ChemComm

Synthesis of 9-Borafluorene Analogues Featuring a Three-Dimensional 1,1'-Bis(o-carborane) Backbone

Journal:	*ChemComm*
Manuscript ID	CC-COM-12-2018-010087.R1
Article Type:	Communication

Journal Name

COMMUNICATION

Synthesis of 9-Borafluorene Analogues Featuring a Three-Dimensional 1,1'-Bis(o-carborane) Backbone

pReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sam Yruegas[a], Jonathan C. Axtell[b], Kent O. Kirlikovali[b], Alexander M. Spokoyny[b,c], and Caleb D. Martin[a]*

The synthesis of [1,1'-bis(*o*-carboranyl)]boranes was achieved through the deprotonation of 1,1'-bis(*o*-carborane) reagents followed by salt metathesis with $(^{i}Pr)_2NBCl_2$. X-ray crystallography confirms planar central BC_4 rings and Gutmann-Beckett studies reveal an increase in Lewis acidity at the boron center in comparison to their biphenyl congener, 9-borafluorene.

Polyhedral carborane clusters are viewed as three-dimensional aromatic analogues to the ubiquitous two-dimensional aromatic arenes (e.g. benzene).[1] These species share high delocalization within the cage and ring resulting in high kinetic stability.[2] The significant difference is that carboranes exhibit three-dimensional aromaticity while benzene is a classical π aromatic molecule. Due to their unique steric profile and electronic structure, *o*-carboranes have been explored as a substitute for phenyl groups in molecules. The lability of the C-H vertices (pKa = 22 *c.f.* benzene = 43) of *o*-carborane facilitates selective derivatization to incorporate carboranes into molecular architectures.[3] 1,1'-Bis(*o*-carborane, **B**) can be viewed as a three-dimensional analogue to a biphenyl unit, a common ligand scaffold in organometallic chemistry (**A**, Fig 1).[4] The facile manipulation and high stability has resulted in complexes featuring **B** being investigated in medicine and electronic materials.[2a, 5]

9-Borafluorenes (**1A**) contain a biphenyl backbone linked by a tricoordinate boron center and have been recognized as attractive targets for molecular sensors[6], reagents for the synthesis of polycyclic aromatic hydrocarbons[7] as well as components in organic light emitting diodes (OLEDs)[8] and organic photovoltaics (OPVs).[9] The vacant p_z orbital on the boron center extends conjugation throughout the three fused rings. We envisioned that 1,1'-bis(*o*-carborane) could replace the biphenyl framework in 9-borafluorenes to generate a species with a three-dimensional backbone.

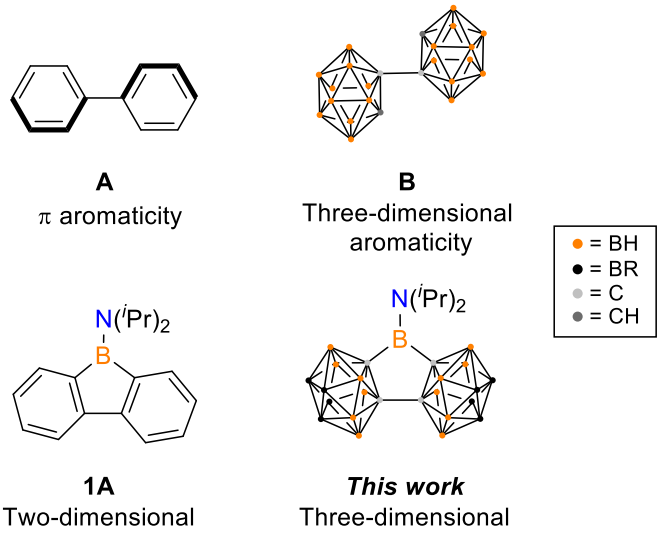
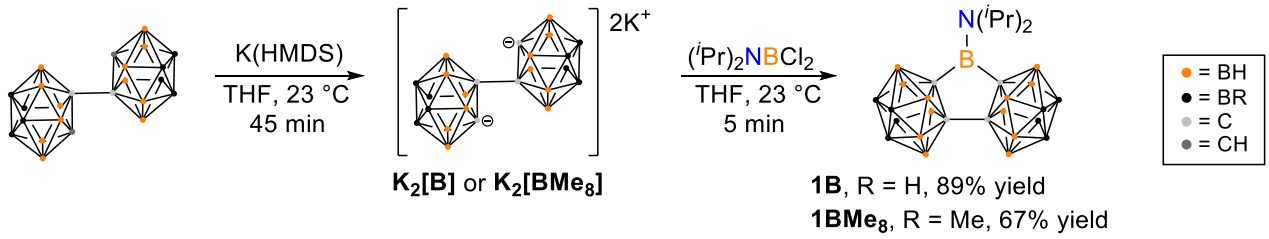


Fig 1. Relationship of biphenyl (**A**) to 1,1'-bis(*o*-carborane) (**B**) and the corresponding chelated boranes investigated in this work.

The initial strategies to access the target [1,1'-bis(*o*-carboranyl)]boranes were inspired by effective methods for the synthesis of 9-borafluorenes, specifically transmetallation of a stannole or dilithiated species with RBX_2.[10] The corresponding [1,1'-bis(*o*-carboranyl)]stannole[4j] was recently reported and the [1,1'-bis(*o*-carboranyl)]dilithium species[11] has been generated and utilized *in situ*. Unfortunately, all attempts to access the [1,1'-bis(*o*-carboranyl)]borane via these reagents were unsuccessful (Tables S-1 and S-2). In addition, the transmetallation reaction with the [1,1'-bis(*o*-carboranyl)]magnesium species did not generate the desired boracycle (Table S-3). Potassium bis(trimethylsilyl)amide [K(HMDS)] is also an effective base for the deprotonation of the C-H vertices and the resultant salt, **K_2[B]**, is easier to generate and offers enhanced solubility in comparison to the dilithiated

[a] Department of Chemistry and Biochemistry, Baylor University, One Bear Place #97348, Waco, Texas 76798, United States. E-mail: caleb_d_martin@baylor.edu
[b] Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095, USA. E-mail: spokoyny@ chem.ucla.edu
[c] California NanoSystems Institute (CNSI), University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, California 90095, USA.
Electronic Supplementary Information (ESI) available: Experimental procedures, multinuclear NMR Spectra, X-ray crystallographic data (CCDC 1884761-1884762), FT-IR spectra, and computational details (PDF). See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of **1B** and **1BMe$_8$**.

reagent.[4k, 12] After several attempts using a variety of conditions (Table S-4), the room temperature generation of **K$_2$[B]** in THF followed by addition of $(^i\text{Pr})_2\text{NBCl}_2$ proved to be an effective method to furnish the desired [1,1'-bis(*o*-carboranyl)]borane **1B**. Acquiring a $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture showed a three-coordinate peak at 32.9 ppm, slightly shifted from $(^i\text{Pr})_2\text{NBCl}_2$ (31.3 ppm), coupled with the disappearance of one of the diagnostic signals corresponding to **B** (-2.2 ppm) and emergence of a singlet at 1.7 ppm, suggesting restricted rotation about the C-C bond in **B**.[13] After isolation, the product was dissolved in $CDCl_3$ and the subsequent ^{1}H NMR spectrum contained no C-H carborane signal at 3.51 ppm, indicating successful deprotonation of the carboranyl moieties and the product was isolated in 89% yield (Scheme 1). The identity of **1B** was further confirmed based on single crystal X-ray diffraction studies (Fig 2). The synthetic route was compatible with the octa-methylated variant **1BMe$_8$**[14] featuring a $^{11}\text{B}\{^1\text{H}\}$ NMR resonance at 33.7 ppm corresponding to the $(^i\text{Pr})_2$NB-center, and a singlet at 6.0 ppm resulting from κ^2-C,C'-chelation of the bis(*o*-carborane). X-ray diffraction studies confirmed the structural identity of **1BMe$_8$**, which was isolated in 67% yield (Fig 2).

A notable structural feature of **1B** and **1BMe$_8$** are highly planar central BC_4 rings (maximum deviation from planarity = 0.029 Å and 0.011 Å, respectively), which is comparable to their borafluorene counterpart **1A** (0.020 Å). The boron atom of the central ring and adjacent nitrogen atom of **1B** are trigonal planar [Σ_{angles}: B(1) = 360.0(18)˚ and N(1) = 360.0(17)˚, Table 1]. Positional disorder of the isopropyl groups on the nitrogen atom of **1BMe$_8$** prevents an in-depth analysis of the metrical parameters of the substituents. The endocyclic carbon-carbon bonds of **1B** and **1BMe$_8$** are longer than **1A**[10b] [**1B**: C(1)–C(2) 1.649(3) Å, C(2)–C(3) 1.528(3) Å, and C(3)–C(4) 1.649(3) Å, **1BMe$_8$**: C(1)–C(2) 1.652(3) Å, C(2)–C(3) 1.524(3) Å, and C(3)–C(4) 1.646(3) Å, **1A**: C(1)–C(2) 1.418(3) Å, C(2)–C(3) 1.474(3) Å, and C(3)–C(4) 1.413(3) Å] but contracted from the parent **B**[3j] [C(1)–C(2) 1.630(3) Å, C(2)–C(3) 1.528(3) Å, and C(3)–C(4) 1.649(3) Å]. The B–N bond lengths of **1B** and **1BMe$_8$** are slightly shorter compared to previously reported B–N length of **1A** [1.371(3) Å and 1.384(4) Å *c.f.* 1.396(3) Å][10b, 15], indicating strong π-donation from the nitrogen lone pair to boron.[16]

The UV-Vis spectra of **1B** and **1BMe$_8$** in CH_2Cl_2 (Fig 3A) exhibit absorption maxima at 232 and 233 nm, respectively, blueshifted from **1A** (248 nm).[10b] Cyclic voltammetry (CV) measurements conducted on **1B** show an irreversible one-electron reduction at -1.86 V versus the ferrocenium/ferrocene couple (Fc^+/Fc). In comparison, **1BMe$_8$** exhibits an irreversible reduction at -2.09 V whereas **1A** showed only a reversible reduction at -2.95 V, indicating that the bis(*o*-carboranyl) backbone imparts an electron-withdrawing effect facilitating reduction (Fig 3B).[10b]

In order to understand the electronic effects of the bis(*o*-carboranyl) ligand scaffold, density functional theory (DFT) calculations were carried out. The geometries of **1A**, **1B**, and **1BMe$_8$** were optimized based on the X-ray structure of **1B** at the PBE-D3(BJ)/TZP level, and single-point calculations were carried out at the B3LYP-D3(BJ)/TZ2P level of theory (Fig S-19). The frontier orbital diagrams for **1B** and **1BMe$_8$** are similar, where

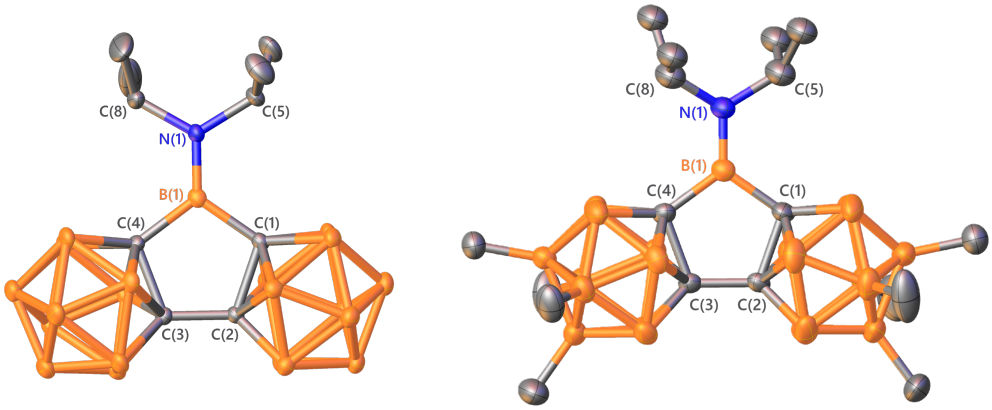


Fig 2. Solid-state structures of **1B** and **1BMe$_8$**. Thermal ellipsoids are depicted at 50% probability and hydrogen atoms are removed for clarity. The diisopropyl group in **1BMe$_8$** is positionally disordered and only the major component is shown.

Table 1. Salient bond lengths (Å) and angles [°] in compounds **1B**, **1BMe$_8$**, and **1A**.

	1B	1BMe$_8$	1A
B(1)-C(1)	1.631(3)	1.622(4)	1.593(3)
C(1)-C(2)	1.649(3)	1.652(3)	1.418(3)
C(2)-C(3)	1.528(3)	1.524(3)	1.474(3)
C(3)-C(4)	1.649(3)	1.646(3)	1.413(3)
C(4)-B(1)	1.630(3)	1.626(4)	1.601(3)
B(1)-N(1)	1.371(3)	1.384(4)	1.396(3)
N(1)-B(1)-C(4)	126.06(19)	125.50(2)	128.97(13)
C(1)-B(1)-N(1)	125.61(18)	125.40(2)	127.51(19)
C(1)-B(1)-C(4)	108.33(16)	109.00(2)	103.44(17)
B(1)-N(1)-C(5)	119.94(17)		120.90(2)
B(1)-N(1)-C(8)	120.09(18)		119.76(18)
C(5)-N(1)-C(8)	119.96(16)		119.35(19)

the highest occupied molecular orbital (HOMO) is predominantly of π-character with respect to the B–N fragment, and the lowest occupied molecular orbital (LUMO) primarily resides on the bis(*o*-carboranyl) borane fragment. In contrast, the HOMO for **1A** is entirely on the biphenyl fragment with no contribution from the amine, and the LUMO for **1A** is localized on the biphenyl borane fragment. The HOMO-LUMO gaps for **1B** and **1BMe$_8$** are comparable (5.99 eV and 6.03 eV, respectively), and significantly larger than **1A** (4.17 eV). These data corroborate similar absorption maxima for **1B** and **1BMe$_8$** as well as a bathochromic shift relative to the absorption maximum of **1A** (Fig 3A). The calculated higher-lying LUMO for **1BMe$_8$** (-1.74 eV) relative to that of **1B** (-2.05 eV) is consistent with the observed more negative reduction potential for **1BMe$_8$** (-2.09 V and -1.86 V, respectively; Fig 3B).

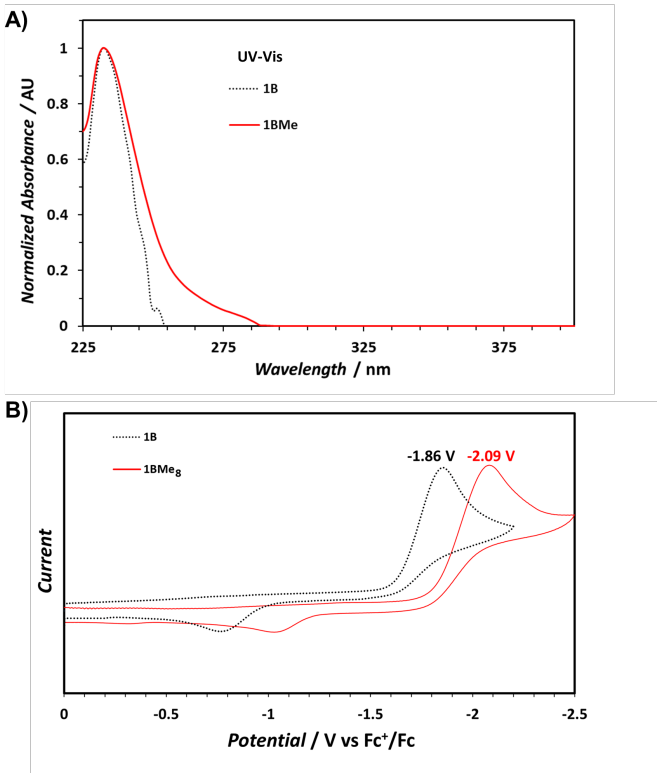


Fig 3. **A**) UV–Vis absorption emission spectra for **1B** and **1BMe$_8$** obtained from solutions of CH_2Cl_2 (λ = 232 and 233 nm respectively). **B**) Cyclic voltammograms of **1B** and **1BMe$_8$** recorded in anhydrous tetrahydrofuran with 0.1 M $[N^nBu_4][PF_6]$ and referenced to the ferrocenium/ferrocene redox couple (Fc^+/Fc; scan rate = 0.1 V/s).

To experimentally gauge Lewis acidity, the Gutmann-Beckett method was utilized.[17] This method involves the addition of an excess of Et_3PO to a solution of the borane and monitoring the change in chemical shift of the $^{31}P\{^1H\}$ NMR signal ($\delta_{31Psample} - 41.0$). Multiplying this value by 2.21 gives the acceptor number (AN), where a greater AN signifies stronger Lewis acidity. The AN of **1A** is 13.5 in C_6D_6[10b] and performing the analogous study with **1B** gave an AN value of 15.3. Methyl substitution at the peripheral boron vertices have an inductive effect, in this case acting as electron-withdrawing groups.[3k, 18] Subsequent Gutmann-Beckett studies of **1BMe$_8$** corroborated this hypothesis with an AN of 20.3, aligning with an increase of Lewis acidity at the boron center.

In summary, we have taken advantage of the lability of the C-H bonds of 1,1'-bis(*o*-carborane) to access 9-borafluorene analogues with a three-dimensional backbone. These species represent the first examples of 1,1'-bis(carboranyl)boranes and feature a highly planar central ring with enhanced Lewis acidity in comparison to 9-borafluorenes. Methyl substitution at the 8,9,10,12-B-vertices results in an increase of the overall Lewis acidity of the molecule. The results demonstrate the potential of utilizing bis(*o*-carboranes) as biphenyl analogues to create unique boracyclic architectures.

‡ C. D. M. and S. Y. are grateful to the Welch Foundation (Grant No. AA-1846) and the National Science Foundation for a CAREER Award (Award No. 1753025) for their generous support of this work. A. M. S. is thankful to 3M for a Non-Tenured Faculty Award, Alfred P. Sloan Foundation for a Fellowship in Chemistry, NIGMS (R35GM124746), and Research Corporation for Science Advancement (RCSA) for a Cottrell Fellowship.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. (a) P. v. R. Schleyer and K. Najafian, *Inorg. Chem.*, 1998, **37**, 3454-3470; (b) R. B. King, *Chem. Rev.*, 2001, **101**, 1119-1152; (c) Z. Chen and R. B. King, *Chem. Rev.*, 2005, **105**, 3613-3642.
2. (a) J. Plesek, *Chem. Rev.*, 1992, **92**, 269-278; (b) M. A. Fox and A. K. Hughes, *Coord. Chem. Rev.*, 2004, **248**, 457-476; (c) R. N. Grimes, *Dalton Trans.*, 2015, **44**, 5939-5956; (d) R. N. Grimes, *Carboranes*, Academic Press, New York, 2016; (e) J. Estrada, C. A. Lugo, S. G. McArthur and V. Lavallo, *Chem. Commun.*, 2016, **52**, 1824-1826.
3. (a) L. I. Zakharkin and A. I. Kovredov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22**, 1396-1396; (b) L. I. Zakharkin and N. F. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26**, 2184-2186; (c) L. I. Zakharkin and N. F. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1267-1268; (d) N. G. Bokii, A. I. Yanovskii, Y. T. Struchkov, N. F. Shemyakin and L. I. Zakharkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 328-334; (e) M. Y. Antipin, N. G. Furmanova, A. I. Yanovskii and Y. T. Struchkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1264-1267; (f) L. I. Zakharkin and N. F. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1525-1527; (g) L. I. Zakharkin and N. F. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 2572-2573; (h) R. A. Love and R. Bau, *J. Am. Chem. Soc.*, 1972, **94**, 8274-8276; (i) D. E. Harwell, J. McMillan, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1997, **36**, 5951-5955; (j)

S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167-5168; (k) A. V. Puga, F. Teixidor, R. Sillanpää, R. Kivekäs, M. Arca, G. Barberà and C. Viñas, *Chem. - Eur. J.*, 2009, **15**, 9755-9763; (l) Z. Qiu, S. Ren and Z. Xie, *Acc. Chem. Res.*, 2011, **44**, 299-309; (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) S. Ren, Z. Qiu and Z. Xie, *J. Am. Chem. Soc.*, 2012, **134**, 3242-3254; (o) M. Asay, C. E. Kefalidis, J. Estrada, D. S. Weinberger, J. Wright, C. E. Moore, A. L. Rheingold, L. Maron and V. Lavallo, *Angew. Chem. Int. Ed.*, 2013, **125**, 11774-11777; (p) A. L. Chan, J. Fajardo, J. H. Wright, M. Asay and V. Lavallo, *Inorg. Chem.*, 2013, **52**, 12308-12310; (q) J. H. Wright, C. E. Kefalidis, F. S. Tham, L. Maron and V. Lavallo, *Inorg. Chem.*, 2013, **52**, 6223-6229; (r) Z.-J. Yao, Y.-Y. Zhang and G.-X. Jin, *J. Organomet. Chem.*, 2015, **798**, 274-277; (s) C. A. Lugo, C. E. Moore, A. L. Rheingold and V. Lavallo, *Inorg. Chem.*, 2015, **54**, 2094-2096; (t) Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. - Eur. J.*, 2016, **22**, 6764-6767; (u) D. Zhao, J. Zhang, Z. Lin and Z. Xie, *Chem. Commun.*, 2016, **52**, 9992-9995; (v) Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. Commun.*, 2016, **52**, 12710-12713; (w) J. C. Axtell, K. O. Kirlikovali, P. I. Djurovich, D. Jung, V. T. Nguyen, B. Munekiyo, A. T. Royappa, A. L. Rheingold and A. M. Spokoyny, *J. Am. Chem. Soc.*, 2016, **138**, 15758-15765; (x) R. M. Dziedzic, J. L. Martin, J. C. Axtell, L. M. A. Saleh, T.-C. Ong, Y.-F. Yang, M. S. Messina, A. L. Rheingold, K. N. Houk and A. M. Spokoyny, *J. Am. Chem. Soc.*, 2017, **139**, 7729-7732; (y) T. L. Chan and Z. Xie, *Chem. Sci.*, 2018, **9**, 2284-2289; (z) R. Cheng, B. Li, J. Wu, J. Zhang, Z. Qiu, W. Tang, S.-L. You, Y. Tang and Z. Xie, *J. Am. Chem. Soc.*, 2018, **140**, 4508-4511; (aa) Y. Quan, Z. Qiu and Z. Xie, *Chem. - Eur. J.*, 2018, **24**, 2795-2805; (ab) S. Duttwyler, *Pure Appl. Chem.*, 2018, **90**, 733.

4. (a) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642-1643; (b) A. M. Spokoyny, *Pure Appl. Chem.*, 2013, **85**, 903-919; (c) G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2015, **44**, 5628-5637; (d) M. J. Martin, W. Y. Man, G. M. Rosair and A. J. Welch, *J. Organomet. Chem.*, 2015, **798**, 36-40; (e) 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; (f) K. O. Kirlikovali, J. C. Axtell, A. Gonzalez, A. C. Phung, S. I. Khan and A. M. Spokoyny, *Chem. Sci.*, 2016, **7**, 5132-5138; (g) I. Sivaev, *Commun. Inorg. Synth.*, 2016, 21-28; (h) L. E. Riley, T. Krämer, C. L. McMullin, D. Ellis, G. M. Rosair, I. B. Sivaev and A. J. Welch, *Dalton Trans.*, 2017, **46**, 5218-5228; (i) G. Thiripuranathar, A. P. Y. Chan, D. Mandal, W. Y. Man, M. Argentari, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2017, **46**, 1811-1821; (j) J. C. Axtell, K. O. Kirlikovali, R. M. Dziedzic, M. Gembicky, A. L. Rheingold and A. M. Spokoyny, *Eur. J. Inorg. Chem.*, 2017, 4411-4416; (k) K. O. Kirlikovali, J. C. Axtell, K. Anderson, P. I. Djurovich, A. L. Rheingold and A. M. Spokoyny, *Organometallics*, 2018, **37**, 3122-3131; (l) A. P. Y. Chan, G. M. Rosair and A. J. Welch, *Inorg. Chem.*, 2018, **57**, 8002-8011.

5. (a) M. Scholz and E. Hey-Hawkins, *Chem. Rev.*, 2011, **111**, 7035-7062; (b) F. Issa, M. Kassiou and L. M. Rendina, *Chem. Rev.*, 2011, **111**, 5701-5722; (c) L. Zhu, W. Lv, S. Liu, H. Yan, Q. Zhao and W. Huang, *Chem. Commun.*, 2013, **49**, 10638-10640; (d) Z. J. Leśnikowski, *J. Med. Chem.*, 2016, **59**, 7738-7758; (e) B. P. Dash, R. Satapathy, E. R. Gaillard, K. M. Norton, J. A. Maguire, N. Chug and N. S. Hosmane, *Inorg. Chem.*, 2011, **50**, 5485-5493; (f) S. G. McArthur, L. Geng, J. Guo and V. Lavallo, *Inorg. Chem. Front.*, 2015, **2**, 1101-1104; (g) S. Mukherjee and P. Thilagar, *Chem. Commun.*, 2016, **52**, 1070-1093; (h) R. Núñez, M. Tarrés, A. Ferrer-Ugalde, F. F. de Biani and F. Teixidor, *Chem. Rev.*, 2016, **116**, 14307-14378; (i) X. Li, H. Yan and Q. Zhao, *Chem. - Eur. J.*, 2016, **22**, 1888-1898; (j) D. Tu, D. Shao, H. Yan and C. Lu, *Chem. Commun.*, 2016, **52**, 14326-14329.

6. (a) S. Muhammad, M. R. Janjua and Z. Su, *J. Phys. Chem. C*, 2009, **113**, 12551–12557; (b) I. A. Adams and P. A. Rupar, *Macromol. Rapid Commun.*, 2015, **36**, 1336-1340; (c) T. Matsumoto, H. Takamine, K. Tanaka and Y. Chujo, *Mater. Chem. Front.*, 2017, **1**, 2368-2375.

7. (a) S. Biswas, C. Maichle-Mössmer and H. F. Bettinger, *Chem. Commun.*, 2012, **48**, 4564-4566; (b) M. Müller, C. Maichle-Mössmer and H. F. Bettinger, *Angew. Chem. Int. Ed.*, 2014, **53**, 9380-9383; (c) S. Yruegas, J. J. Martinez and C. D. Martin, *Chem. Commun.*, 2018, **54**, 6808-6811; (d) S. Yruegas, J. H. Barnard, K. Al-Furaiji, J. L. Dutton, D. J. D. Wilson and C. D. Martin, *Organometallics*, 2018, **37**, 1515-1518; (e) K. R. Bluer, L. E. Laperriere, A. Pujol, S. Yruegas, V. A. K. Adiraju and C. D. Martin, *Organometallics*, 2018, **37**, 2917-2927; (f) E. von Grotthuss, A. John, T. Kaese and M. Wagner, *Asian J. Org. Chem.*, 2018, **7**, 37-53; (g) W. Zhang, G. Li, L. Xu, Y. Zhuo, W. Wan, N. Yan and G. He, *Chem. Sci.*, 2018, **9**, 4444-4450; (h) J. Radtke, S. K. Mellerup, M. Bolte, H.-W. Lerner, S. Wang and M. Wagner, *Org. Lett.*, 2018, **20**, 3966-3970.

8. (a) C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574-4585; (b) K. S. Thanthiriwatte and S. R. Gwaltney, *J. Phys. Chem. A.*, 2006, **110**, 2434-2439; (c) S. Yamaguchi and A. Wakamiya, *Pure Appl. Chem.*, 2006, **78**, 1413.

9. M. Lorenz-Rothe, K. S. Schellhammer, T. Jägeler-Hoheisel, R. Meerheim, S. Kraner, M. P. Hein, C. Schünemann, M. L. Tietze, M. Hummert, F. Ortmann, G. Cuniberti, C. Körner and K. Leo, *Adv. Electron. Mater.*, 2016, **2**, 1600152-1600163.

10. (a) P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo and M. Parvez, *Organometallics*, 2003, **22**, 1266-1274; (b) M. F. Smith, S. J. Cassidy, I. A. Adams, M. Vasiliu, D. L. Gerlach, D. A. Dixon and P. A. Rupar, *Organometallics*, 2016, **35**, 3182-3191; (c) W. Zhang, D. Yu, Z. Wang, B. Zhang, L. Xu, G. Li, N. Yan, E. Rivard and G. He, *Org. Lett.*, 2018, DOI: 10.1021/acs.orglett.8b03538.

11. J. R. Reiner, R. P. Alexander and H. Schroeder, *Inorg. Chem.*, 1966, **5**, 1460-1462.

12. A.-R. Popescu, A. D. Musteti, A. Ferrer-Ugalde, C. Viñas, R. Núñez and F. Teixidor, *Chem. - Eur. J.*, 2012, **18**, 3174-3184.

13. F. Teixidor, C. Vinas and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 3339-3345.

14. A. Herzog, A. Maderna, G. N. Harakas, C. B. Knobler and M. F. Hawthorne, *Chem. - Eur. J.*, 1999, **5**, 1212-1217.

15. (a) T. Araki, A. Wakamiya, K. Mori and S. Yamaguchi, *Chem. - Asian J.*, 2012, **7**, 1594-1603; (b) F. Ge, G. Kehr, C. G. Daniliuc, C. Mück-Lichtenfeld and G. Erker, *Organometallics*, 2015, **34**, 4205-4208.

16. P. Paetzold, *Pure Appl. Chem.*, 1991, **63**, 345-350.

17. (a) M. A. Beckett, G. C. Strickland, J. R. Holland and K. Sukumar Varma, *Polymer*, 1996, **37**, 4629-4631; (b) I. B. Sivaev and V. I. Bregadze, *Coord. Chem. Rev.*, 2014, **270-271**, 75-88.

18. (a) S. Hermanek, *Chem. Rev.*, 1992, **92**, 325-362; (b) S. Heřmánek, *Inorganica Chim. Acta*, 1999, **289**, 20-44; (c) F. Teixidor, G. Barberà, A. Vaca, R. Kivekäs, R. Sillanpää, J. Oliva and C. Viñas, *J. Am. Chem. Soc.*, 2005, **127**, 10158-10159.