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Hydroboration of carbon dioxide with catechol- and pinacolborane using an Ir-CNP* pincer complex. Water influence on the catalytic activity

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Iridium complexes based on deprotonated lutidine-derived CNP* pincers **2a**/**2b** selectively catalyze the hydroboration of CO_2 under mild conditions (1-2 bar CO_2, 30 °C) to methoxyborane using HBcat (TOF up to 56 h^{-1}) and to the formate level with HBpin (TOF up to 1245 h^{-1}). Interestingly, an intriguing, positive water effect on the reaction rates has been observed. NMR spectroscopy and ESI-MS analysis of the hydroboration reactions have shown the formation of ligand-protonated $[Ir(CNP)(CO)(BR_2)H][B(R_2)_2]$ (R_2 = catecholate, pinacolate) derivatives under catalytic conditions. Control experiments, however, have demonstrated that these derivatives are not catalytically competent species in the hydroboration of CO_2.

Introduction

Carbon dioxide is the C1 carbon source par excellence for chemicals and fuels production due to its abundant, renewable and non-toxic nature.[1] However, the chemical transformation of CO_2 is significantly hampered by its high thermodynamic and kinetic stability. While conversion of CO_2 by non-redox processes such as the production of carbonates, carbamates and urethanes are relatively well-established processes,[1] the reduction of CO_2 to synthetically and energetically relevant products such as formic acid derivatives and methanol still represents an important challenge.[2] Among potential reductants, dihydrogen provides the most atom-economical alternative, and consequently it is not surprising that hydrogenation of CO_2 to formates and, to a lesser extent, to MeOH has been profusely studied.[2] Since hydrogenation of CO_2 usually involves the use of high temperatures and pressures, other reducing agents such as hydrosilanes[3] or hydroboranes[4] have also received a significant attention due to the milder reaction conditions that can be employed with these species. Furthermore, their reactivity can be adjusted by varying the silane or borane substituents facilitating access to different C1 products including CO, CH_2O, MeOH and CH_4.[3,4] In this vein, particularly appealing for synthetic purposes is the reduction of CO_2 to formate and acetal derivatives that serve for the development of reductive functionalizations of CO_2.[5]

Reduction of carbon dioxide can be accomplished in the absence of a catalyst with metal borohydrides.[6] On the contrary, the hydroboration of CO_2 with even very reactive BH_3 adducts should be carried out in the presence of a catalyst.[7,8] Since the seminal work of Guan *et al.* reporting the reduction of CO_2 with HBcat (catecholborane) to methanol mediated by pincer nickel complexes,[9] there has been an intense impetus for the development of non-metal,[8,10] main group metal,[11] and transition metal catalysts for CO_2 hydroboration.[12-21] Among these catalytic systems, thiolate nickel[12] and palladium[13] pincer complexes have provided the highest TOFs, in the range of 1780 to 2400 h^{-1}, for the reduction of CO_2 to methoxyborane using HBcat as reductant. Also, while hydroboration of CO_2 with BH_3 and HBcat proceeds to the methoxide level, the reduction process can be controlled to some extent by the use of less reactive boranes such as HBpin (pinacolborane). Thus, selective reduction of CO_2 to formoxyborane, which has been proven to serve as a formate source for synthetic purposes,[14] has been achieved with HBpin and a metal catalyst.[11c,14-17] It is also worth mentioning attempts to generate acetal derivatives that can be employed as methylene transfer reagents.[18-20]

It is interesting to note that although catalysts for the hydroboration of CO_2 based on different metals, including most of groups 8-11 elements, have been reported, it is surprising that iridium complexes, which have been frequently employed in hydroboration reactions,[22-24] have not been investigated in the reduction of CO_2 by hydroboranes. While being less attractive in terms of cost and environmental aspects, noble metal catalysts should not be ignored since higher catalytic efficiencies and stabilities may compensate for

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† Dedicated to Prof. Ernesto Carmona on occasion of his 70th anniversary.

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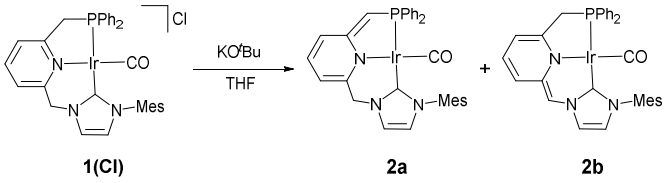
their increase price and be useful for small scale applications. Herein, we report an Ir catalyst precursor based on a deprotonated lutidine-derived *N*-heterocyclic carbene/phosphine CNP* pincer that selectively catalyzes the hydroboration of CO_2 to methoxy- or formoxyborane depending on the employed hydroborane (HBcat or HBpin). Interestingly, an unexpected positive influence of the presence of small amounts of water in the reaction rates has been observed. Finally, iridium species formed under catalytic conditions have been investigated and their participation in the catalytic cycle has been evaluated.

Results and discussion

Synthesis of the catalyst precursor

Reaction of the carbonyl iridium complex **1(Cl)**[25] with KO^{t}Bu in THF yielded the formation of a mixture of the deprotonated "tautomeric" species **2a** and **2b** (Scheme 1). The ratio, as determined by ^{1}H NMR spectroscopy, between these species depends on the solvent. In the ^{1}H NMR spectrum registered in THF-d_8, **2a** and **2b** appear in a 9:1 ratio, whereas a **2a**/**2b** ratio of 4 was observed in C_6D_6. In the former solvent, the CH_2N bridge of the pincer of **2a** produces in the ^{1}H NMR spectrum a singlet signal at 4.72 ppm (2H) and the methyne CHP arm gives rise to a doublet resonance at 3.84 ppm ($^2J_{HP}$ = 1.9 Hz, 1H), meanwhile **2b** exhibits a singlet peak at 6.17 ppm (1H) for the CHN pincer arm and a doublet signal at 3.51 ppm ($^2J_{HP}$ = 11.4 Hz, 2H) for the hydrogens of the methylene CH_2P moiety. For both complexes, the resonances corresponding to the pyridine derived fragments appear significantly shifted upfield (6.30-5.37 ppm) in comparison to **1(Cl)**, in agreement with the presence of dearomatized central rings. In the $^{13}C\{^1H\}$ NMR spectrum, derivative **2a** exhibits the resonance produced by the carbenic carbon atom as a doublet at 182.8 ppm (J_{CP} = 92 Hz) and that of the CO ligand at 182.0 ppm (d, J_{CP} = 10 Hz). Further support for the inferred structure of **2a** was obtained by a X-ray diffraction study of a single crystal of the complex (Fig. 1).[26] Deprotonation of the methylene P-arm is reflected in short C(19)-P(1) and C(19)-C(18) bond lengths of 1.743 and 1.370 Å, respectively. Furthermore, alternating C-C distances in the pyridine moiety evidence ring dearomatization as shown by the elongated C(18)-C(17) and C(16)-C(15) distances of 1.460 and 1.396 Å, and shorten C(17)-C(16) and C(15)-C(14) bond lengths of 1.343 and 1.378 Å, respectively (average C-C bond in the pyridine molecule: 1.38 Å).

As inferred from the different **2a**/**2b** ratios observed in distinct solvents, complexes **2a** and **2b** are in equilibrium in solution. This observation is further manifested in the ^{1}H,^{1}H-exchange spectroscopy (EXSY) spectrum (mixing time = 0.8 s) of the **2a**/**2b** mixture in wet THF-d_8 registered at 25 °C, where intense exchange cross-peaks are observed between: i) signals corresponding to the methyne and methylene bridges of **2a**, ii) resonances caused by the CHP and CH_2N moieties of **2a** with those of the CH_2P and CHN bridges of **2b**, respectively, and iii) the signals of the methyne and methylene fragments of **2a** and **2b** with those of water (Fig. S1). These observations support that the tridentate ligand bridges can get involved in reversible protonation/deprotonation mediated by water molecules acting as proton transfer assistants.[27]



Scheme 1 Synthesis of complexes **2a** and **2b**.

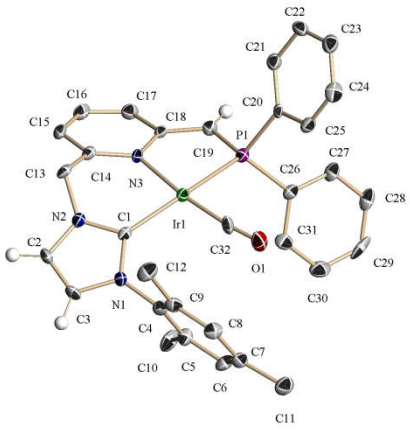


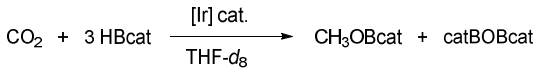
Fig. 1 ORTEP drawing at 30% ellipsoid probability of complex **2a**. Most hydrogen atoms and solvent molecule (THF) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)-C(1) 2.034(8), Ir(1)-N(3) 2.127(5), Ir(1)-P(1) 2.285(2), Ir(1)-C(32) 1.818(8), C(1)-Ir(1)-P(1) 168.3(2), C(1)-Ir(1)-C(32) 97.2(3), C(32)-Ir(1)-N(3) 172.9(3), C(1)-Ir(1)-N(3) 89.7(2), P(1)-Ir(1)-N(3) 82.64(16).

Catalytic hydroboration of CO_2

Hydroboration of CO_2 catalyzed by the mixture of complexes **2a**/**2b** was investigated. Initial reactions were carried out with HBcat in THF-d_8 (2 bar CO_2, 30 °C) using 1.0 mol% of **2a**/**2b**. Selective CO_2 reduction to the corresponding methoxyborane (CH_3OBcat) was established by ^{1}H NMR spectroscopy after the observation of a singlet resonance at 3.81 ppm, and the appearance of a broad signal in the ^{11}B NMR spectrum at 22.5 ppm. Also, the expected concomitant formation of diboroxane (catBOBcat) was confirmed by the appearance of a white precipitate after removal of THF-d_8 under vacuum and addition of C_6H_6 (δ_H (THF-d_8) = 6.83, 6.93 ppm; δ_B (THF-d_8) = 16.5 ppm).[28] Although significant care was exercised in the set-up of the catalytic experiments, these reactions were initially found difficult to reproduce. However, after scrupulous control of the reaction parameters, a marked influence of the presence of water in the hydroboration reaction was noticed.[29] Therefore, catalytic reactions were performed in the presence of variable amounts of water (Table 1). Reactions were followed up by $^1H\{^{11}B\}$ NMR spectroscopy, and for a meaningful comparison of the catalytic activity, TON values were determined after 1.5 h

although upon extended reaction times all the reactions proceeded to completion. Thus, when the catalytic reaction was performed in the presence of 1 mol% of water, formation of 18% of methoxyborane was observed (TON = 54; TOF = 36 h^{-1}) (entry 1). By increasing the water content, faster transformation of CO_2 to methoxyborane was evidenced, providing up to 28% conversion to methoxyborane in the presence of 5 mol% of water (TON = 84; TOF = 56 h^{-1}) (entries 2 and 3). It should be noted that for the latter reaction the maximum yield is 30% after considering the amount of borane that is hydrolyzed to catBOBcat. Further increase in the water content of the reaction to 6 mol% somewhat decreased the catalytic activity (TOF = 50 h^{-1}) (entry 4). Interestingly, complex **1(Cl)** was found a poorer catalyst than **2a**/**2b** providing 78 turnovers after 16 h (TOF = 4.9 h^{-1}) (entry 5). Control experiments showed that **2a**/**2b** catalyzes the hydrolysis of HBcat to yield catBOBcat as the sole product.

Table 1 Catalytic hydroboration of CO_2 with HBcat

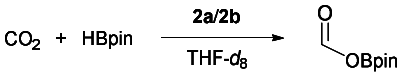


Entry	Catalyst	H_2O (mol%)	Yield (%)	TON
1	**2a**/**2b**	1	18	54
2		3	24	72
3		5	28	84
4		6	25	75
5[a]	**1(Cl)**	3	26	78

Reaction conditions: 1.0 mol% [Ir], 2 bar CO_2, 30 °C, THF-d_8, [HBcat] = 0.5 M. Reaction time: 1.5 h, unless otherwise noted. Yields were determined by $^1H\{^{11}B\}$ NMR spectroscopy using hexamethylbenzene as internal standard. TON values based on moles of B-H bonds reacted per mole catalyst: (mmol methoxyborane x 3)/(mmol cat). [a] Reaction time: 16 h.

Next, the catalytic performance of **2a**/**2b** in the hydroboration of CO_2 with HBpin was examined under 1 bar of CO_2 at 30 °C (Table 2). These reactions were carried out with low catalyst loadings of 0.2 mol%. While previous reports have shown that reduction of CO_2 with pinacolborane may yield formate (HCO_2Bpin), acetal ($H_2C(OBpin)_2$) and methoxy (CH_3OBpin) derivatives, or mixtures thereof, reactions with **2a**/**2b** gave solely formoxyborane. Moreover, as in the case of the reactions with HBcat, the presence of small amounts of water significantly increases the reaction rate. All reactions proceeded to conversions of HBpin higher than 90%, although TON values were compared after a reaction time of 20 min. For example, reaction in the presence of 1 mol% of water provided the formoxyborane derivative in 30% yield (TOF = 450 h^{-1}, entry 1), whereas upon addition of increasing amounts of water up to 7 mol% a *ca.* three-fold rise of the catalytic activity (TOF = 1245 h^{-1}) was observed (entries 2-5). Moreover, when the catalyst loading was further reduced to 0.1 mol%, formoxyborane was obtained in 74% yield after 1 h, what represents a notable TOF of 740 h^{-1}. Among the few catalysts that selectively produces formoxyborane,[11c,14-17] only the palladium pincer complex reported by Hazari *et al.* provides faster reaction rates with low catalyst loadings (TOF = 8500 h^{-1}, 0.01 mol% catalyst).[15]

Table 2 Catalytic hydroboration of CO_2 with HBpin

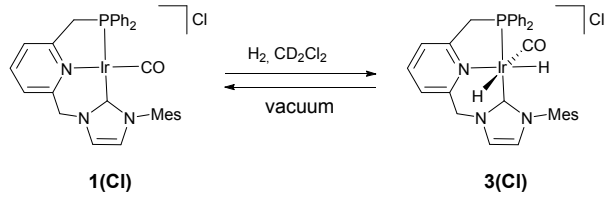


Entry	H_2O (mol%)	Yield (%)	TON
1	1	30	150
2	2	72	360
3	3	79	395
4	6	80	400
5	7	83	415
6[a]	3	74	740

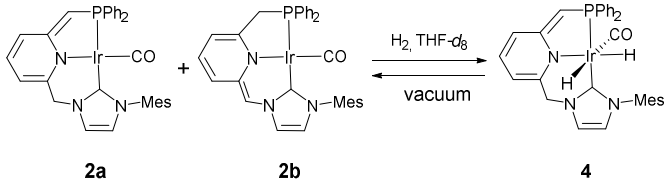
Reaction conditions, unless otherwise noted: 0.2 mol% **2a**/**2b**, 1 bar CO_2, 30 °C, THF-d_8, [HBpin] = 0.4 M. Reaction time: 20 min. Yields were determined by $^1H\{^{11}B\}$ NMR spectroscopy using hexamethylbenzene as internal standard. TON values as determined by (mmol formoxyborane)/(mmol cat). [a] 0.1 mol% **2a**/**2b**. Reaction time: 1.0 h.

Study of metal species formed under catalytic conditions

To shed light on the metal species formed under catalytic conditions, the hydroboration of CO_2 (2 bar) with HBcat was carried out using 20 mol% of **2a**/**2b** in THF-d_8. Upon reaction completion only a singlet signal is observed in the $^{31}P\{^1H\}$ NMR spectrum at 16.9 ppm that corresponds to a dihydride species, as deduced by the appearance of two doublets of doublets signals appearing at 17.5 ($^2J_{HP}$ = 12 Hz, $^2J_{HH}$ = 2 Hz) and 8.3 ppm ($^2J_{HP}$ = 22 Hz, $^2J_{HH}$ = 2 Hz) in the ^1H NMR spectroscopy experiment. Therefore, we hypothesized whether the species observed after reaction completion was a dihydride Ir complex based on a protonated CNP (**3**$^+$, Scheme 2) or deprotonated CNP* (**4**, Scheme 3) ligand, and consequently an independent synthesis of both complexes was pursued. For the study of complex **3(Cl)**, a CD_2Cl_2 solution of **1(Cl)** was exposed to 1 bar of H_2 (Scheme 2). The ^1H NMR spectrum of the newly formed species showed a doublet of doublets at 17.45 ppm ($^2J_{HP}$ = 11.7 Hz, $^2J_{HH}$ = 1.6 Hz) attributable to the IrH *trans* to the pyridine moiety, and a doublet of doublets of doublets appearing at 8.32 ppm ($^2J_{HP}$ = 22.2 Hz, $^2J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.6 Hz) caused by the hydride ligand placed *cis* to the N-donor fragment that couples with the other IrH hydrogen and one of the hydrogens of the CH_2P bridge.[30] Meanwhile, the $^{31}P\{^1H\}$ NMR spectrum displays a singlet signal at 16.9 ppm. These data agree well with the observed signals at the end of the catalytic reaction and demonstrates that ligand protonation occurs under catalysis. Complex **3(Cl)** could not be isolated since its attempted purification yielded mixtures of **3(Cl)** and **1(Cl)**, indicating that the dihydrido complex loses H_2 under vacuum.



Scheme 2 Reaction with H_2 of complex **1(Cl)**.

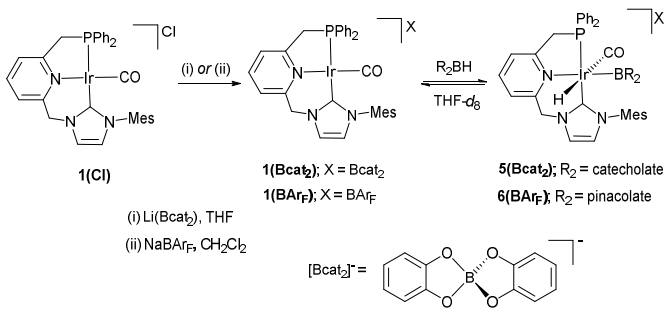


Scheme 3 Reaction with H_2 of complexes **2a**/**2b**.

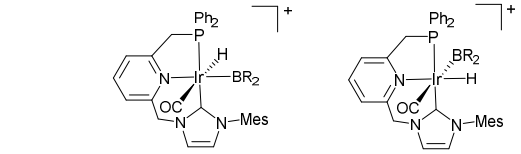
Additionally, formation of a deprotonated dihydride complex **4** was ruled out since exposure of the **2a**/**2b** mixture to H_2 (5 bar) in THF-d_8 produced in the $^{31}P\{^1H\}$ NMR spectrum a singlet at 8.8 ppm. Furthermore, in the ^1H NMR spectrum derivative **4** showed two doublet of doublets appearing at 8.64 ($^2J_{HP}$ = 20.8 Hz, $^2J_{HH}$ = 1.5 Hz) and 16.59 ($^2J_{HP}$ = 11.3 Hz, $^2J_{HH}$ = 1.5 Hz),[30] whereas the signals for the dearomatized pyridine ring are significantly shifted to high field appearing in the range between 6.56 and 5.71 ppm. Complex **4** also readily loses H_2 under vacuum leading to the regeneration of the **2a**/**2b** mixture.

Furthermore, analysis by ESI-MS (positive mode) of the catalytic reaction between CO_2 and HBcat in the presence of 20 mol% of **2a**/**2b** provided a peak at *m/z* 698 attributable to the cationic fragment $[IrH_2(CNP)(CO)]^+$ (**3**$^+$), while in the negative mode a peak at *m/z* 227 was observed that has been assigned to the arylspiroboronate ester $[Bcat_2]$. Degradation of HBcat promoted by nucleophiles, including complexes containing anionic ligands, have been shown to provide the above anion along with other boron species such as B_2cat_3 and BH_3.[23,24,31] However, formation of these, or other, boron derivatives could not be unequivocally detected by MS or NMR spectroscopy. Moreover, although HBpin has been shown to be less prone to degradation than HBcat,[22d,32] ESI-MS analysis of a catalytic reaction with HBpin using 20 mol% of **2a**/**2b** allowed for the detection of the cationic fragment **1**$^+$ and the anion $[Bpin_2]$ (*m/z* 243).[33] We speculate that formation of $[Bcat_2]$ and $[Bpin_2]$ anions might initially involve nucleophilic attack to the hydroborane by the methyne carbon of the deprotonated CNP* ligand,[27] and ligand-assisted B-H activation, as shown by Milstein *et al.* for related Ru complexes.[34] However, direct evidence of these processes has remained elusive in our system.

Since the hydroboration reaction is significantly faster using HBpin than with HBcat, the later process was chosen to get insight into the formation of other metal species during the catalytic reaction. Hydroboration of CO_2 (2 bar) with HBcat using 10 mol% of **2a**/**2b** in THF-d_8 was monitored by ^1H NMR spectroscopy, showing the formation of a hydride complex that produces a doublet resonance at 6.9 ppm ($^2J_{HP}$ = 21 Hz), and which could be the result of the oxidative addition of HBcat to **1**$^+$. In order to unequivocally determine the structure of this derivative, complex **1(Bcat$_2$)** was readily isolated after anion exchange of **1(Cl)** with Li[Bcat$_2$][35] and made react with HBcat (Scheme 4). Addition of a slight excess of HBcat (1.5 equiv) to a THF-d_8 solution of **1(Bcat$_2$)** produced the decoloring of the initially yellow solution to yield the boryliridium hydride complex **5(Bcat$_2$)**.[24,36] This derivative was spectroscopically characterized since attempts to isolate **5(Bcat$_2$)** yielded mixtures of **1(Bcat$_2$)** and **3(Bcat$_2$)**. Diagnostic signals for complex **5(Bcat$_2$)** in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra registered in THF-d_8 include the presence of a doublet resonance at 6.90 ppm ($^2J_{HP}$ = 21.1 Hz) attributable to the hydrido ligand, and a doublet at 154.3 ppm (J_{CP} = 96 Hz) due to the carbenic carbon, respectively. The presence of the carbonyl ligand is manifested in the $^{13}C\{^1H\}$ NMR spectrum by a broad resonance at 176.8 ppm, and in the IR spectrum by an absorption at 2005 cm^{-1}. Moreover, in addition to the HBcat and biscatecholborate resonances appearing in the ^{11}B NMR spectrum at 22.5 (d, J_{BH} = 189 Hz) and 15.1 ppm respectively, a broad signal at 12.9 ppm is also observed, which have been assigned to the boryl ligand. Also, while these spectroscopic data do not allow for a straightforward differentiation between the two possible isomers resulting from the oxidative addition of HBcat to **1(Bcat$_2$)**, i.e. trans (**5-I**) or cis (**5-II**) coordination of the boryl ligand to the pyridine fragment (Fig. 2), comparison of the chemical shift of the resonance of the hydrido ligand with those of complex **3(Cl)** suggests a cis coordination of the Bcat moiety to the carbonyl ligand. This ligand disposition prevents the trans coordination of the two potentially π-accepting boryl and carbonyl ligands.[36b,37] Moreover, DFT calculations (B3LYP-D3, 6-31g(d,p)/SDD) of **5-I** and **5-II** indicate that the former cationic species is more stable by 3.2 kcal/mol (Fig. 2). Also of note, in the $^1H,^1H$-exchange spectroscopy (EXSY) spectrum of the reaction mixture of **1(Bcat$_2$)** and HBcat in THF-d_8 registered at 25 ^oC, exchange cross peaks are observed between the signal of the aromatic hydrogens corresponding to HBcat and those of the $[Bcat_2]$ anion indicative of the existence of a boron substituent scrambling process. Upon registering the same experiment at 50 ^oC, a cross-peak signal caused by the exchange between free HBcat and the hydrido ligand is also observed pointing out to the reversibility of the B-H oxidative addition.



Scheme 4 Synthesis of **1(Bcat$_2$)** and **1(BAr$_F$)**, and reactions with boranes.



R_2 = catechol	**5-I** *(0.0)*	**5-II** *(3.2)*
R_2 = pinacol	**6-I** *(3.5)*	**6-II** *(0.0)*

Fig. 2 Relative thermodynamic stability of cationic fragments **5-I** and **5-II**, and **6-I** and **6-II**. Data in parenthesis are ΔG in THF (kcal mol^{-1}).

To test the formation of analogous species to **5(Bcat$_2$)** with HBpin, complex **1(BAr$_F$)**, previously prepared by anion exchange of **1(Cl)** with NaBAr$_F$, was reacted with an excess of HBpin (2.4 equiv) (Scheme 4). The newly formed species **6(BAr$_F$)** provided comparable NMR spectra to those of **5(Bcat$_2$)**, with the logical differences of the signals due to the [BAr$_F$]$^-$ anion and the boryl ligand, evincing the cis arrangement of the boryl and CO ligands. However, DFT calculations (B3LYP-D3, 6-31g(d,p)/SDD) shows that the isomer **6-I** is 3.5 kcal/mol less stable than **6-II**, what can be ascribed to the presence of non-stabilizing interactions in **6-I** between the more sterically demanding pinacol moiety with the substituents of the NHC and phosphino fragments (Fig. 2). Also of interest, exchange cross-peaks between the resonances of the free borane and the hydrido ligand of **6(BAr$_F$)** are observed in the ^{1}H,^{1}H-EXSY spectrum.

NMR spectra of the reaction of complexes **5(Bcat$_2$)** and **6(BAr$_F$)** with CO_2 did not show any noticeable changes, i.e. insertion of CO_2 into the Ir-H bond to yield a formato complex was not observed. Therefore, in order to determine whether species **5(Bcat$_2$)** and **6(BAr$_F$)** participate in the reduction of CO_2 with boranes, complexes **1(Bcat$_2$)** and **1(BAr$_F$)** were employed as pre-catalyst in lieu of **2a**/**2b** in the hydroboration of CO_2 with HBcat and HBpin, respectively. Under the reaction conditions of Table 1, entry 5, **1(Bcat$_2$)** provided a significantly lower TOF of 6.8 h^{-1} (89% conv. after 13 h). Similarly, complex **1(BAr$_F$)** was also found a poorer catalyst precursor than **2a**/**2b** in the reduction of CO_2 since negligible formation of formoxypinacolborane was observed (<5% conv. after 21 h). Overall, these results support that **5(Bcat$_2$)** and **6(BAr$_F$)** are not significantly involved in the hydroboration of CO_2 using **2a**/**2b** as catalytic precursors. Marder, Baker *et al.* have similarly observed that while $[Ir(Cl)(COE)_2]_2$/PPh_3 mixtures promote HBcat degradation and are active in alkene hydroborations, isolated iridium boryl compounds generated from the reaction of this catalytic system and hydroboranes produce innefective catalysts.[24] Similarly, for thiolate Ni and Pd pincer complexes, which are very active catalytic precursors in the hydroboration of CO_2 to CH_3OBcat, it has been shown that the corresponding hydride species are probably not involved in the catalytic process.[12,13]

As previously reported, catalytic hydroboration of CO_2 with HBpin can proceed to the methoxide level (CH_3OBpin),[4] although with a proper choice of the catalyst partially reduced products including the corresponding formoxyborane derivative can be obtained.[14-20] Guan *et al.* have computationally studied the reduction of CO_2 with HBcat to CH_3OBcat mediated by a pincer nickel hydride complex.[9b] The delineated mechanism is composed of three successive cycles. The first cycle involves CO_2 insertion into the Ni-H bond to yield a Ni-formate intermediate that upon interaction with HBpin yields HCO_2Bcat. The subsequent reduction of formoxyborane implies the insertion into a Ni-H bond to produce formaldehyde, which is finally reduced to CH_3OBcat by a third molecule of HBcat. Analogous steps have also been proposed for the hydroboration of CO_2 with HBpin catalyzed by a Ru complex.[38] Based on the mechanism proposed by the Guan group, Hazari *et al.* have assumed that the high selectivity provided by a pincer Pd complex in the hydroboration of CO_2 with HBpin to the formate level is determined by the larger size of the pinacol fragment that prevents further reduction of HCO_2Bpin.[15] Furthermore, selective reduction of CO_2 to formoxyborane with HBpin has only been achieved with metal based catalysts.[14-17] Therefore, since a highly selective CO_2 hydroboration with HBpin to formoxyborane takes place using **2a**/**2b**, it can be expected that metal species should be involved in the catalytic reactions. Furthermore, considering the degradation of the hydroboranes as well as the observed influence of water, it can be proposed that the catalytically active species are iridium derivatives formed by reaction of **2a**/**2b** with the hydroboranes and water. However, since in addition to frustrated Lewis pairs containing boron-based moieties capable of catalyzing the hydroboration of CO_2,[8a,8b,8g] other boron species have been shown to catalyze hydroboration reactions, as reported for the catalytic addition of hydroboranes to alkenes and alkynes,[39] reduction of CO_2 mediated by boron species derived from hydroborane degradation promoted by **2a**/**2b**, or their participation in accelerating an Ir-catalyzed reaction,[40] cannot be fully ruled out.

Conclusions

The iridium complexes supported by deprotonated lutidine-derived CNP* pincers **2a**/**2b** catalyze the hydroboration of CO_2. A marked influence of the hydroborane is observed in the selectivity and rate of the reactions. More interestingly,

significant reaction rate accelerations have been observed after optimization of the water content of the reactions, suggesting that water is involved in the formation of the catalytically active species. Thus, upon using HBcat selective reduction of CO_2 to the methanol equivalent is observed (TOF up to 58 h^{-1}), whereas the most sterically demanding HBpin yields the corresponding formoxyborane as the sole product with notable catalytic activities (TOF up to 1245 h^{-1}).

Under catalytic conditions, iridium species resulting from the oxidative addition of the hydroborane to ligand-protonated [Ir(CNP)(CO)][$B(R_2)_2$] (R_2 = catechol, pinacol) complexes has been observed. However, control experiments indicate that these species are inefficient catalysts in the hydroboration of CO_2. Taking into account the observed water effect, the hydroborane degradation leading to the formation of $[B(R_2)_2]^-$ anions, and the different selectivity observed in the reduction of CO_2 with HBcat and HBpin, we feel inclined to consider that the hydroboration reactions are catalyzed by Ir-containing species formed after reaction of **2a**/**2b** with the hydroborane in the presence of water. Unfortunately, we have been unable to detect such as species by NMR spectroscopy or MS, suggesting that they are formed in low concentrations.

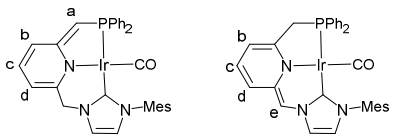
Experimental

General procedures

All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodium-benzophenone-ketyl for diethyl ether (Et_2O) and tetrahydrofuran (THF); sodium for pentane and toluene; CaH_2 for dichloromethane and acetonitrile (CH_2Cl_2, CH_3CN); and NaOMe for methanol (MeOH). For the preparation of wet THF-d_8 solutions, commercial THF-d_8 (Eurisotop, <0.05% water) was dried with sodium-benzophenone-ketyl and distilled under argon, and known amounts of water were added. Water content in the thus prepared solutions was confirmed by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard. Complex **1(Cl)**,[25] Li[$Bcat_2$][35] and Na[BAr_F][41] were synthetized following previously reported methods. All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on Bruker DPX-300, DRX-400, AVANCEIII/ASCEND 400R or DRX-500 spectrometers. $^{31}P\{^1H\}$ and ^{11}B NMR shifts were referenced to external 85% H_3PO_4 and BF_3 Et_2O respectively, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. All NMR measurements were carried out at 25 °C, unless otherwise stated. NMR signal assignations were confirmed by 2D NMR spectroscopy (^1H-^1H COSY, ^1H-^1H NOESY, ^1H-^{13}C HSQC and ^1H-^{13}C HMBC) and $^1H\{^{31}P\}$ and $^1H\{^{11}B\}$ NMR experiments. HRMS data were obtained on a JEOL JMS-SX 102A mass spectrometer at the Instrumental Services of Universidad de Sevilla (CITIUS). ESI-MS experiments were carried out in a Bruker 6000 apparatus by the Mass Spectrometry Service of the Instituto de Investigaciones Químicas. Elemental analyses were run by the Analytical Service of the Instituto de Investigaciones Químicas in a Leco TrueSpec CHN elemental analyzer. IR spectra were acquired on a Bruker Tensor 27 instrument.

Synthesis of complexes

Complexes 2a/2b. To a solution of **1(Cl)** (0.075 g, 0.10 mmol) in THF (5 mL) was added a solution of KO^{t}Bu (0.013 g, 0.11 mmol) in THF (5 mL) giving rise to a red solution. The resulting solution was stirred for 2 h, and solvent was evaporated under reduced pressure. The residue was extracted with toluene (2 × 10 mL), and volatiles were removed under vacuum. The solid obtained was washed with pentane (2 × 10 mL) and dried under vacuum to give the mixture of complexes **2a** and **2b** as a red solid (0.050 g, 70%). Crystals of **2a** suitable for X-ray diffraction analysis were grown from a saturated solution of the complexes **2a**/**2b** in THF. Anal. calcd (%) for $C_{32}H_{29}IrN_3OP$: C 55.32, H 4.21, N 6.05; found: C 55.10, H 4.56, N 6.09. IR (nujol): 1938 (ν_{CO}) cm^{-1}.



*NMR spectroscopy data for **2a**:* ^{1}H NMR (500 MHz, THF-d_8): δ 7.57 (m, 4H, 4 H arom PPh), 7.41 (s, 1H, H arom NHC), 7.20 (m, 6H, 6 H arom PPh), 7.09 (s, 1H, H arom NHC), 6.92 (s, 2H, 2 H arom Mes), 6.30 (m, 2H, H^b + H^c), 5.37 (dd, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 3.7 Hz, 1H, H^d), 4.72 (s, 2H, CH_2N), 3.84 (d, $^2J_{HP}$ = 1.9 Hz, 1H, H^a), 2.28 (s, 3H, CH_3), 2.09 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, THF-d_8): δ 28.3. $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8): δ 182.8 (d, J_{CP} = 92 Hz, C-2 NHC), 182.0 (d, J_{CP} = 10 Hz, CO), 156.3 (d, J_{CP} = 24 Hz, C_q arom), 150.8 (d, J_{CP} = 1 Hz, C_q arom), 140.6 (d, J_{CP} = 58 Hz, 2 C_q arom), 139.6 (C_q arom), 137.5 (C_q arom), 136.9 (2 C_q arom), 132.9 (d, J_{CP} = 11 Hz, 4 CH arom), 131.9 (d, J_{CP} = 2 Hz, C^c), 129.4 (2 CH arom), 129.3 (d, J_{CP} = 2 Hz, 2 CH arom), 128.3 (d, J_{CP} = 10 Hz, 4 CH arom), 121.8 (d, J_{CP} = 3 Hz, CH arom), 121.1 (d, J_{CP} = 3 Hz, CH arom), 117.8 (d, J_{CP} = 19 Hz, C^b), 101.7 (C^d), 69.1 (d, J_{CP} = 69 Hz, C^a), 57.3 (CH_2N), 21.2 (CH_3), 18.6 (2 CH_3).

*NMR spectroscopy data for **2b**:* ^{1}H NMR (500 MHz, THF-d_8): δ 7.64 (m, 4H, 4 H arom PPh), 7.49 (s, 1H, H arom NHC), 7.32 (m, 6H, 6 H arom PPh), 7.06 (s, 1H, H arom NHC), 6.91 (s, 2H, 2 H arom Mes), 6.17 (s, 1H, H^e), 6.17 (d, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, H^c), 6.05 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H^d), 5.53 (d, $^3J_{HH}$ = 6.1 Hz, 1H, H^b), 3.51 (d, $^2J_{HP}$ = 11.4 Hz, 1H, CH_2P), 2.25 (s, 3H, CH_3), 2.12 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, THF-d_8): δ 33.3.

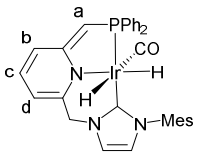
Complex 1(Bcat$_2$). A solution of **1(Cl)** (0.100 g, 0.14 mmol) and Li[$Bcat_2$] (0.035 g, 0.15 mmol) in MeCN (8 mL) was stirred for 1 h. The resulting suspension was filtered, and solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2 × 10 mL), and the solution was brought to dryness. The resulting solid was washed with pentane (2 × 8 mL) and dried under vacuum. Complex **1(Bcat$_2$)** was obtained as an orange solid (0.073 g, 58%). IR (nujol): 1973 cm^{-1} (ν_{CO}). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.79 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.65 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.59 (m, 6H, 6 H arom), 7.52 (m, 2H, 2 H arom), 7.44 (m, 4H, 4 H arom), 7.04 (s, 2H, 2 H arom Mes), 7.01 (s, 1H, H arom NHC), 6.55 (m, 8H, $Bcat_2$), 5.42 (s, 2H, CH_2N), 4.09 (d, $^2J_{HP}$ = 10.1 Hz, 2H,

CH_2P), 2.36 (s, 3H, CH_3), 2.13 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 45.4. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2): δ 14.4. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 178.6 (d, J_{CP} = 98 Hz, C-2 NHC), 177.1 (d, J_{CP} = 9 Hz, CO), 165.0 (d, J_{CP} = 7 Hz, C_q arom), 155.3 (C_q arom), 152.3 (4 C_q arom $Bcat_2$), 141.5 (CH arom), 140.3 (C_q arom), 136.3 (2 C_q arom), 135.6 (C_q arom), 133.2 (d, J_{CP} = 12 Hz, 4 CH arom), 132.0 (2 CH arom), 130.2 (d, J_{CP} = 54 Hz, 2 C_q arom), 129.5 (d, J_{CP} = 11 Hz, 4 CH arom), 129.3 (2 CH arom), 124.7 (d, J_{CP} = 10 Hz, CH arom), 124.6 (CH arom), 122.8 (CH arom), 122.5 (CH arom), 118.2 (4 CH arom $Bcat_2$), 108.7 (4 CH arom $Bcat_2$), 55.5 (CH_2N), 42.6 (d, J_{CP} = 31 Hz, CH_2P), 21.3 (CH_3), 18.5 (2 CH_3). HRMS (ESI): *m/z* 696.1743 [(*M* $Bcat_2$)$^+$] (exact mass calculated for $C_{32}H_{30}IrN_3OP$: 696.1750).

Complex 1(BAr_F). A solution of **1(Cl)** (0.096 g, 0.13 mmol) and Na[BAr_F] (0.116 g, 0.13 mmol) in CH_2Cl_2 (7 mL) was stirred for 2 h. The resulting suspension was filtered, and solvent was removed under reduced pressure. The resulting solid was washed with pentane (2 × 10 mL) and dried under vacuum. Complex **1(BAr_F)** was isolated as an orange solid (0.186 g, 91%). Anal. calcd (%) for $C_{64}H_{42}BF_{24}IrN_3OP$: C 49.31; H 2.72; N 2.70; found: C 49.20; H 2.92; N 2.78. IR (nujol): 1979 (ν_{CO}) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.95 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.76 (s, 8H, 8 H arom BAr_F), 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 7.63 (m, 4H, 4 H arom), 7.59 (s, 4H, 4 H arom BAr_F), 7.51 (m, 7H, 7 H arom), 7.44 (dd, $^3J_{HH}$ = 1.8 Hz, $^5J_{HP}$ = 0.8 Hz, 1H, H arom NHC), 7.17 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H arom NHC), 7.09 (s, 2H, 2 H arom Mes), 5.39 (s, 2H, CH_2N), 4.14 (d, $^2J_{HP}$ = 10.1 Hz, 2H, CH_2P), 2.40 (s, 3H, CH_3), 2.16 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 45.6. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2): δ 6.6. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 179.3 (d, J_{CP} = 99 Hz, C-2 NHC), 176.4 (d, J_{CP} = 10 Hz, CO), 165.9 (d, J_{CP} = 7 Hz, C_q arom), 162.2 (q, J_{CB} = 50 Hz, 4 BC_q arom BAr_F), 154.9 (C_q arom), 141.5 (CH arom), 140.8 (C_q arom), 136.1 (2 C_q arom), 135.2 (m, 8 CH arom BAr_F), 133.2 (d, J_{CP} = 12 Hz, 4 CH arom), 132.3 (2 CH arom), 129.6 (overlapped, 2 C_q arom), 129.6 (d, J_{CP} = 11 Hz, 4 CH arom), 129.5 (2 CH arom), 129.3 (q, J_{CF} = 32 Hz, 8 C_q arom BAr_F), 125.0 (q, J_{CF} = 272 Hz, 8 CF_3), 124.9 (d, J_{CP} = 10 Hz, CH arom), 123.9 (CH arom), 123.3 (CH arom), 121.8 (CH arom), 117.9 (m, 4 CH arom BAr_F), 56.3 (CH_2N), 43.1 (d, J_{CP} = 31 Hz, CH_2P), 21.3 (CH_3), 18.5 (2 CH_3); signal for one quaternary aromatic carbon could not be identified.

Complex 3(Cl). In a J.Young-valved NMR tube, a solution of **1(Cl)** (0.050 g, 0.07 mmol) in CD_2Cl_2 (0.5 mL) was charged with 1 bar of H_2. The resulting solution was immediately analyzed by NMR spectroscopy indicating complete formation of **3(Cl)**. Complex **3(Cl)** loses hydrogen upon exposure to vacuum. IR (CD_2Cl_2): 2338 (ν_{IrH}), 2085 (ν_{IrH}), 1987 (ν_{CO}) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2): δ 8.45 (s, 1H, H arom NHC), 8.29 (d, $^3J_{HH}$ = 6.4 Hz, 1H, H arom Py), 7.99 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, H arom Py), 7.82 (d, $^3J_{HH}$ = 6.4 Hz, 1H, H arom Py), 7.60 (dd, $^3J_{HP}$ = 12.8 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, 2 H arom PPh), 7.51 (dd, $^3J_{HH}$ = 7.6 Hz, J_{HP} = 6.3 Hz, 1H, H arom PPh), 7.40 (m, 5H, 5 H arom PPh), 7.27 (m, 2H, 2 H arom PPh), 7.12 (d, $^2J_{HH}$ = 15.4 Hz, 1H, C*H*HN), 7.07 (s, 1H, H arom NHC), 7.05 (s, 2H, 2 H arom Xyl), 4.89 (d, $^2J_{HH}$ = 15.3 Hz, 1H, C*H*HN), 4.82 (dd, $^2J_{HH}$ = 17.1 Hz, $^2J_{HP}$ = 12.5 Hz, 1H, C*H*HP), 3.63 (dd, $^2J_{HH}$ = 17.1 Hz, $^2J_{HP}$ = 10.2 Hz, 1H, C*H*HP), 2.42 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 8.32 (ddd, $^2J_{HP}$ = 22.2 Hz, $^2J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, IrH *cis* to Py), 17.45 (dd, $^2J_{HP}$ = 11.7 Hz, $^2J_{HH}$ = 1.6 Hz, 1H, IrH *trans* to Py). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 16.9. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 175.0 (CO), 163.4 (d, J_{CP} = 3 Hz, C_q arom), 156.9 (d, J_{CP} = 100 Hz, C-2 NHC), 155.8 (C_q arom), 140.3 (CH arom), 139.6 (C_q arom), 136.8 (C_q arom), 135.7 (C_q arom), 135.5 (C_q arom), 134.9 (d, J_{CP} = 12 Hz, 2 CH arom), 134.4 (d, J_{CP} = 49 Hz, C_q arom), 132.3 (d, J_{CP} = 2 Hz, CH arom), 131.3 (d, J_{CP} = 2 Hz, CH arom), 130.4 (d, J_{CP} = 11 Hz, 2 CH arom), 130.1 (d, J_{CP} = 63 Hz, C_q arom), 129.5 (d, J_{CP} = 10 Hz, 2 CH arom), 129.4 (CH arom), 129.2 (CH arom), 129.1 (d, J_{CP} = 12 Hz, 2 CH arom), 125.7 (CH arom), 124.1 (d, J_{CP} = 3 Hz, CH arom), 123.4 (d, J_{CP} = 10 Hz, CH arom), 121.8 (d, J_{CP} = 3 Hz, CH arom), 58.1 (CH_2N), 46.1 (d, J_{CP} = 37 Hz, CH_2P), 21.3 (CH_3), 18.4 (CH_3), 18.2 (CH_3). MS (ESI, CH_2Cl_2/MeCN): *m/z* (%): 698 (100) [(*M* Cl)$^+$].

Complex 4. In a J.Young-valved NMR tube, a solution of **2a**/**2b** (0.010 g, 0.014 mmol) in THF-d_8 (0.5 mL) was charged with 5 bar of H_2. The resulting solution was immediately analyzed by NMR spectroscopy showing complete formation of **4**. Complex **4** readily loses hydrogen upon removal of the H_2 atmosphere.



^1H NMR (500 MHz, THF-d_8): δ 7.58 (m, 3H, 3 H arom), 7.41 (dd, J_{HP} = 10.1 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, 2 H arom), 7.19 (m, 7H, 7 H arom), 7.06 (m, 2H, 2 H arom), 6.56 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, H^c), 6.43 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H^b), 5.71 (d, $^3J_{HH}$ = 6.2 Hz, 1H, H^d), 5.01 (d, $^2J_{HH}$ = 14.1 Hz, 1H, C*H*HN), 4.70 (d, $^2J_{HH}$ = 14.3 Hz, 1H, C*H*HN), 3.93 (d, $^2J_{HP}$ = 2.7 Hz, 1H, H^a), 2.43 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 8.64 (dd, $^2J_{HP}$ = 20.8 Hz, $^2J_{HH}$ = 1.5 Hz, 1H, IrH), 16.59 (dd, $^2J_{HP}$ = 11.3 Hz, $^2J_{HH}$ = 1.6 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (202 MHz, THF-d_8): δ 8.8. $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8): δ 176.5 (br m, CO), 174.7 (d, J_{CP} = 19 Hz, C_q arom), 162.7 (d, J_{CP} = 92 Hz, C-2 NHC), 150.3 (C_q arom), 145.0 (d, J_{CP} = 50 Hz, C_q arom), 140.7 (d, J_{CP} = 71 Hz, C_q arom), 139.2 (C_q arom), 138.4 (C_q arom), 136.7 (C_q arom), 136.0 (C_q arom), 134.7 (d, J_{CP} = 11 Hz, 2 CH arom), 132.0 (d, J_{CP} = 2 Hz, C^c), 131.4 (d, J_{CP} = 12 Hz, 2 CH arom), 129.5 (CH arom), 129.3 (CH arom), 129.0 (CH arom), 128.6 (CH arom), 128.0 (d, J_{CP} = 10 Hz, 2 CH arom), 127.8 (d, J_{CP} = 11 Hz, 2 CH arom), 122.0 (CH arom), 121.8 (d, J_{CP} = 3 Hz, CH arom), 115.3 (d, J_{CP} = 18 Hz, C^b), 102.0 (C^d), 66.6 (d, J_{CP} = 78 Hz, C^a), 60.3 (CH_2N), 21.2 (CH_3), 18.7 (CH_3), 18.4 (CH_3).

Complex 5($Bcat_2$). In a J.Young-valved NMR tube, a solution of **1($Bcat_2$)** (0.035 g, 0.04 mmol) in THF-d_8 (0.5 mL) was treated with HBcat (5.0 μL, 0.05 mmol). Complete conversion of **1($Bcat_2$)** to **5($Bcat_2$)** was determined by NMR spectroscopy. IR (CH_2Cl_2): 2101 (ν_{IrH}), 2005 (ν_{CO}) cm^{-1}. ^1H NMR (500 MHz, THF-d_8): δ 7.91 (d, $^3J_{HH}$ = 1.1 Hz, 1H, H arom NHC), 7.86 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H arom Py), 7.82 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, 1H, H arom Py), 7.74 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H arom Py), 7.48 (m, 4H, 4 H arom), 7.36 (m, 4H, 4 H arom), 7.24 (m, 2H, 2 H arom), 7.11 (br, H arom HBcat), 7.05 (d, $^3J_{HH}$ = 1.1 Hz, 1H, H arom NHC), 6.97 (br, H arom HBcat), 6.82 (s, 1H, H arom Mes), 6.76 (m, 2H, 2 H arom IrBcat), 6.70 (m, 2H, 2 H arom

IrBcat), 6.39 (br m, 8H, 8 H arom $Bcat_2$), 6.00 (d, $^2J_{HH}$ = 15.7 Hz, 1H, NC*H*H), 5.97 (s, 1H, H arom Mes), 5.01 (dd, $^2J_{HH}$ = 17.3 Hz, $^2J_{HP}$ = 12.5 Hz, 1H, PC*H*H), 5.00 (d, $^2J_{HH}$ = 15.7 Hz, 1H, NC*H*H), 4.37 (q, $^1J_{HB}$ = 190 Hz, *H*Bcat), 3.98 (dd, $^2J_{HH}$ = 17.1 Hz, $^2J_{HP}$ = 10.2 Hz, 1H, PC*H*H), 2.01 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 6.90 (d, $^2J_{HP}$ = 21.1 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (202 MHz, THF-d_8): δ 15.7. ^{11}B NMR (96 MHz, THF-d_8): δ 22.5 (d, J_{BH} = 189 Hz, HBcat), 15.1 (br, $Bcat_2$), 12.9 (IrBcat). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 176.8 (br, CO), 162.0 (C_q arom), 155.1 (C_q arom), 154.3 (d, J_{CP} = 96 Hz, C-2 NHC), 153.3 (4 C_q arom $Bcat_2$), 151.0 (2 C_q arom IrBcat), 149.5 (2 C_q arom HBcat), 141.3 (CH arom), 140.1 (C_q arom), 136.2 (C_q arom), 135.8 (C_q arom), 135.2 (C_q arom), 133.7 (d, J_{CP} = 11 Hz, 2 CH arom), 132.4 (d, J_{CP} = 11 Hz, 2 CH arom), 132.2 (CH arom), 131.9 (CH arom), 131.8 (d, J_{CP} = 50 Hz, C_q arom), 130.0 (d, J_{CP} = 11 Hz, 2 CH arom), 129.9 (CH arom), 129.4 (CH arom), 129.2 (d, J_{CP} = 62 Hz, C_q arom), 129.1 (d, J_{CP} = 12 Hz, 2 CH arom), 125.0 (CH arom), 124.9 (CH arom), 124.7 (d, J_{CP} = 10 Hz, CH arom), 123.9 (CH arom), 122.6 (br, 2 CH arom HBcat), 121.4 (2 CH arom IrBcat), 118.0 (4 CH arom $Bcat_2$), 112.4 (br, 2 CH arom HBcat), 111.3 (2 CH arom IrBcat), 108.7 (4 CH arom $Bcat_2$), 59.1 (CH_2N), 46.1 (d, J_{CP} = 39 Hz, CH_2P), 21.3 (CH_3), 18.6 (CH_3), 17.6 (CH_3).

Complex 6(BAr$_F$). In a J.Young-valved NMR tube, a solution of **1(BAr$_F$)** (0.023 g, 0.015 mmol) in THF-d_8 (0.5 mL) was treated with pinBH (5.3 μL, 0.036 mmol). Complete conversion of **1(BAr$_F$)** to **6(BAr$_F$)** was determined by NMR spectroscopy. IR (CH_2Cl_2): 2089 (ν_{IrH}), 1993 (ν_{CO}) cm^{-1}. ^1H NMR (400 MHz, THF-d_8): δ 8.03 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.79 (s, 8H, 8 H arom BAr_F), 7.73 (m, 2H, 2 H arom), 7.68 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H arom Py), 7.61 (m, 2H, 2 H arom), 7.57 (s, 4H, 4 H arom BAr_F), 7.45 (m, 8H, 8 H arom), 7.25 (s, 1H, H arom), 7.06 (s, 1H, H arom), 7.01 (s, 1H, H arom), 5.79 (d, $^2J_{HH}$ = 15.8 Hz, 1H, NC*H*H), 5.19 (d, $^2J_{HH}$ = 15.8 Hz, 1H, NC*H*H), 4.86 (dd, $^2J_{HH}$ = 16.9 Hz, $^2J_{HP}$ = 12.5 Hz, 1H, PC*H*H), 3.83 (dd, $^2J_{HH}$ = 17.1 Hz, $^2J_{HP}$ = 10.4 Hz, 1H, PC*H*H), 3.75 (q, $^1J_{HB}$ = 172 Hz, *H*Bpin), 2.33 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.22 (s, 4 CH_3 HBpin), 0.74 (s, 6H, 2 CH_3 IrBpin), 0.71 (s, 6H, 2 CH_3 IrBpin), 6.81 (d, $^2J_{HP}$ = 22.1 Hz, 1H, IrH). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8): δ 18.1. ^{11}B NMR (128 MHz, THF-d_8): δ 30.1 (d, J_{BH} = 173 Hz, HBpin), 23.2 (br, IrBpin), 4.6 ppm (BAr_F). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 178.0 (br, CO), 162.6 (q, J_{CB} = 50 Hz, 4 BC_q arom BAr_F), 162.4 (C_q arom), 156.8 (d, J_{CP} = 102 Hz, C-2 NHC), 155.6 (C_q arom), 140.8 (CH arom), 139.8 (C_q arom), 137.2 (C_q arom), 135.9 (C_q arom), 135.4 (m, 8 CH arom BAr_F), 133.8 (d, J_{CP} = 11 Hz, 2 CH arom), 132.1 (m, 2 CH arom), 132.0 (CH arom), 131.8 (CH arom), 129.8 (m, 4 CH arom + 8 C_q arom BAr_F), 128.8 (d, J_{CP} = 11 Hz, 2 CH arom), 125.2 (q, J_{CF} = 272 Hz, 8 CF_3), 125.0 (CH arom), 123.6 (CH arom), 123.4 (CH arom), 123.3 (CH arom), 118.0 (m, 4 CH arom BAr_F), 83.6 (2 C_q HBpin), 82.8 (2 C_q IrBpin), 59.7 (CH_2N), 47.3 (d, J_{CP} = 37 Hz, CH_2P), 25.0 (4 CH_3 HBpin), 24.9 (overlapped with solvent signal, 2 CH_3 IrBpin), 24.2 (2 CH_3 IrBpin), 20.9 (CH_3), 18.9 (CH_3), 18.8 (CH_3); signals for three quaternary aromatic carbons could not be detected due to significant spectrum complexity.

Representative procedure for CO_2 hydroboration with HBcat

In a glovebox, a J.Young-valved NMR tube was charged with a solution of **2a**/**2b** (1.6 mg, 2.3 μmol) and hexamethylbenzene (3.8 mg, 0.023 mmol) in THF-d_8 containing 0.2% of water (0.5 mL) (total water content: 5 mol%), and catecholborane (25 μL, 0.23 mmol) was added. The NMR tube was submitted to vacuum to remove the N_2 atmosphere, charged with CO_2 (2 bar) and heated to 30 °C. Reaction progress was monitored by $^1H\{^{11}B\}$ and ^{11}B NMR spectroscopies.

Representative procedure for CO_2 hydroboration with HBpin

In a glovebox, a J.Young-valved NMR tube was charged with 300 μL of a freshly prepared 1.3 mM stock solution of **2a**/**2b** (0.4 μmol) in THF-d_8 containing 0.2% of water, hexamethylbenzene (3.8 mg, 0.023 mmol) and THF-d_8 (0.2 mL) containing 0.2% of water (total water content: 5 mol%). Pinacolborane (32 μL, 0.22 mmol) was added, and the NMR tube was submitted to vacuum to remove the N_2 atmosphere, charged with CO_2 (1 bar) and heated to 30 °C. Reaction progress was monitored by $^1H\{^{11}B\}$ and ^{11}B NMR spectroscopies.

DFT calculations

DFT calculations were carried out with the Gaussian 09 program.[42] The hybrid functional B3LYP[43] was used, with dispersion effects taken into account by adding the D3 version of Grimme's empirical dispersion.[44] C, H, N, B, O and P atoms were represented by the 6-31g(d,p) basis set,[45] whereas Ir was described using the Stuttgart/Dresden Effective Core Potential and its associated basis set SDD.[46] All geometry optimizations were performed without restrictions in THF (bulk solvent effects modelled with the SMD continuum model).[47]

Conflicts of interest

There are no conflicts to declare.

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