. Ed.*, 2016, **55**, 1751–1754.

18 D. Zhao, J. Zhang and Z. Xie, *Chem.–Eur. J.*, 2015, **21**, 10334–10337.

19 CCDC 2052100 (**3h**), CCDC 2052101 (**3i**), CCDC 2052102 (**3k**), CCDC 2052103 (**3l**), CCDC 2052104 (**3m**), CCDC 2052105 (**3q**), CCDC 2052106 (**3s**), CCDC 2052107 (**3t**), CCDC 2052108 (**3w**), CCDC 2052109 (**3y**), CCDC 2052110 (**3jm**), CCDC 2052111 (**5**) and CCDC 2052112 (**7**) contain the supplementary crystallographic data for this paper.

20 (*a*) A. Ajaz, A. Z. Bradley, R. C. Burrell, W. H. H. Li, K. J. Daoust, L. B. Bovee, K. J. DiRico and R. P. Johnson, *J. Org. Chem.*, 2011, **76**, 9320–9328; (*b*) V. P. Ananikov, *J. Phys. Org. Chem.*, 2001, **14**, 109–121; (*c*) V. P. Ananikov and E. G. Gordeev, *Chem. Sci.*, 2011, **2**, 2332–2341.

21 (*a*) R. P. Johnson, *Chem. Rev.*, 1989, **89**, 1111–1124; (*b*) S. L. Skraba and R. P. Johnson, *J. Org. Chem.*, 2012, **77**, 11096–11100; (*c*) T. L. Jacobs, J. R. McClenon and O. J. Muscio Jr, *J. Am. Chem. Soc.*, 1969, **91**, 6038–6041.