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Insertion of CO_2 into the carbon–boron bond of a boronic ester ligand†

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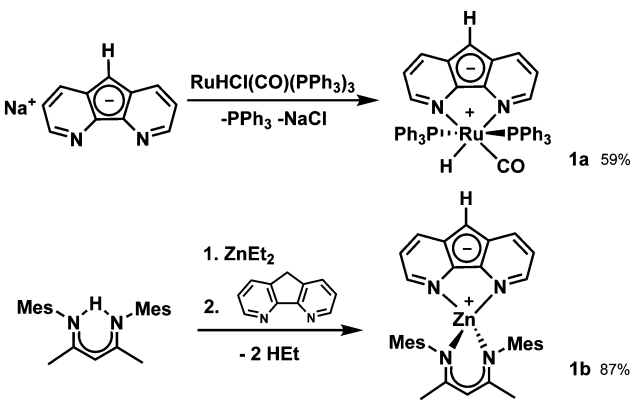
New Ru and Zn diazafluorenyl complexes undergo C–H borylation of the diazafluorenyl ligand to form the corresponding diazafluorenylboronic ester complexes, which can insert CO_2 into their C–B bonds to form boryl ester functionalities. The relevance of these new reactivities towards catalytic CO_2 reduction has also been explored.

Discovery of new fundamental reactivity of CO_2 is of interest because it may lead to new ways to sequester CO_2 and utilize CO_2 as a C_1 feedstock for synthesis.[1] Known reactivity of CO_2 includes coordination to metal centres,[2] insertion into M–X bonds (where M is a metal center and X is an element, most commonly H or C)[3–5] and adduct formation with a Lewis base (with or without the assistance of a Lewis acid).[6,7] These fundamental reactivities have resulted in the catalytic conversion of CO_2 into a variety of reduced products, which is a topic that has been reviewed[5,7–11] and has seen a flurry of recent progress.[12–31] Our group has demonstrated formal insertion of CO_2 into the C–H bond of an actor diazafluorenyl (L^-) ligand supported by a spectator metal center.[32] We elaborated this work to include metal-free insertions,[33] and catalytic hydroboration[28] of CO_2. Although we have not yet studied the catalytic mechanism in detail, one plausible pathway involves borylation of the diazafluorenyl moiety and subsequent insertion of CO_2 into the newly formed C–B bond. To our knowledge, the direct insertion of CO_2 into a C–B bond is unknown prior to this work, and represents a new mode of reactivity for the thermodynamically stable CO_2 molecule.

Related yet distinct C–B bond reactivity was reported by Shoji *et al.* who employed salts containing the electrophilic Mes_2B^+ in a deoxygenation-arylation of CO_2.[34] In this reaction, one mesityl group is transferred to the carbon of CO_2, generating MesC≡O$^+$. Piers *et al.* recently activated CO_2 in ring expansion reactions using the reactive C–B bonds of isomeric doubly reduced diborole and bis-cycloborabutylidene derivatives.‡[35] Two examples of related insertions of CO_2 have also recently emerged: Waterman *et al.* observed an unexpected insertion of CO_2 into reactive C–Si bonds in Zn complexes chelated by a pair of 2-(phosphinomethyl)-pyridine ligands,[36] and Knopf and Cummins demonstrated formal insertion of CO_2 into three B–H bonds in borohydride salts to form $[HB(OCHO)_3]^-$.[37]

Herein we report the reactivity of $[Ru(CO)(H)L(PPh_3)_2]$, **1a** and $[ZnL(Mes_2nacnac)]$, **1b** toward pinacolborane (HBpin) to generate the corresponding complexes **2a** and **2b** of an actor diazafluorenylboronic ester ligand. This actor ligand inserts CO_2 into its C–B bond, which is an unprecedented mode of reactivity for the boronic ester functional group. We also report the catalytic activities of these complexes towards CO_2 reduction with catecholborane (HBcat) and HBpin.

As shown in Scheme 1, **1a** was synthesized in 59% yield from the reaction of NaL and $[RuHCl(CO)(PPh_3)_3]$. The spectroscopic properties of **1a** are similar to those of $[Ru(H)L(N_2)(PPh_3)_2]$ ($\nu(N_2)$ = 2092 cm^{-1}),[38] except that its characteristic infrared absorption occurs at 1918 cm^{-1} due to stretching of the CO ligand.



Scheme 1 Syntheses of **1a** (top) and **1b** (bottom).

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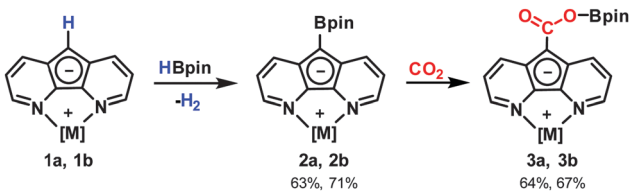
1b was synthesized by protonolysis in two steps from diethylzinc with an overall 87% yield. In the ^{1}H NMR spectrum of **1b** one resonance exists for each pair of pyridyl protons, which are related to each other through a mirror plane of symmetry. Protons on nacnac are similarly related, consistent with C_{2v} symmetry in solution. The solid state structure of **1b** (see ESI†) features a ZnN_4 core with distorted tetrahedral geometry.

With **1a** and **1b** in hand, we investigated the stoichiometric reactivity of the diazafluorenyl complexes towards HBpin: when a toluene solution of complex **1a** is heated with HBpin, **2a** is formed with concomitant formation of H_2 (Scheme 2). Presumably the formation of **2a** starts with the formation of an adduct between the carbanion of **1a** and HBpin. This interaction brings B–H and C–H bonds into close proximity, which allows the loss of H_2. In the transformation from **1a** to **2a** the diazafluorenyl ligand acts and the Ru centre spectates.

The borylation of **1a** brings about a change in the carbonyl stretching frequency from 1918 cm^{-1} in the starting material to 1936 cm^{-1} in the product. The higher C–O bond strength in **2a** indicates the electron-withdrawing nature of the newly formed diazafluorenylboronic ester ligand relative to the parent L$^-$ ligand in **1a**. In C_6D_6 at ambient temperature, complex **2a** displays a singlet at 48.47 ppm in its ^{31}P{^{1}H} NMR spectrum; the hydride resonates at −11.68 ppm as a triplet ($^2J_{P-H}$ = 20 Hz) and the diazafluorenyl moiety shows one signal for each of its six protons in its ^{1}H NMR spectrum.

As shown in Fig. 1, the solid state structure of **2a** has been confirmed with X-ray crystallography. The structure of **2a** features a pseudo-octahedral Ru centre with two mutually *trans* phosphine ligands and the hydride and carbonyl ligands oriented in a *cis* fashion. The diazafluorenylboronic ester ligand chelates the Ru centre through its two nitrogen donor atoms. The Ru1–N1 bond length of 2.171(2) is shorter than the Ru1–N2 bond length of 2.266(2) due to the greater *trans* influence of the hydride ligand relative to CO. The sum of the bond angles around C5 is 359.9(5)° which suggests sp^2 hybridization. The B atom is three-coordinate and the O2–B1–O3 group is nearly coplanar with diazafluorenyl (a dihedral angle of 6°) such that π-donation of the carbanion into the vacant p orbital on B is possible. The C5–B1 bond length is 1.512(4) Å, which is similar to pinacol esters of other borylated cyclopentadienyl (Cp) compounds (12-crown-4)LiCpBpin (1.488(8) Å) and (Cp_2Ru)Bpin (1.537(12) Å).[39,40] In such compounds the boratafulvene resonance form also contributes to the bonding picture, having C–B bond lengths between a typical C(sp^2)–B(sp^2) single bond (*e.g.*, 1.58 Å in $BMes_3$)[41] and a formal C(sp^2)–B(sp^2) double bond (*e.g.*, 1.444(8) Å in simple borataalkene [$Mes_2B{=}CH_2$]$^-$).[42]



Scheme 2 Borylation and carboxylation of diazafluorenyl complexes.

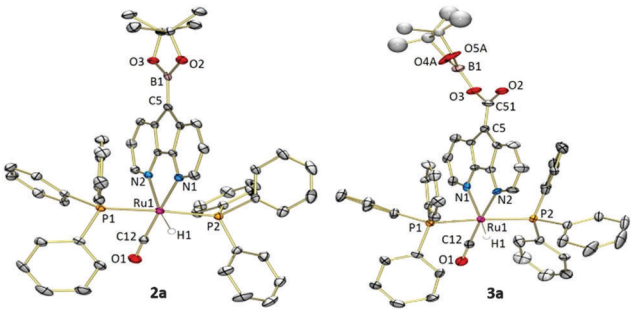


Fig. 1 Molecular structures of **2a** and **3a**. Ellipsoids are shown at 30% probability. Hydrogen atoms except for hydrides omitted for clarity. Only one disordered component is shown. Co-crystallized molecules are removed for clarity.

Similarly, when **1b** was heated in THF in the presence of HBpin an analogous borylation of diazafluorenyl occurred and **2b** formed. Similar to **1b**, the NMR data for **2b** reveal a symmetric structure in solution. **2b** crystallizes from toluene/pentane with two molecules in the asymmetric unit (see ESI†). The distorted tetrahedral ZnN_4 core persists; the metric parameters around Zn are similar to those in **1b**, and the metric parameters of the diazafluorenylboronic ester ligand are similar to those in **2a**.

With **2a** and **2b** in hand we set about investigating their reactivity towards CO_2. When CO_2 is introduced to a solution of **2a** in toluene–diethylether (1 : 1 v/v), the colour of the solution changes from pink to orange (Scheme 2). The formation of **3a** can be confirmed by NMR experiments, in which all the ^{1}H signals have shifted slightly compared to those of **2a** and an additional ^{13}C signal appears at 162.29 ppm corresponding to the newly formed ester group from CO_2. In the infrared spectrum of **3a**, the ester carbonyl stretch appears at 1647 cm^{-1}, and the CO ligand stretch is shifted to 1942 cm^{-1}. X-ray crystallography confirmed the structure of **3a** as shown in Fig. 1. Diazafluorenyl is nearly coplanar with its appended carboxylate group, and the B atom is canted out of this plane, giving an O2–C51–O3–B1 dihedral angle of ∼37°. When CO_2 is introduced to a C_6D_5Br solution of **2b**, a similar change in colour and in spectral data occurs as the boryl ester product **3b** forms; we confirmed the structure by X-ray crystallography (see ESI†).

The insertion of CO_2 into the C–B bond of **2a** and **2b** is intriguing from the standpoint of providing a new type of reactivity for the thermodynamically stable and environmentally deleterious CO_2 molecule. To understand this transformation further, DFT calculations have been used to locate the transition state of the insertion reaction from **2a** to **3a** and to obtain the thermodynamic data (see ESI† for details). The transition state of the insertion features a C–C–O–B four-membered ring (Fig. 2). The CO_2 moiety is off linear by 46.4° with the endocyclic C–O bond elongated by 0.09 Å, while the Bpin moiety is bent away from its original position in **2a** by 32.6° (measured by the change in $Cp_{centroid}$–C–B angle) to accommodate the incoming CO_2 with the B–C bond elongated by 0.08 Å. The endocyclic B–O and C–C distances are 2.11 and 1.66 Å, respectively, indicating that the C–C bond is largely formed in the transition state, but the B–O bond formation is far from complete. This result prompted us to

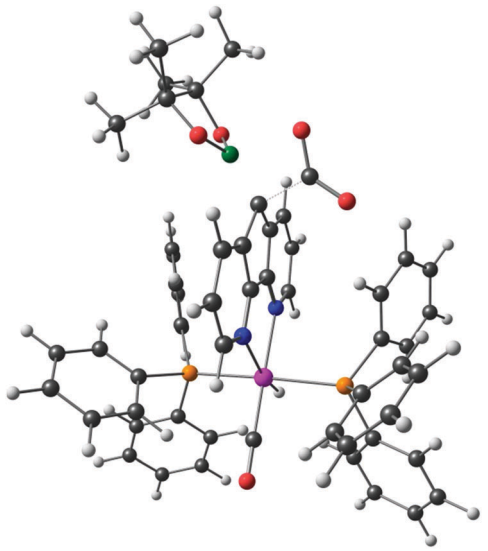


Fig. 2 Computed transition state structure of the CO_2 insertion reaction from **2a** to **3a** Colour key: O, red; N, blue; P, orange; B, green; Ru, pink; C, gray; H, white.

examine the possibility of a two-step mechanism for the insertion reaction, *i.e.*, C–C bond formation first, followed by the migration of the Bpin moiety. All attempts to locate the C–C formation intermediate failed. Although it is still possible that such an intermediate may sit in an extremely shallow well, our computation is consistent with the one-step CO_2 insertion mechanism. The ΔH of the overall reaction is -15.9 kcal mol^{-1}, while the $\Delta H^{\neq}$ is 13.1 kcal mol^{-1}, so it is unsurprising that the insertion reaction occurs readily at ambient temperature.

This unique reactivity led us to investigate whether borylester **3a** is sufficiently reactive towards further reduction of the CO_2-derived moiety. Heating a C_6D_6 solution of **3a** to 110 °C in the presence of 20 equivalents of HBpin led to a 0.9 : 1 ratio of **2a** : **3a** in 8 hours as detected by ^{1}H NMR spectroscopy, accompanied by the formation of CH_3OBpin and pinBOBpin. This reactivity represents the closing of a synthetic loop: the reactive diazafluorenylboronic ester **2a** inserts CO_2 to make boryl ester **3a**, which upon reaction with HBpin regenerates **2a** and liberates the product of CO_2 reduction.

With the synthetic loop established, we tested the performance of complexes **1** and **2** in catalytic hydroboration of CO_2 with HBcat and HBpin (Table 1). **1a** and **1b** perform similarly as catalysts: their average turnover frequencies (avg. TOF) are on the order of one per hour, and the methoxyborane derivative CH_3OBR_2 was the major CO_2 reduction product in all cases. In the hydroboration of CO_2 with HBcat, **1a** and **1b** are not as active as (*N*-methyl)diazafluorenide (avg. TOF = 16 h^{-1} at 25 °C). However, when HBpin is used as the reductant, **1a** and **1b** are capable of more turnovers compared to (*N*-methyl)diazafluorenide (avg. TOF = 0.28 at 100 °C in $CDCl_3$).[28] Interestingly, **2a** and **2b** showed comparable catalytic performance for CO_2 hydroboration with HBpin under the same respective conditions compared to the parent compounds **1a** and **1b** (Table 1). In the Ru case the borylated species led to a slight increase in total TON (from 39 to 60). In the Zn case the borylated version led to a slight decrease in total TON (from 48 to 40). Unfortunately, we could not identify any metal containing species from the catalytic reaction mixtures. Therefore, the relevance of the steps in the synthetic loop to the actual catalytic runs has yet to be determined through further mechanistic studies.

In summary, new compounds **1a** and **1b** undergo C–H bond borylation to yield diazafluorenylboronic ester complexes **2a** and **2b**, which feature the unquenched π-basicity of a carbanionic group directly bound to a boron centre. It is this structural feature that facilitates the unprecedented insertion of CO_2 into their C–B bonds to yield boryl ester products **3a** and **3b**. DFT calculations suggest the insertion occurs in a concerted fashion. Compound **3a** can be converted to **2a** when reacted with HBpin, releasing the CO_2 reduction product CH_3OBpin and closing a synthetic loop of CO_2 reduction. Furthermore, compounds **1** and **2** all displayed catalytic activity toward CO_2 hydroboration with HBpin and HBcat. Further mechanistic studies of the catalytic CO_2 reduction, the insertion of other unsaturated substrates into the C–B bond in our diazafluorenylboronic ester ligand, the related reactivities of other C–E bonds, and the corresponding catalytic reactions are under investigation in our laboratory.

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Table 1 Results for the catalytic hydroboration of CO_2 by HBcat and HBpin[a]

					TON from formation of each product[b]			
Entry	Cat.	Borane	T (°C)	Time (h)	HCO_2BR_2	$CH_2(OBR_2)_2$	CH_3OBR_2	Total TON[b]
1	**1a**	HBcat	90	45			29	29
2	**1a**	HBpin	100	45	2		37	39
3	**2a**	HBpin	100	45	5	2	54	60
4	**1b**	HBcat	60	20			16	16
5	**1b**	HBpin	90	20	3	0.1	45	48
6	**2b**	HBpin	90	20	5	4	31	40

[a] Reactions were carried out in Schlenk bombs charged with catalyst (0.01 M), borane (1 M), hexamethylbenzene (2–10 mg as an internal standard), C_6D_5Br (0.6 mL) and CO_2 (~1.5 atm). [b] TON is based on the number of C–H bonds formed in the reduced product per molecule of catalyst, determined by integration of the ^{1}H NMR signals against the internal standard. R_2BOBR_2 is formed in all cases in addition to the carbon-containing CO_2-derived products.

Notes and References

‡ The authors posit that CO_2 catalyzes the rearrangement of the biscycloborabutylidene into the diborole, which reacts with CO_2 in a pair of ring expansions from five to six members, distinct from from simple insertion into the reactive C–B bonds.

1 M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, 2010.
2 J. Mascetti, Metal Coordination of CO_2, *Encyclopedia of Inorganic and Bioinorganic Chemistry*, Wiley, Chichester, 2014.
3 X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
4 S. P. Bew, *Compr. Org. Funct. Group Transform. II*, 2005, 19–125.
5 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510.
6 J. L. Murphy, K. N. Robertson, R. A. Kemp, H. M. Tuononen and J. A. C. Clyburne, *Chem. Commun.*, 2015, **51**, 3942.
7 D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625–2641.
8 E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89.
9 A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621.
10 D. Yu, S. P. Teong and Y. Zhang, *Coord. Chem. Rev.*, 2015, **293**, 279.
11 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
12 Z. Lu, H. Hausmann, S. Becker and H. A. Wegner, *J. Am. Chem. Soc.*, 2015, **137**, 5332.
13 J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin and S. Aldridge, *Angew. Chem., Int. Ed.*, 2015, **54**, 5098.
14 M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Kohn, D. J. Liptrot, M. F. Mahon and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826.
15 J. R. Khusnutdinova, J. A. Garg and D. Milstein, *ACS Catal.*, 2015, **5**, 2416.
16 N. M. Rezayee, C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 1028.
17 S. Wesselbaum, V. Moha, M. Meuresch, S. Brosinski, K. M. Thenert, J. Kothe, T. vom Stein, U. Englert, M. Holscher, J. Klankermayer and W. Leitner, *Chem. Sci.*, 2015, **6**, 693.
18 K. Beydoun, G. Ghattas, K. Thenert, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2014, **53**, 11010.
19 E. Blondiaux, J. Pouessel and T. Cantat, *Angew. Chem., Int. Ed.*, 2014, **53**, 12186.
20 M.-A. Courtemanche, M.-A. Légaré, E. Rochette and F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858.
21 R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K. S. Nahi, N. Bouchard, F.-G. Fontaine and L. Maron, *ACS Catal.*, 2015, **5**, 2513.
22 C. Liu, J. Xie, G. Tian, W. Li and Q. Zhou, *Chem. Sci.*, 2015, **6**, 2928.
23 F. A. LeBlanc, W. E. Piers and M. Parvez, *Angew. Chem., Int. Ed.*, 2014, **53**, 789.
24 T. T. Metsänen and M. Oestreich, *Organometallics*, 2015, **34**, 543.
25 S. Bontemps, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2014, **136**, 4419.
26 K. Fujiwara, S. Yasuda and T. Mizuta, *Organometallics*, 2014, **33**, 6692.
27 C. C. Chong and R. Kinjo, *Angew. Chem., Int. Ed.*, 2015, **54**, 12116.
28 Y. Yang, M. Xu and D. Song, *Chem. Commun.*, 2015, **51**, 11293.
29 X. Frogneux, E. Blondiaux, P. Thuéry and T. Cantat, *ACS Catal.*, 2015, **5**, 3983.
30 G. Jin, C. G. Werncke, Y. Escudié, S. Sabo-Etienne and S. Bontemps, *J. Am. Chem. Soc.*, 2015, **137**, 9563.
31 S. Bagherzadeh and N. P. Mankad, *J. Am. Chem. Soc.*, 2015, **137**, 10898.
32 V. T. Annibale and D. Song, *Chem. Commun.*, 2012, **48**, 5416.
33 V. T. Annibale, D. A. Dalessandro and D. Song, *J. Am. Chem. Soc.*, 2013, **135**, 16175.
34 Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama and T. Fukushima, *Nat. Chem.*, 2014, **6**, 498.
35 J. F. Araneda, W. E. Piers, M. J. Sgro and M. Parvez, *Organometallics*, 2015, **34**, 3408.
36 G. I. McGrew, P. A. Khatri, W. E. Geiger, R. A. Kemp and R. Waterman, *Chem. Commun.*, 2015, **51**, 15804.
37 I. Knopf and C. C. Cummins, *Organometallics*, 2015, **34**, 1601.
38 E. Stepowska, H. Jiang and D. Song, *Chem. Commun.*, 2010, **46**, 556.
39 G. E. Herberich and A. Fischer, *Organometallics*, 1996, **15**, 58.
40 M. Sato, G. Maruyama and A. Tanemura, *J. Organomet. Chem.*, 2002, **655**, 23.
41 J. F. Blount, P. Finocchiaro, D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 1973, **95**, 7019.
42 M. M. Olmstead, P. P. Power, K. J. Weese and R. J. Doedens, *J. Am. Chem. Soc.*, 1987, **109**, 2541.