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 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$_2$.\(^\ddagger\) Two examples of related insertions of CO$_2$ have also recently emerged: Waterman \textit{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$_2$nacnac)], 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$_3$)$_2$] (\(r(N_2) = 2092\) 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).
1b was synthesized by protonolysis in two steps from diethylzinc with an overall 87% yield. In the 1H 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 C2v symmetry in solution. The solid state structure of 1b (see ESI†) features a ZnN4 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 H2 (Scheme 2). Presumably the formation of 2a starts with the formation of an adduct between the carbonyl of 1a and HBpin. This interaction brings B–H and C–H bonds into close proximity, which allows the loss of H2. 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 L1 ligand in 1a. In C6D6 at ambient temperature, complex 2a displays a singlet at 48.47 ppm in its 31P{1H} NMR spectrum; the hydride resonates at –11.68 ppm as a triplet (JP–H = 20 Hz) and the diazafluorenyl moiety shows one signal for each of its six protons in its 1H 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) Å is shorter than the Ru1–N2 bond length of 2.266(2) Å 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 sp² 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 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,Ru)Bpin (1.537(12) Å).19,40 In such compounds the boratafulvene resonance form also contributes to the bonding picture, having C–B and C–H bonds into close proximity, which allows the loss of H2. I n the 13C signal appears at 162.29 ppm corresponding to the newly formed ester group from CO2. In the infrared spectrum of 3a, the CO2 moiety is off linear by 46.4° (measured by the change in Cpcentroid–C–B angle) to accommodate the incoming CO2 with the endocyclic C–O bond elongated by 0.09 Å, while the C–O bond of the boron ester bond is bent away from its original position in 2a (by 32.6° measured by the change in C·BO–C angle) to accommodate the incoming CO2 with the B–O 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

![Scheme 2](image-url)

**Scheme 2** Borylation and carboxylation of diazafluorenyl complexes.

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 ZnN4 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 CO2. When CO2 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 1H signals of 1a, the ester carbonyl 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 CO2 is introduced to a Cd3Br 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 CO2 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 CO2 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 CO2 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 C·BO–C angle) to accommodate the incoming CO2 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. 1](image-url)
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 $\Delta H$ of the overall reaction is $-15.9$ kcal mol$^{-1}$, while the $\Delta H^\circ$ 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$_6$D$_6$ 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$_3$OBpin 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$_3$OBBr$_2$ 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)diazafluorene (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)diazafluorene (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 carbamionic 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$_3$OBpin 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$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Borane</th>
<th>$T$ (°C)</th>
<th>Time (h)</th>
<th>TON from formation of each product$^b$</th>
<th>Total TON$^b$</th>
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<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>HBcat</td>
<td>90</td>
<td>45</td>
<td>HCO$_2$Br$_2$ : 29</td>
<td>CH$_3$(OBBr)$_2$ : 54</td>
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<tr>
<td>2</td>
<td>1a</td>
<td>HBpin</td>
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</tr>
<tr>
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<td>6</td>
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<td>HBpin</td>
<td>90</td>
<td>20</td>
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<td>40</td>
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$^a$ 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$_6$D$_5$Br (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$_n$BOBr$_2$ is formed in all cases in addition to the carbon-containing CO$_2$-derived products.
Notes and References

‡ The authors posit that CO₂ catalyzes the rearrangement of the bicycloborabutylidene into the diborole, which reacts with CO₂ in a pair of ring expansions from five to six members, distinct from simple

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