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Metal-free binding and coupling of carbon monoxide at a boron–boron triple bond

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Many metal-containing compounds, and some metal-free compounds, will bind carbon monoxide. However, only a handful of metal-containing compounds have been shown to induce the coupling of two or more CO molecules, potentially a method for the use of CO as a one-carbon-atom building block for the synthesis of organic molecules. In this work, CO was added to a boron–boron triple bond at room temperature and atmospheric pressure, resulting in a compound into which four equivalents of CO are incorporated: a flat, bicyclic, bis(boralactone). By the controlled addition of one CO to the diboryne compound, an intermediate in the CO coupling reaction was isolated and structurally characterized. Electrochemical measurements confirm the strongly reducing nature of the diboryne compound.

Carbon monoxide has long been available on an industrial scale in the form of synthesis gas (syngas), a mixture of CO and H_2 traditionally produced from coal. Efforts to use CO as a one-carbon-atom (or C_1) building block by coupling multiple CO units arguably began in the early 1800s, with reports of reductive coupling of CO molecules by both Gmelin[1] and Liebig[2] to form salts of the dianion $[C_nO_n]^{2-}$. Currently, CO is the major C_1 feedstock of the chemical industry, partly due to the prominence of the Fischer–Tropsch process for the production of alkanes of varying lengths using CO and dihydrogen. Although the Fischer–Tropsch process generally uses late transition-metal catalysts, coupling of CO is also possible using strongly-reducing early transition-metal complexes, beginning with samarium and later lanthanum complexes (Evans and Atwood)[3,4] (**I**, Fig. 1). Other reductive CO coupling reactions have involved yttrium, niobium and tantalum (Lippard)[5], uranium (Cloke, **II**, **III**, **V**; Arnold, **VI**; Fig. 1)[6–9], rhenium (Labinger and Bercaw)[10] and tantalum (Kawaguchi, **IV**; Fig. 1)[11].

Reduction of CO with neutral p-block compounds is potentially a route to neutral CO-coupled products. However, to our knowledge, the only CO-coupling processes using p-block (albeit metallic) elements are those presented by Power with a germylene compound, which can head-to-head couple two CO units (**VII**, Fig. 1)[12,13]. Siebert showed that CO could be inserted into a cyclic diborane, but this led to unusual rearrangements rather than CO coupling[14]. Transient triplet carbenes[15] and certain stable singlet carbenes[16] react with CO, in some cases leading to reduction, but no coupling has been observed. Some 'frustrated Lewis pairs' (FLPs)[17] also react with CO, and a compound was recently reported in which two CO units and 1 equiv. of H_2 derived from syngas were coupled in a head-to-tail manner using such an FLP[18]. The disilyne (Si≡Si) of Sekiguchi has been found to couple some unsaturated compounds, but no reactivity with CO has been reported[19]. Here, we provide a report of CO coupling by a single main-group compound, a reaction in which a boron–boron triple bond is broken and four CO molecules assemble a planar, carbene-stabilized, bis(boralactone). The reaction is formally an oxidation of two zerovalent boron atoms to B(III), corresponding to a six-electron reduction of CO, and is one of only a few instances of undisputable boron-centred reduction. This rare reactivity pattern has only been observed previously with electron-rich compounds such as the boryl anions[20] and boron radicals[21] of Yamashita and Nozaki, and the base-stabilized borylene[22] of Bertrand.

Results and discussion

As a preliminary experiment to test the reactivity of our recently reported diboryne compound **1**[23] with simple small molecules, we treated a benzene solution of this with an excess of CO (Fig. 2) at room temperature. A red-orange solid sample of $B_2C_4O_4(IDip)_2$ (**3**, IDip = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene; Fig. 2a, Supplementary Fig. S1) was isolated with one signal in its ^{11}B NMR spectrum ($\delta = -3.6$) found at a much lower frequency than that of precursor **1** ($\delta = 39$), in the region usually restricted to tetrahedrally coordinated boron atoms. The ^1H-decoupled ^{13}C spectrum of **3** indicated the addition of two new quaternary carbon nuclei to the molecule. The connectivity of compound **3** was identified by single-crystal X-ray crystallography (Fig. 3). The most salient features of the molecular structure of **3** are the planarity of the bicyclic $C_6B_2O_4$ bis(boralactone) core including the carbene carbon atoms and the multiple bonding in the B–C–C–B portion of the molecule. The boron atoms are in an environment reminiscent of borataalkenes of the form $[R_2B{=}CR'_2]^-$, previously reported by the groups of Power[24] and Gabbaï[25,26]. In both cases, planar, tricoordinate boron atoms bear one very short B–C distance that can be described as a double bond (B1–C1 distance in **3**, 1.4507(18) Å; B–C distance in borataalkenes, 1.438(9)–1.475(6) Å). However, the similarity between **3** and borataalkenes does not extend to their ^{11}B NMR parameters, signals of which range from 35.0 to 45.5 ppm in the latter. The C1–C1′ distance (1.426(2) Å) is much shorter than a regular C–C single bond, and is even shorter than the central C–C single bond in a comparable bis(lactam) derived from pulvinic acid (1.489(4) Å)[27], suggesting a certain amount of double-bond character between these two atoms. Overall, the three B–C–C–B

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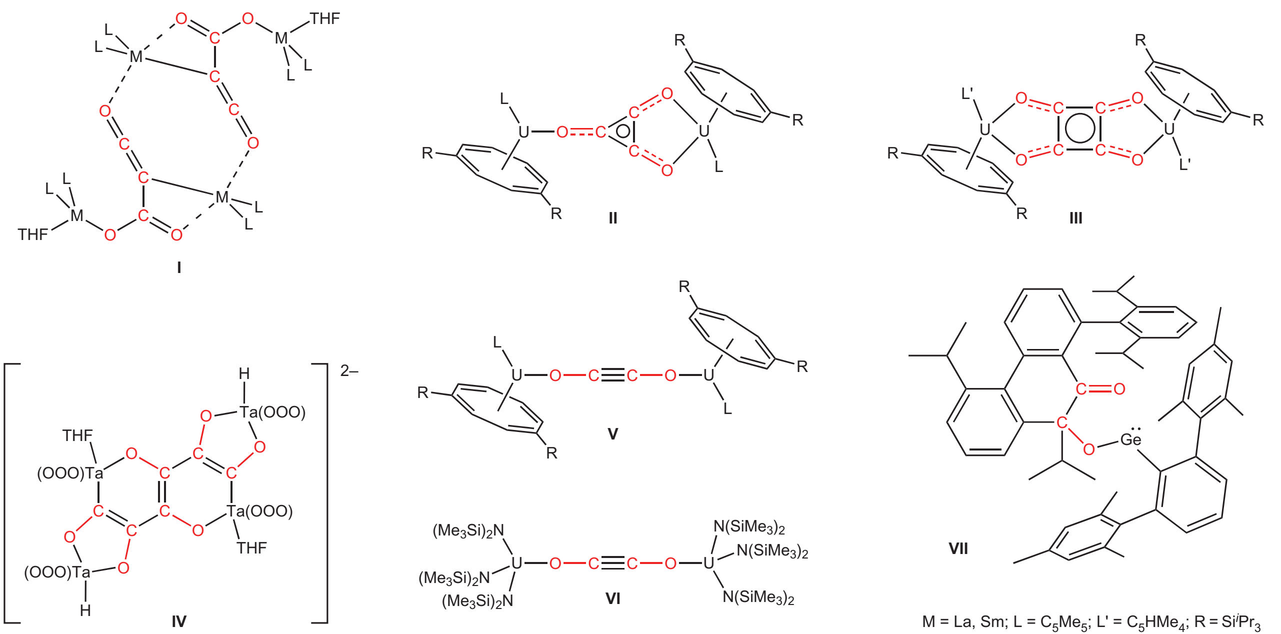

M = La, Sm; L = C_5Me_5; L' = C_5HMe_4; R = Si^iPr_3
H_3(OOO) = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-*tert*-butylphenol

Figure 1 | Selected products of published metal-mediated CO-coupling reactions. Note that most of these coupling procedures function in a head-to-head (C-to-C) manner. The coupled CO units are highlighted in red.

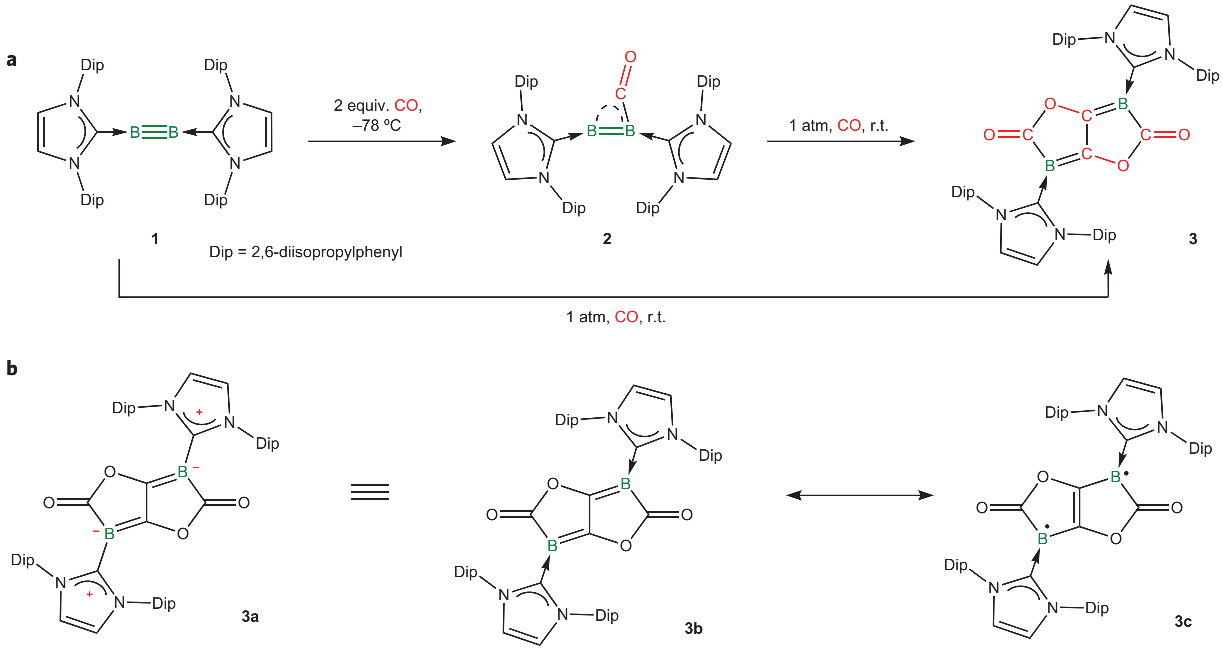

Figure 2 | Synthesis of 2 and 3 and some plausible electronic descriptions of 3. a, Ambient temperature and pressure CO coupling by a main group species. It should be noted that 2 equivalents of CO were added to the reaction forming 2, but only 1 equivalent is incorporated into the product, presumably due to its low solubility and precipitation from the solvent, and/or the high stability of 2 relative to any dicarbonyl compounds. **b**, Some plausible electronic descriptions of 3.

bonds are too short to be considered conventional single bonds, leading us to infer some delocalization over this area of the molecule and propose the two resonance forms **3b** and **3c** (Fig. 2b) as possible contributors to the electronic structure of 3. At ambient temperature, no signal corresponding to a diradical as in resonance form **3c** could be detected in the electron paramagnetic resonance (EPR) spectrum of 3, although this does not exclude a diradical structure completely.

Determination of the frontier orbital topology of 3 by density functional theory (DFT) confirms the description of the B–C–C–B core of the molecule as a 1,4-dibora-1,3-butadiene as in structure **3b**. The central B_2C_2 core of the HOMO-1, HOMO and LUMO (Supplementary Fig. S4) resemble the same three orbitals of 1,3-butadiene, albeit with a small amount of participation from π orbitals of the carbene and carboxylate carbons in 3. The bis(boralactone) 3 was also found to be fluorescent, in analogy to the structurally very similar pulvinic acid lactones found in fluorescent lichens[28,29]. Ultraviolet-visible (UV-vis) and fluorescent spectra, as well as time-dependent DFT calculations of 3, are provided in Supplementary Fig. S6 and Table S2.

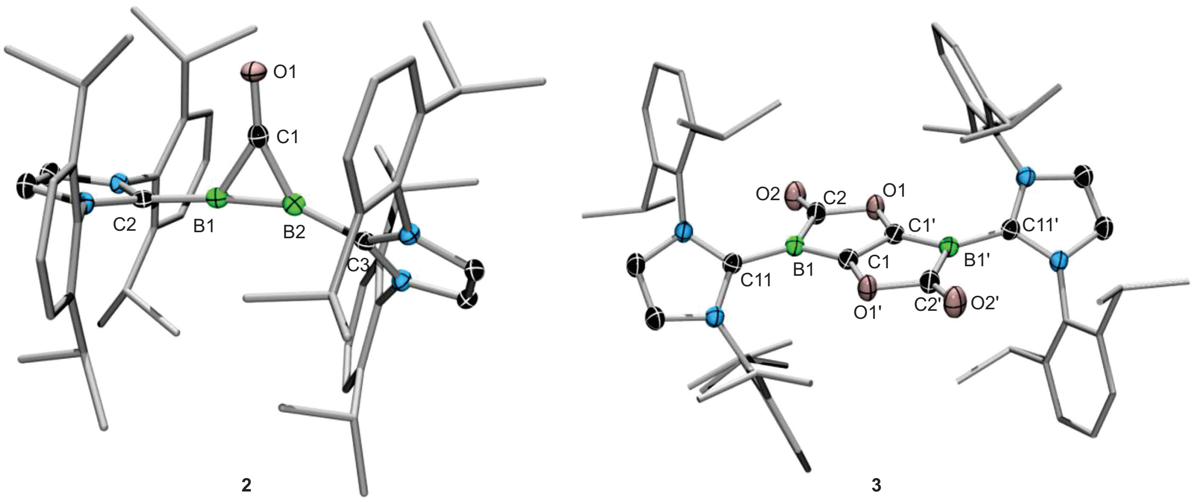

Figure 3 | Molecular structures of 2 and 3. Thermal ellipsoids in the structures represent the 50% probability level. For clarity, hydrogen atoms and one molecule of benzene solvent (structure of **3**) have been removed. Bond lengths (Å) and angles (deg) relevant to the B–B–C–O core of **2**: B1–B2, 1.549(3); C1–B1, 1.565(3); C1–B2, 1.485(3); O1–C1, 1.249(2); O1–C1–B2, 155.38(17); O1–C1–B1, 143.62(16); B2–C1–B1, 61.00(13). The CO is bound unsymmetrically, with a C1–B2 distance that is significantly shorter than the C1–B1 distance. Nevertheless, the B–B distance still corresponds to a double-bond description. Bond lengths (Å) relevant to the B–C–C–B core of **3**: B1–C1, 1.4507(18); B1–C2, 1.5742(18); B1–C11, 1.5471(18); C1–C1′, 1.426(2). The three B–C–C–B bonds are very short—too short to be considered conventional single bonds, and we propose some delocalization as illustrated by the resonance forms in Fig. 2b.

Although the aforementioned reaction of **1** with a vast excess of CO proceeds rapidly at room temperature, we sought to slow the reaction down by adding discrete amounts of CO at lower temperatures. Two equivalents of CO were added using a glass tube of measured volume to a hexane solution of **1** at −78 °C, leading to the precipitation of an orange-brown solid (**2**, Fig. 2a). This solid was stable at room temperature under inert conditions. Although a single ^{11}B NMR signal ($\delta = 17$) was observed for **2**, multinuclear NMR techniques did not provide enough information to unambiguously ascertain its structure. However, single-crystal X-ray crystallography confirmed that **2** was the product of a single CO addition to **1** containing an unsymmetrically bridging CO (Fig. 3). The B–B distance in **2** (1.549(3) Å) corresponds to a double-bond description (B$=$B bond distances in doubly-carbene-stabilized diborenes: 1.546(6), 1.561(18) Å)[23,30]. The C–O distance of **2** (1.249(2) Å) is much longer than those calculated for CO adducts of boranes ($F_3B \leftarrow CO$, 1.128 Å; $(F_5C_6)_3B \leftarrow CO$, 1.131 Å)[31], clearly indicating strong backdonation from the B_2 unit into the π^* orbital of CO. A band in the infrared spectrum of **2** at 1,926 cm^{-1} is clearly attributable to the semi-bridging carbonyl group.

Compound **2** could then be converted quantitatively to the bis(boralactone) **3** by treatment with an excess of CO at room temperature, confirming its intermediacy in the CO-coupling reaction. Alternatively, when **1** was treated with 2 equiv. of CO in toluene at room temperature, a mixture of **2** and **3** was observed by ^{11}B NMR. The coexistence of intermediate **2** and product **3** in this reaction suggests that **2** is probably the most stable, and perhaps the only isolable, intermediate species in this reaction. Compounds **1**–**3** were evaluated using Kohn–Sham DFT methods at the OLYP/DZP level, giving excellent reproduction of the geometries (Supplementary Table S1, Figs S3, S5 and S7). These calculations showed that the conversion of **1** + CO to **2** is exothermic by 26.23 kcal mol^{-1}, and the conversion of **2** + 3CO to **4** is exothermic by 66.50 kcal mol^{-1}, indicating that the overall reaction (**1** + 4CO to **4**) is exothermic by 92.73 kcal mol^{-1}.

To quantify the apparent strongly reducing properties of **1**, cyclic voltammetric measurements on diboryne compound **1** show an extremely facile and reversible one-electron oxidation step ($E_{1/2} = -1.3$ V versus ferrocene/ferrocenium, Fc/Fc$^+$) followed by a second, irreversible oxidation ($E_{pa} = +0.1$ V) (Supplementary Fig. S2). The potential of the first oxidation step is close to those of cobaltocene $[(\eta^5\text{-}C_5H_5)_2Co]$[32] and samarium diiodide[33], the latter a common reagent for organic reductions, indicating that **1** is a potent neutral, metal-free reductant. Strong main-group reductants such as the bis(monovalent) magnesium (Mg^IMg^I) reagent of Jones[34] have attracted much attention lately and, based on the results herein, diboryne **1** is potentially a useful new member of this family.

The reaction of CO with the triply bonded diboryne compound **1** shows that CO coupling is both possible and highly favoured energetically on a non-metallic framework. The reaction is facile under mild conditions and at atmospheric pressure. Both the CO-coupling reaction and electrochemical measurements confirm the strongly reducing nature of **1**. Additionally, the binding of one molecule of CO to **1** elucidates the first step of the CO-coupling reaction. There is mounting recent evidence that low-valent boron species are able to act like transition metals by binding traditional ligands of inorganic chemistry[35]. Both intermediate **2** and product **3** presented herein provide further support for this hypothesis.

Methods

Synthetic methods. All manipulations were conducted under an atmosphere of dry argon or under vacuum using standard Schlenk line or glovebox techniques. Solvents (pentane, hexane, toluene and tetrahydrofuran) were purified by distillation from appropriate drying agents ($NaK_{2.8}$ alloy and sodium/benzophenone) under dry argon immediately before use. C_6D_6 was degassed by three freeze–pump–thaw cycles and stored over molecular sieves.

Spectroscopic methods. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external tetramethylsilane via the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. UV-vis spectra were measured on a JASCO V-660 UV-vis spectrometer. Elemental analyses were measured on an Elementar Vario MICRO cube instrument. Starting material **1** was synthesized according to literature methods[23].

Crystallographic methods. The crystal data of **2** and **3** were collected on a Bruker X8Apex II diffractometer with a charge-coupled device (CCD) area detector and multilayer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, and allocated the reference numbers CCDC 935712 (**2**) and 913268 (**3**). These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical methods. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are referenced to the $\mathrm{Fc/Fc^+}$ redox couple. Tetra-*n*-butylammonium hexafluorophosphate ($[n\text{-}\mathrm{Bu_4N}][\mathrm{PF_6}]$) was used as the supporting electrolyte.

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References

1. Gmelin, L. Über einige merkwürdige, bei der Darstellung des Kaliums nach der Brunnerschen Methode, erhaltene Substanzen. *Ann. Phys. Chem.* **4,** 31–62 (1825).
2. Liebig, J. Über das Verhalten des Kohlenoxyds zu Kalium. *Ann. Pharm.* **11,** 182–189 (1834).
3. Evans, W. J., Grate, J. W., Hughes, L. A., Zhang, H. & Atwood, J. L. Reductive homologation of CO to a ketenecarboxylate by a low-valent organolanthanide complex—synthesis and X-ray crystal-structure of $[(\mathrm{C_5Me_5})_4\mathrm{Sm_2(O_2CCCO)(THF)}]_2$. *J. Am. Chem. Soc.* **107,** 3728–3730 (1985).
4. Evans, W. J., Lee, D. S., Ziller, J. W. & Kaltsoyannis, N. Trivalent $[(\mathrm{C_5Me_5})_2(\mathrm{THF})\mathrm{Ln}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{N_2})$ complexes as reducing agents including the reductive homologation of CO to a ketene carboxylate, $(\mu\text{-}\eta^4\text{-}\mathrm{O_2C{-}C{=}C{=}O})^{2-}$. *J. Am. Chem. Soc.* **128,** 14176–14184 (2006).
5. Bianconi, P. A. *et al.* Reductive coupling of carbon monoxide ligands to form coordinated bis(trimethylsiloxy)ethyne in seven-coordinate niobium(I) and tantalum(I) $[\mathrm{M(CO)_2(dmpe)_2Cl}]$ complexes. *Organometallics* **6,** 1968–1977 (1987).
6. Summerscales, O. T., Cloke, F. G. N., Hitchcock, P. B., Green, J. C. & Hazari, N. Reductive cyclotrimerization of carbon monoxide to the deltate dianion by an organometallic uranium complex. *Science* **311,** 829–831 (2006).
7. Summerscales, O. T., Cloke, F. G. N., Hitchcock, P. B., Green, J. C. & Hazari, N. Reductive cyclotetramerization of CO to squarate by a U(III) complex: the X-ray crystal structure of $[(\mathrm{U}(\eta\text{-}\mathrm{C_8H_6}\{(\mathrm{SiPr_3})\text{-}\mathrm{Pr}\text{-}i\text{-}1{,}4\}_2)(\eta\text{-}\mathrm{C_5Me_4H})]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{C_4O_4})$. *J. Am. Chem. Soc.* **128,** 9602–9603 (2006).
8. Frey, A. S. *et al.* Mechanistic studies on the reductive cyclooligomerisation of CO by U(III) mixed sandwich complexes; the molecular structure of $[\mathrm{U}(\eta\text{-}\mathrm{C_8H_6}\{\mathrm{Si}i\mathrm{Pr_3}\text{-}1{,}4\}_2)(\eta\text{-}\mathrm{Cp^*})]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}\mathrm{C_2O_2})$. *J. Am. Chem. Soc.* **130,** 13816–13817 (2008).
9. Arnold, P. L., Turner, Z. R., Bellabarba, R. M. & Tooze, R. P. Carbon monoxide coupling and functionalisation at a simple uranium coordination complex. *Chem. Sci.* **2,** 77–79 (2011).
10. Miller, A. J. M., Labinger, J. A. & Bercaw, J. E. Reductive coupling of carbon monoxide in a rhenium carbonyl complex with pendant Lewis acids. *J. Am. Chem. Soc.* **130,** 11874–11875 (2008).
11. Watanabe, T., Ishida, Y., Matsuo, T. & Kawaguchi, H. Reductive coupling of six carbon monoxides by a ditantalum hydride complex. *J. Am. Chem. Soc.* **131,** 3474–3475 (2009).
12. Wang, X. *et al.* Room-temperature reaction of carbon monoxide with a stable diarylgermylene. *J. Am. Chem. Soc.* **131,** 6912–6913 (2009).
13. Brown, Z. D. & Power, P. P. Mechanisms of reactions of open-shell, heavier group 14 derivatives with small molecules: $n-\pi^*$ back-bonding in isocyanide complexes, C–H activation under ambient conditions, CO coupling, and ancillary molecular interactions. *Inorg. Chem.* **52,** 6248–6259 (2013).
14. Teichmann, J., Stock, H., Pritzkow, H. & Siebert, W. Carbon monoxide and isonitrile insertion into the B–B bond of five-membered cyclic organo-1,2-diboranes. *Eur. J. Inorg. Chem.* 459–463 (1998).
15. Sander, W., Bucher, G. & Wierlacher, S. Carbenes in matrices—spectroscopy, structure, and reactivity. *Chem. Rev.* **93,** 1583–1621 (1993).
16. Lavallo, V., Canac, Y., Donnadieu, B., Schoeller, W. W. & Bertrand, G. CO fixation to stable acyclic and cyclic alkyl amino carbenes: stable amino ketenes with a small HOMO–LUMO gap. *Angew. Chem. Int. Ed.* **45,** 3488–3491 (2006).
17. Sajid, M. *et al.* Facile carbon monoxide reduction at intramolecular frustrated phosphane/borane Lewis pair templates. *Angew. Chem. Int. Ed.* **52,** 2243–2246 (2013).
18. Dobrovetsky, R. & Stephan, D. W. Stoichiometric metal-free reduction of CO in syn-gas. *J. Am. Chem. Soc.* **135,** 4974–4977 (2013).
19. Asay, M. & Sekiguchi, A. Recent developments in the reactivity of stable disilynes. *Bull. Chem. Soc. Jpn* **85,** 1245–1261 (2012).
20. Segawa, Y., Suzuki, Y., Yamashita, M. & Nozaki, K. Chemistry of boryllithium: synthesis, structure, and reactivity. *J. Am. Chem. Soc.* **130,** 16069–16079 (2008).
21. Aramaki, Y. *et al.* Synthesis and characterization of B-heterocyclic π-radical and its reactivity as a boryl radical. *J. Am. Chem. Soc.* **134,** 19989–19992 (2012).
22. Kinjo, R., Donnadieu, B., Celik, M. A., Frenking, G. & Bertrand, G. Synthesis and characterization of a neutral tricoordinate organoboron isoelectronic with amines. *Science* **333,** 610–613 (2011).
23. Braunschweig, H. *et al.* Ambient-temperature isolation of a compound with a boron–boron triple bond. *Science* **336,** 1420–1422 (2012).
24. Olmstead, M. M., Power, P. P., Weese, K. J. & Doedens, R. J. Isolation and X-ray crystal structure of the boron methylidenide ion $[\mathrm{Mes_2BCH_2}]^-$ (Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$)—a boron–carbon double bonded alkene analogue. *J. Am. Chem. Soc.* **109,** 2541–2542 (1987).
25. Hoefelmeyer, J. D., Sole, S. & Gabbaï, F. P. Reactivity of the dimesityl-1,8-naphthalenediylborate anion: isolation of the borataalkene isomer and synthesis of 1,8-diborylnaphthalenes. *Dalton Trans.* 1254–1258 (2004).
26. Chiu, C. W. & Gabbaï, F. P. Structural changes accompanying the stepwise population of a B–C π bond. *Angew. Chem. Int. Ed.* **46,** 6878–6881 (2007).
27. Wuckelt, J., Doring, M., Langer, P., Gorls, H. & Beckert, R. Lactam analogues of pentalene. A new one-pot synthesis of pyrrolo[3,2-*b*]pyrrole-2,5-diones deriving from pulvinic acid. *Tetrahedron Lett.* **38,** 5269–5272 (1997).
28. Gaylord, M. C., Benedict, R. G., Hatfield, G. M. & Brady, L. R. Isolation of diphenyl-substituted tetronic acids from cultures of *Paxillus atrotomentosus*. *J. Pharm. Sci.* **59,** 1420–1423 (1970).
29. Lunak, S., Vynuchal, J. & Hrdina, R. Geometry and absorption of diketo-pyrrolo-pyrrole isomers and their pi-isoelectronic furo-furanone analogues. *J. Mol. Struct.* **919,** 239–245 (2009).
30. Wang, Y. *et al.* A stable neutral diborene containing a B=B double bond. *J. Am. Chem. Soc.* **129,** 12412–12413 (2007).
31. Jacobsen, H. *et al.* Lewis acid properties of tris(pentafluorophenyl)borane. Structure and bonding in L-$\mathrm{B(C_6F_5)_3}$ complexes. *Organometallics* **18,** 1724–1735 (1999).
32. Connelly, N. G. & Geiger, W. E. Chemical redox agents for organometallic chemistry. *Chem. Rev.* **96,** 877–910 (1996).
33. Enemaerke, R. J., Daasbjerg, K. & Skrydstrup, T. Is samarium diiodide an inner- or outer-sphere electron donating agent? *Chem. Commun.* 343–344 (1999).
34. Green, S. P., Jones, C. & Stasch, A. Stable magnesium(I) compounds with Mg–Mg bonds. *Science* **318,** 1754–1757 (2007).
35. Braunschweig, H., Radacki, K., Shang, R. & Tate, C. W. Reversible intramolecular coupling of the terminal borylene and a carbonyl ligand of $[\mathrm{Cp(CO)_2Mn{=}B}\text{-}t\mathrm{Bu}]$. *Angew. Chem. Int. Ed.* **52,** 729–733 (2012).

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Author contributions

H.B. conceived and supervised the study. J.M., T.D., K.H. and W.C.E. performed the syntheses and spectroscopic studies. J.O.C.J.H., A.V. and A.K.P. performed the DFT computational studies. I.K. performed the EPR spectroscopic and cyclic voltammetry. T.K. performed the X-ray crystallographic measurements. R.D.D. wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.B.

Competing financial interests

The authors declare no competing financial interests.