Journal Name

COMMUNICATION

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Boryl Substituted Group 13 Metallylenes: Complexes with an Iron Carbonyl Fragment

Deepak Dange,[a] Christian P. Sindlinger,[b] Simon Aldridge[b] and Cameron Jones*,[a]

The first examples of boryl substituted aluminylene and gallylene complexes, [(DAB)B(THF)Al{Fe(CO)$_3$(μ-CO)}]$_2$ and [(DAB)BGa{μ-Fe(CO)$_4$}]$_2$ (DAB = {(C$_6$H$_3$Pr$^i_2$-2,6)NCH}$_2$) have been prepared by reduction of MX$_2$(THF){B(DAB)} (M = Al or Ga, X = Cl or Br) with K$_2$[Fe(CO)$_4$]. Spectroscopic and crystallographic analyses of the compounds show them to be structurally distinct dimers, the latter of which possesses a close Ga···Ga separation that computational analyses reveal has negligible bonding character.

The chemistry of group 13 metallylenes, RM: (R = alkyl, aryl, silyl, amido etc.), is now well developed, and numerous complexes of these carbene analogues, involving metals from across the periodic table, have been prepared and studied in depth.[1,2] While monomeric, uncomplexed examples of such systems are known for all the group 13 metals, these typically incorporate bi- or polydentate anionic ligands (e.g. β-diketiminate (Nacnac), guanidinate or tris(pyrazolyl)borate) at the metal(I) centre.[3-5] With that said, a handful of one-coordinate metallylenes (M = Ga, In or Tl) have been kinetically stabilised by extremely bulky, mono-dentate terphenyl or amide ligands, although no one-coordinate aluminylenes have yet been reported.[6] Given that two-coordinate aluminylenes (e.g. (Nacnac)Al:) are emerging as powerful reagents for the activation of an array of catalytically relevant bonds (e.g. E-H (E = H, N, B, Si, P) and C-F linkages),[7] it would be of considerable interest to access one-coordinate aluminylenes, which should be markedly more electrophilic, and thus more reactive, than their two-coordinate counterparts.

In recent years, we have had significant success in stabilising a variety of low oxidation state/low-coordinate groups 13-15 complexes (e.g. **I**-**III**,[8] Figure 1), by utilising Yamashita's reagent, (THF)$_2$Li{B(DAB)} (DAB = {(C$_6$H$_3$Pr$^i_2$-2,6)NCH}$_2$),[9] as the source of the boryl ligand in those compounds. In light of the imposing steric profile of this ligand (*cf.* Power's terphenyls[10]), its high nucleophilicity, and the fact that a range of aluminium complexes incorporating it have recently come forward,[11] we postulated that monomeric boryl-aluminylenes and their heavier analogues, *viz.* (DAB)BM: (M = group 13 metal), might be isolable species. Although our efforts to achieve this goal have so far proved fruitless, we have prepared the first examples of metal complexes derived from these systems, as detailed below.

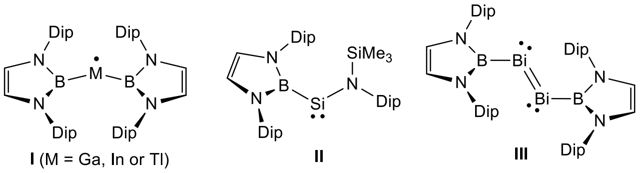


Figure 1. Examples of low oxidation state group 13-15 complexes stabilised by Yamashita's heterocyclic boryl ligand (Dip = 2,6-diisopropylphenyl).

As logical precursors to the target compounds, the boryl aluminium and gallium halides, **1**-**3** (Scheme 1) were prepared in moderate to good yields *via* 1:1 reactions of (THF)$_2$Li{B(DAB)} with group 13 metal trihalides in toluene. Attempts to remove the THF of coordination from the complexes by heating them under vacuum were not successful. This is in contrast to the related gallium alkyl complex, GaMe$_2$(THF){B(DAB)}, which does undergo a desolvation process *in vacuo*.[11(b)] It is noteworthy that indium analogues of **1**-**3** could not be prepared in our hands, as even 1:1 reactions of (THF)$_2$Li{B(DAB)} with indium halides led to bis(boryl) complexes, InX{B(DAB)}$_2$ (X = Cl[8(a)] or Br, see ESI for full details), and unreacted InX$_3$. Complexes **1**-**3** represent the first examples of crystallographically characterised boryl group 13 metal dihalides (see ESI for details), and all are monomeric, possessing distorted tetrahedral metal geometries, as is the case for the isostructural methyl analogues, MMe$_2$(THF){B(DAB)} (M = Al or Ga).[11(c),12] In line with the

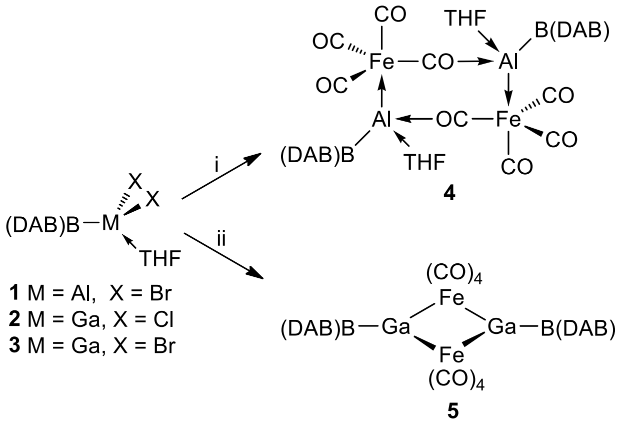
---

[a] *Monash Centre for Catalysis, School of Chemistry, PO Box 23, Monash University, VIC, 3800, Australia.*
[b] *Department of Chemistry, Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QR, UK.*
[c] *Email: cameron.jones@monash.edu*

† Electronic Supplementary Information (ESI) available: Full details and references for synthetic, crystallographic and computational studies. CCDC xxx-xxx. See DOI: 10.1039/b000000x

planar three-coordinate geometries for the boron centres of the complexes are their $^{11}B\{^{1}H\}$ NMR spectra, all of which exhibit broad resonances between δ 27-28 ppm (*cf.* δ 32.0 ppm for $GaMe_2(THF)\{B(DAB)\}$[12])

With **1**-**3** in hand, their reductions with a variety of reducing agents (e.g. magnesium(I) dimers,[13] KC_8 and K(naphthalenide)) were carried out. However, in all cases complex product mixtures resulted, the $^{11}B\{^{1}H\}$ NMR spectra of which revealed to include (DAB)BH and (DAB)BX as significant components. It is noteworthy that the apparent instability of the boryl metallylenes, (DAB)BM:, has previously been suggested from the reactions of $(THF)_2Li\{B(DAB)\}$ with heavier group 13 metal(I) halides or amides. These yielded the radical species, **I**, which were proposed to form *via* disproportionation of putative metal(I) boryl intermediates.[8(a)]



Scheme 1. Preparation of compounds **4** and **5**; i) M = Al, $K_2[Fe(CO)_4]$, THF, -KBr; ii) M = Ga, $K_2[Fe(CO)_4]$, THF, -KCl or -KBr.

A common strategy used to stabilise group 13 metallylenes has been to coordinate them to transition metal carbonyl fragments, through their metal-centred lone pair.[14] This tactic was adopted in the current study by carrying out reactions of **1**-**3** with $K_2[Fe(CO)_4]$ in THF. These led to the formation of boryl metallyne complexes, **4** and **5**, in low isolated crystalline yields (Scheme 1). In these reactions the ferrate starting material acts as a reducing agent, in a similar fashion to that previously reported for the preparations of both aluminylene and gallylene-iron carbonyl complexes.[14] Although the dimeric structures of **4** and **5** are ostensibly similar, they differ in the fact that the μ-Fe(CO)$_4$ fragments of **4** bridge both Al centres through intermolecular isocarbonyl O-Al bonds, giving rise to an eight membered $Fe_2Al_2C_2O_2$ ring, while the iron centres of **5** symmetrically bridge the galyllene fragments, yielding a four-membered Fe_2Ga_2 ring. These differences possibly occur due to the higher Lewis acidity of Al over Ga, which leads to THF ligation of the Al centres in **4**, thereby supressing the formation of Al-(μ-Fe)-Al bridges.

Both **4** and **5** are thermally stable in the solid state, and do not show any signs of decomposition in toluene solutions over 1 week. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are consistent with the compounds retaining their solid state structures in solution, while the $^{11}B\{^{1}H\}$ NMR signals (**4**: δ 30.5 ppm; **5**: δ 27.0 ppm) are at fields reminiscent of three-coordinate boron systems. The infrared spectrum of **4** exhibits strong CO stretching bands that were assigned to terminal (ν = 2005, 1937, 1902 cm^{-1}) and bridging (ν = 1653 cm^{-1}) carbonyl ligands. The latter band is at a wavenumber characteristic of bridging isocarbonyl units O-ligated to aluminium centres, (e.g. ν = 1650 cm^{-1} for $\{CpW(CO)(\mu\text{-}CO)_2AlMe_2\}_2$[15]). In contrast, the infrared spectrum of **5** highlights a terminal CO stretching band pattern (ν = 2036, 1965, 1938, 1920(sh) cm^{-1}) similar to those reported for closely related iron bridged systems (e.g. $[(THF)ClGa\{\mu\text{-}Fe(CO)_4\}]_2$[16]).

The X-ray crystal structures of **4** and **5** were determined and their molecular structures are depicted in Figures 2 and 3. As mentioned above, the monomeric units of compound **4** associate through Al-(μ-CO)-Fe isocarbonyl bridges, yielding eight-membered heterocycles. Similar bridging motifs have been observed previously in main group metal-first row transition metal carbonyl systems.[15,17] As in those compounds, there is a significant shortening and lengthening of the bridging Fe-C (1.687(3) Å) and C-O bonds (1.232(3) Å), respectively, relative to the means for those bonds in the terminal FeCO fragments (1.782 Å and 1.162 Å). This is consistent with increased $Fe(d_{\pi})\rightarrow CO(\pi^*)$ back-bonding in the bridging carbonyl unit. The geometry of the Al centres of **4** is distorted tetrahedral, while that of the Fe centres is trigonal bipyramidal. Both unique Al-O bonds, and the Al-Fe linkage, are in the normal ranges for such interactions,[18] while the Al-B separation (2.128(3) Å) is similar to all other such bonds involving the same boryl ligand (2.119-2.167 Å, 6 examples[18]).

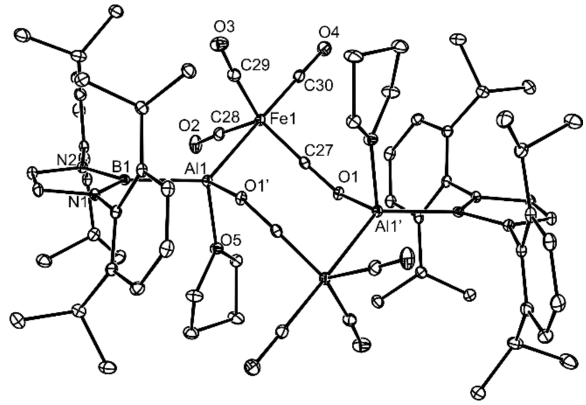


Figure 2. Molecular structure of **4** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Al(1)-O(1)' 1.896(2), Al(1)-O(5) 1.912(2), Al(1)-B(1) 2.128(3), Fe(1)-Al(1) 2.394(1), Fe(1)-C(27) 1.687(3), C(27)-O(1) 1.232(3), B(1)-Al(1)-Fe(1) 130.82(9), O(1)'-Al(1)-B(1) 104.5(1), O(5)-Al(1)-B(1) 102.2(1), C(27)-Fe(1)-Al(1) 78.42(9).

Compound **5** is also dimeric, but unlike **4**, its monomeric units associate through bridging octahedral Fe centres, generating a planar Fe_2Ga_2 four-membered ring, in which the Ga atoms have distorted trigonal planar geometries. Several structurally related compounds have been previously reported (e.g. $[(THF)ClGa\{\mu\text{-}Fe(CO)_4\}]_2$[16]), though the Ga centres in each are four-coordinate. The central rings of the boryl substituents in **5** are close to orthogonal to the Fe_2Ga_2 plane, and coordinate the iron centres with B-Ga bond lengths (2.067(2) Å) that are within the narrow range reported for (DAB)B-Ga bonds (2.045-2.121 Å, 11 examples[18]). Similarly, the Fe-Ga bond lengths in **5** (2.472 Å, mean) are unexceptional (*cf.* 2.472 Å for [(THF)ClGa{μ-Fe(CO)$_4$}]$_2$[16]), while the trans-annular Ga···Ga separation (2.9239(4) Å, *cf.* 2.881 Å in [(THF)ClGa{μ-Fe(CO)$_4$}]$_2$[16]) is short enough to suggest a possible metal-metal interaction in that compound.

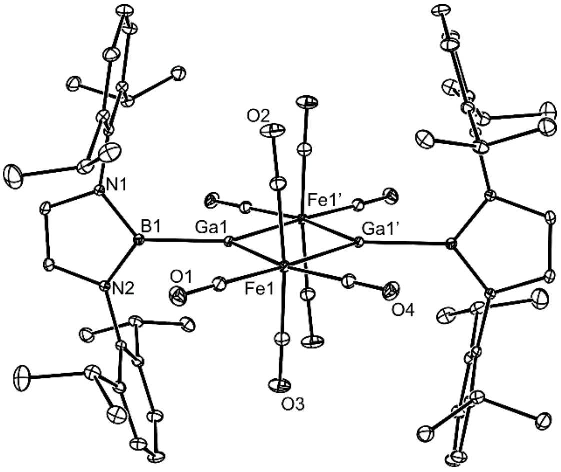


Figure 3. Molecular structure of **5** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ga(1)-B(1) 2.067(2), Ga(1)-Fe(1) 2.4684(4), Ga(1)-Fe(1)' 2.4757(4), Ga(1)···Ga(1)' 2.9239(4), B(1)-Ga(1)-Fe(1) 127.88(5), B(1)-Ga(1)-Fe(1)' 124.63(5), Fe(1)-Ga(1)-Fe(1)' 107.49(1), Ga(1)-Fe(1)-Ga(1)' 72.51(1).

In order to investigate this possibility, DFT calculations (BP86-D3(BJ)/TZ2P) were carried out on **5** in the gas phase (i.e. **5'**). The geometry of **5'** optimised to be similar to that of **5**, but with a slightly shorter Ga···Ga separation (2.865 Å). An orbital analysis of **5'** revealed a number of filled MO's that exhibit significant Ga-Fe σ-bonding character (e.g. HOMO-6 and HOMO-11, Figure 4), while there is what appears to be a small degree of trans-annular Ga-Ga σ-bonding derived from overlap of the two B-Ga σ-bonds (HOMO-21).[19] Despite this, a Bader analysis of **5'** did not show a bond critical point between the two Ga centres, so any interaction is likely to be negligible. Character of the empty p-orbitals at the Ga centres is displayed in the LUMO and LUMO+1, which show a small degree of Ga-Ga π-bonding and π*-antibonding character, respectively. In consideration of this, and in an attempt to populate the LUMO of **5**, the compound was treated with two equivalents of potassium naphthalenide in THF. However, this led only to an intractable mixture of products.

In summary, the first examples of boryl substituted aluminylene and gallylene complexes have been prepared and analysed by spectroscopic, crystallographic and computational techniques. Both prepared compounds are dimers, though they are structurally distinct in that the aluminylene adduct dimerises through Al-(μ-CO)-Fe isocarbonyl bridges, while the gallylene complex associates through Ga-{μ-Fe(CO)$_4$}-Ga linkages. The latter gives rise to a relatively short Ga···Ga separation within the generated Fe$_2$Ga$_2$ four-membered ring, though computational studies do not point to any significant bonding character between the two gallium centres. We continue to explore the ability of the nucleophilic boryl ligand, -B(DAB), to stabilise low oxidation state/low coordinate main group systems, and will report on our efforts in this direction in the due course.

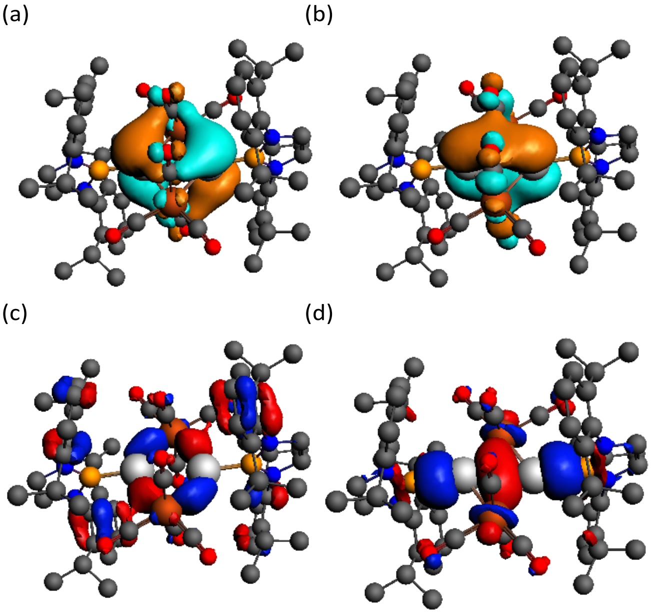


Figure 4 (a) LUMO+1, (b) LUMO, (c) HOMO-11, and (d) HOMO-21 of **5'**.

CJ and SA gratefully acknowledge financial support from the Australian Research Council, while CJ acknowledges support from the U.S. Air Force Asian Office of Aerospace Research and Development (FA2386-14-1-4043). CS acknowledges support of a Feodor Lynen Research fellowship from the Alexander von Humboldt Stiftung. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, Victoria, Australia.

Notes and references

1 C. Jones, A. Stasch in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities*, S. Aldridge, A. J. Downs (Eds), Wiley, Sussex, Chap. 5, 2011, pp 285-341
2 Selected reviews (a) M. Asay, C. Jones, M. Driess, *Chem. Rev.*, 2011, **111**, 354; (b) S. Gonzalez-Gallardo, G. Prabusankar, T. Cadenbach, C. Gemel, M. von Hopffgarten, G. Frenking, R. A. Fischer, *Struct. Bond. (Berlin)*, 2010, **136**, 147; (c) C. Jones, *Coord. Chem. Rev.*, 2010, **254**, 1273; (d) R. J. Baker, C. Jones, *Coord. Chem. Rev.*, 2005, **249**, 1857; (e) C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R. A. Fischer, *Eur. J. Inorg. Chem.*, 2004, 4161; (f) H. W. Roesky, *Inorg. Chem.*, 2004, **43**, 7284.
3 Selected examples of Al^{I} and Ga^{I} Nacnac complexes: (a) D. Dange, S. L. Choong, C. Schenk, A. Stasch, C. Jones, *Dalton Trans.*, 2012, **41**, 9304; (b) X. Li, X. Cheng, H. Song, C. Cui, *Organometallics*, 2007, **26**, 1039; (c) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.*, 2000, **39**, 4274; (d) N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.*, 2000, 1991.
4 Guanidinato Ga^{I} complexes: (a) J. Overgaard, C. Jones, D. Dange, J. A. Platts, *Inorg. Chem.*, 2011, **50**, 8418; (b) G. Jin, C. Jones, P. C. Junk, A. Stasch, W. D. Woodul, *New. J. Chem.*, 2008, **32**, 835; (c) C. Jones, P. C. Junk, J. A. Platts, A. Stasch, *J. Am. Chem. Soc.*, 2006, **128**, 2206.
5 A Ga^{I} tris(pyrazoly)lborate complex: M. C. Kuchta, J. B. Bonanno, G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 10914.

6 Selected examples of one-coordinate group 13 metallylenes: (a) D. Dange, J. Li, C. Schenk, H. Schnöckel, C. Jones, *Inorg. Chem.*, 2012, **51**, 13050; (b) Z. Zhu, R. C. Fischer, B. D. Ellis, E. Rivard, W. A. Merrill, M. M. Olmstead, P. P. Power, J. D. Guo, S. Nagase, L. Pu, *Chem. Eur. J.*, 2009, **15**, 5263; (c) R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.*, 2006, **128**, 12498; (d) S. T. Haubrich, P. P. Power, *J. Am. Chem. Soc.*, 1998, **120**, 2202.

7 See for example: (a) M. R. Crimmin, M. J. Butler, A. J. P. White, *Chem. Commun.*, 2015, **51**, 15994; (b) T. Chu, I. Korobkov, G. I. Nikonov, *J. Am. Chem. Soc.*, 2014, **136**, 9195.

8 (a) A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Nature Chem.*, 2014, **6**, 315; (b) A. V. Protchenko, K. H. Birjkumar, H. Krishna, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500; (c) D. Dange, A. Davey, J. A. B. Abdalla, S. Aldridge, C. Jones, *Chem. Commun.*, 2015, **51**, 7128.

9 Y. Segawa, M. Yamashita, K. Nozaki, *Science*, 2006, **314**, 113.

10 E. Rivard, P. P. Power, *Inorg. Chem.*, 2007, **46**, 10047.

11 (a) N. Dettenrieder, C. O. Hollfelder, L. N. Jende, C. Maichle-Mossmer, R. Anwander, *Organometallics*, 2014, **33**, 1528; (b) N. Dettenrieder, C. Schadle, C. Maichle-Mossmer, R. Anwander, *Dalton Trans.*, 2014, **43**, 15760; (c) N. Dettenrieder, H. M. Dietrich, C. Schadle, C. Maichle-Mossmer, K. W. Tornroos, R. Anwander, *Angew. Chem. Int. Ed.*, 2012, **51**, 4461.

12 N. Dettenrieder, C. Schaedle, C. Maichle-Moessmer, P. Sirsch, R. Anwander, *J. Am. Chem. Soc.*, 2014, **136**, 886.

13 Reviews: (a) C. Jones, A. Stasch, *Top. Organomet. Chem.*, 2013, **45**, 73; (b) A. Stasch, C. Jones, *Dalton Trans.*, 2011, **40**, 5659.

14 See for example: (a) G. Tan, T. Szilvasi, S. Inoue, B. Blom, M. Driess, *J. Am. Chem. Soc.*, 2014, **136**, 9732; (b) J. Weiss. D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 70.

15 A. J. Conway, G. J. Gainsford, R. R. Schrieke, J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1975, 2499.

16 T. Adamczyk, G.-M. Li, G. Linti, H. Pritzkow, A. Seifert, T. Zessin, *Eur, J. Inorg. Chem.*, 2011, 3480.

17 See for example: (a) M. P. Blake, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.*, 2015, **137**, 12352; (b) J. A. B. Abdalla, I. M. Riddlestone, J. Turner, P. A. Kaufman, R. Tirfoin, N. Philips, S. Aldridge, *Chem. Eur. J.*, 2014, **20**, 17624.

18 As determined from a survey of the Cambridge Crystallographic Database, October, 2016.

19 N.B. Both the HOMO and HOMO-1 of **5'** largely encompass π-bonding interactions within the boryl heterocycles.

Graphical Abstract

The first examples of boryl substituted aluminylene and gallylene complexes (see picture, DAB = $\{(C_6H_3Pr^i{}_2\text{-}2,6)NCH\}_2$) have been prepared by reduction of boryl-group 13 dihalide compounds with $K_2[Fe(CO)_4]$.