CO_2 Reduction

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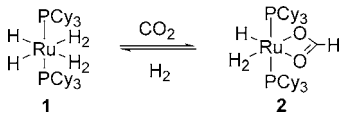
Borane-Mediated Carbon Dioxide Reduction at Ruthenium: Formation of C_1 and C_2 Compounds**

*Sébastien Bontemps, Laure Vendier, and Sylviane Sabo-Etienne**

There is a growing interest in considering the use of carbon dioxide as a carbon source, because it is an abundant, cheap, and nontoxic molecule.[1] Recently, significant advances have been made towards the production of formic acid[2] and in promoting the insertion of CO_2 into C–H bonds.[3] In all of these systems, the OCO unit is maintained, and it is thus desirable to broaden the substrate scope through the abstraction of oxygen atom(s) from carbon dioxide.[4] Following the report in 2005 by Sadighi and co-workers of the copper-catalyzed reduction of CO_2 into CO,[5] transformations of CO_2 under mild conditions (1 atm, RT) into C_1 building blocks such as CO, CH_3OH, or CH_4 were mediated by transition-metal catalysis[5a,6] and organocatalysis,[7] by using silanes, boranes, or aldehydes as oxygen scavengers.

Ruthenium complexes are known to be efficient catalysts for the conversion of CO_2 into formic acid and formate derivatives.[8] In our group, we have extensively studied the chemistry of ruthenium polyhydrides such as the bis(dihydrogen) complex $[RuH_2(H_2)_2(PCy_3)_2]$ (**1**; Cy = cyclohexyl).[9] The unique properties of the bound dihydrogen as a labile ligand and a hydrogen source have been illustrated in the reactivity of **1** and related complexes toward E–H bonds (E = H, BR_2, SiR_3, CR_3).[10] We had shown that **1** can reversibly insert CO_2 into the Ru–H bond by simple gas bubbling, thereby affording the formate complex $[RuH(\kappa^2\text{-}CO_2H)(\eta^2\text{-}H_2)(PCy_3)_2]$ (**2**; Scheme 1).[11] Herein we report the catalyzed reduction of CO_2 by **1** with pinacolborane (HBpin) as the activator and oxygen scavenger. A detailed NMR spectroscopy study, using labeled $^{13}CO_2$, allows us to disclose an unprecedented reductive coupling of two CO_2 molecules, which leads to the formation of $pinBO^{13}CH_2O^{13}CHO$. Mechanistic investigation combining in situ monitoring of the catalytic mixture and stoichiometric experiments highlights the role of a series of carbonyl ruthenium species **3**–**6**.



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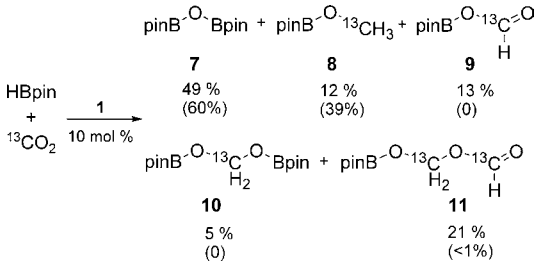
Scheme 1. Reversible insertion of CO_2 into complex **1** affording complex **2**.

In an NMR tube, HBpin readily reacts with $^{13}CO_2$ (1 atm) in the presence of 10 mol% of complex **1** in C_6D_6 at room temperature. Complete conversion of HBpin was observed after 30 min and multinuclear NMR spectroscopy analyses unambiguously demonstrated the formation of $(pinB)_2O$ (**7**), $pinBO^{13}CH_3$ (**8**), and the new compounds $pinBO^{13}CHO$ (**9**), $pinBO^{13}CH_2OBpin$ (**10**), and $pinBO^{13}CH_2O^{13}CHO$ (**11**; Scheme 2).

As depicted in Figure 1, a comparison of the ^1H and $^1H\{^{13}C\}$ NMR spectra provides clear visual proof of the presence of ^{13}C-labeled atoms in the resulting compounds. It is worth mentioning that no reaction occurred in the absence of **1** and that deuterium labeling of HBpin supported the



Scheme 2. Compounds **7**–**11** obtained from the reaction of HBpin with $^{13}CO_2$ (1 atm) using complex **1** (10 mol%) as the catalyst precursor. Relative proportions are given after total consumption of HBpin after 30 min, whereas values in parentheses are obtained after 22 days at room temperature or five hours at 70°C.

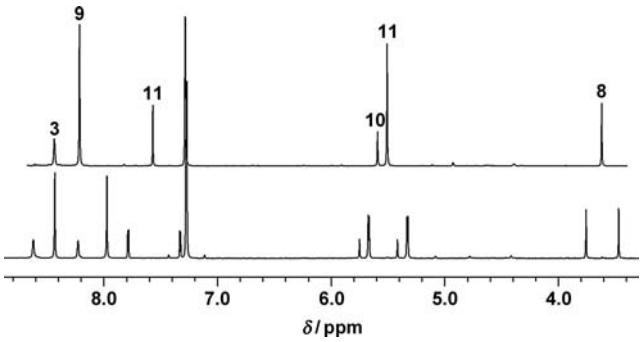


Figure 1. ^1H (bottom) and $^1H\{^{13}C\}$ (top) NMR spectra (C_6D_6) in the downfield region that result from the reaction of HBpin with $^{13}CO_2$ using **1** as catalyst: formation of the boron compounds **8**–**11** and of the ruthenium complex **3**.

[*] Dr. S. Bontemps, Dr. L. Vendier, Dr. S. Sabo-Etienne
CNRS, LCC (Laboratoire de Chimie de Coordination)
205 route de Narbonne, 31077 Toulouse (France)
and
Université de Toulouse, UPS, INPT
31077 Toulouse (France)
E-mail: sylviane.sabo@lcc-toulouse.fr
Homepage: http://www.lcc-toulouse.fr/lcc/spip.php?article433

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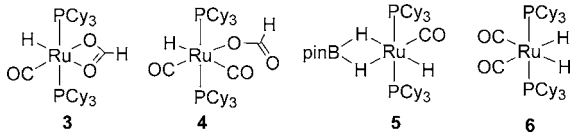
formation of **8**–**11** from the reduction with the borane reagent.[12] Particularly diagnostic for the C_2 compound **11** are the ^1H and ^{13}C chemical shifts indicative of -O^{13}CHO and -O^{13}CH$_2$O- units ($\delta_H = 7.42$ ppm, $^1J_{HC} = 228.9$ Hz and $\delta_H = 5.39$ ppm, $^1J_{HC} = 170.4$ Hz; $\delta_C = 159.2$ and 82.5 ppm, respectively) and the observed coupling constants $^3J_{HC}$ (4.0 and 4.4 Hz, respectively) and $^2J_{CC}$ (2.3 Hz), which support the connectivity between the two units.[13] Interestingly, after 22 days in the NMR tube at room temperature or five hours at 70 °C, the products **9**–**11** are cleanly transformed into **7** and **8**.[12]

Because complexes **1** and **2** were never detected at the end of the catalysis, we sought mechanistic information. Three new complexes **3**–**5** and the known dicarbonyl complex [RuH$_2$(CO)$_2$(PCy$_3$)$_2$] (**6**;[14] Scheme 3) were found in various proportions depending on the catalyst loading (see below). Complexes **3**–**5** were synthesized independently and fully



Scheme 3. Complexes **3**–**6**.

characterized by X-ray diffraction and IR and multinuclear NMR spectroscopy.[12] The signals of the hydride ligands of **3** and **4** are detected at $\delta = -17.76$ and -4.68 ppm, respectively, and the formate protons appear at $\delta = 8.35$ and 8.58 ppm, respectively. The X-ray diffraction structures of **3** and **4** show an octahedral environment with the two PCy$_3$ ligands in *trans* positions (Figure 2). In complex **3**, the equatorial plane is

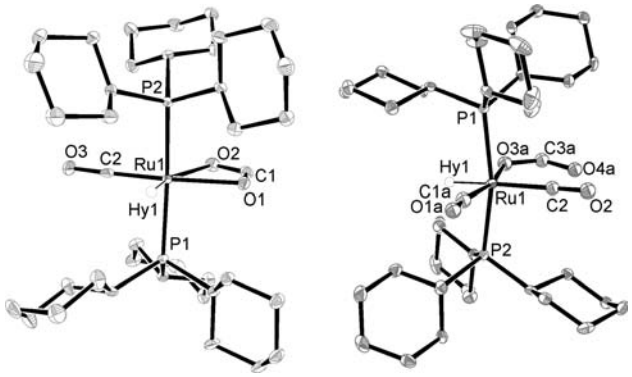


Figure 2. X-ray structures of complex **3** (left) and **4** (right; ellipsoids at 30% probability). Selected bond lengths [Å] and angles [°]: (**3**) Ru–O1 2.2256(16), Ru–O2 2.3409(17), Ru–C2 1.811(2), Ru–Hy1 1.499(19), C1–O1 1.266(2), C1–O2 1.258(2); P1-Ru-P2 165.41(17), O1-Ru-O2 57.71(5), O1-C1-O2 121.91(17). (**4**) Ru–C2 1.959(4), Ru–Hy1 1.42(3); P1-Ru-P2 166.32(3).

occupied by a κ^2-formate, a carbonyl, and a hydride ligand. The κ^2 coordination of the formate ligand is also evidenced by a band in the IR spectrum at 1559 cm^{-1}.[15] In contrast, complex **4** exhibits a second carbonyl ligand, the formate group now adopting a κ^1 coordination mode. The IR spectrum of **4** displays a band at higher frequency (1621 cm^{-1}), as expected for a κ^1 coordination mode and authenticated by labeling studies.[15,16] Previous studies have shown that **1** reversibly coordinates HBpin to produce the complex [RuH{(μ-H)$_2$Bpin}(η^2-HBpin)(PCy$_3$)$_2$], with HBpin incorporated in two different coordination modes, σ-borane and dihydroborate.[17] When complexes **2** or **3** were used as catalyst precursors (10 mol%), both complexes reacted with HBpin to afford, before the introduction of CO_2, the new dihydroborate complex [RuH{(μ-H)$_2$Bpin}(CO)(PCy$_3$)$_2$] (**5**), which was independently isolated by addition of HBpin to the carbonyl complex [RuH$_2$(H$_2$)(CO)(PCy$_3$)$_2$]. Complex **5** is characterized in the ^1H NMR spectrum by three broad signals at $\delta = -6.68$, -8.67, and -10.04 ppm for the three different hydrides.[18] The X-ray diffraction analysis shows that the ruthenium center also displays two PCy$_3$ ligands in *trans* positions, the equatorial plane being occupied by a hydride, a carbonyl, and a κ^2-coordinated dihydridopinacolborate ligand with a Ru–B bond distance of 2.231(3) Å (Figure 3).

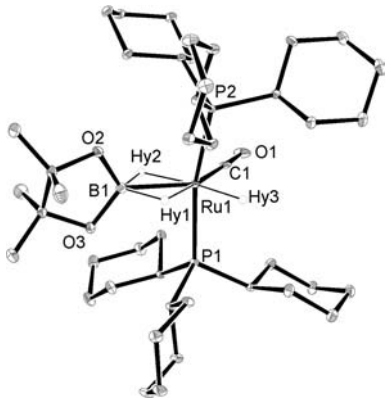


Figure 3. X-ray structure of complex **5** (ellipsoids at 30% probability). Selected bond lengths [Å] and angles [°]: Ru–Hy1 1.65(2), Ru–Hy2 1.64(3), Ru–Hy3 1.55 (3), B–Hy1 1.37(2), B–Hy2 1.42(3), Ru–C1 1.866(3), C1–O1 1.155(3); P1-Ru-P2 166.45(2).

As shown in Table 1 (entry 1), when 10 mol% of complex **1** were used, complex **3** (see also Figure 1) along with a very small amount of complex **6** (<5%) were detected after 30 min and with total consumption of HBpin. In contrast, when 1 mol% of **1** was used, complexes **3**, **5**, and **6** were observed in roughly a 1:4:1 ratio after 30 min (Table 1, entry 2). After a longer reaction time (10 h), only complexes **4** and **6** were detected and HBpin conversion stopped at 89% (Table 1, entry 3). Complexes **3**–**6** feature ^{13}C-labeled car-

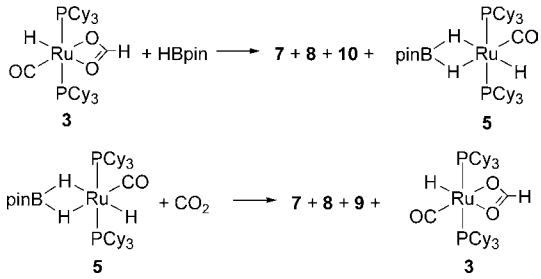
Table 1: Ruthenium species resulting from the use of **1** as the catalyst precursor under 1 atm of CO_2.

Entry	1:HBpin ratio	Relative amount of formed complex [%]			
		3	**4**	**5**	**6**
1	1:10[a]	95	0	0	5
2	1:100[a]	17	0	66	17
3	1:100[b]	0	40	0	60

[a] After 30 min. [b] After ten hours.

bonyl ligands, thus indicating that $^{13}CO_2$ has been decarbonylated during the reaction. Transient formation of formaldehyde is a likely possibility to explain such a decarbonylation,[19] and it should be noted that free formaldehyde and formic acid were detected after three hours during the slow transformation of compounds **9**–**11** into **7**–**8**. Control experiments showed that complex **3** exhibits very similar catalyst activity as **1** or **2**, whereas complexes **4** and **6** are poorly active. When using complex **3** as catalyst precursor, NMR spectroscopy control prior to the introduction of CO_2 indicates the complete and very clean transformation of **3** into the dihydroborate **5**. During the course of the catalysis complexes **3** and **5** coexist, and the activity is maintained until the dicarbonyl complexes **4** and **6** are the only complexes detected in the mixture, thereby causing a drop in catalytic activity.

Stoichiometric experiments were then conducted to gain information on the selectivity (Scheme 4). The reaction of complex **3** with one equivalent of HBpin affords compounds **7** (63%), **8** (24%), and **10** (13%). No trace of **9** or **11** was



Scheme 4. Stoichiometric experiments with complexes **3** and **5**.

detected, and the dihydroborate species **5** is the main ruthenium species (>95%). The exposure of complex **5** to one atmosphere of CO_2 affords compounds **7** (29%) and **8** (10%) along with **9** (60%). No trace of **10** and **11** was detected and the formoxy complex **3** is the main ruthenium species (>95%). The precoordination of HBpin to the metal center appears thus a prerequisite for the formation of the formoxy compound **9**. When CO_2 inserts into a Ru–H bond, the reaction with HBpin likely gives rise to the formation of a {$RuOCH_2OBpin$} species, which had been previously suggested.[6b,c] The observation of the acetal compound **10** is thus an indirect proof of such an intermediate as it likely results from the reaction of the {$RuOCH_2OBpin$} fragment with a second equivalent of HBpin. The mechanism of the formation of compound **11** remains unclear, but the nature of our ruthenium precursor, which allows the access to two vacant sites, could be a key factor to explain such a coupling.

In summary, the formation of the pinacol compounds **7**, **8**, and **9** is reminiscent of the catechol compounds observed by Guan and co-workers,[6b] but the activity and selectivity are much more modest. However, our system broadens the panel of compounds accessible from CO_2 reduction.[20] Indeed, whereas acetals are key structures that have been studied in various CO_2 reduction processes,[4a–c,6a,7] a species such as **10** has not been reported with boron so far,[4h] and compound **11** represents the first direct reductive coupling of two CO_2 units.[21] Mechanistic investigation shows that borane coordination competes with CO_2 insertion and that decarbonylation is readily achieved, which ultimately results in catalyst deactivation. Studies are ongoing to elucidate the mechanism leading to the C_2 compound and to extend the scope of this system.

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[13] ROESY experiments indicate the spatial connectivity of the methyl groups of the pinacol backbone with the $^{13}CH_2$ and $^{13}CH_3$ of **10**, **11**, or **8**. For the formoxy compound **9**, the carbon resonance and the large $^1J_{HC}$ coupling constant ($\delta_H = 8.21$ ppm; $\delta_C = 159.7$ ppm, $^1J_{HC} = 227.3$ Hz) compare well to the related values reported for the analogous CatBOCHO compound (δ_C 162.1, $^1J_{HC} = 214.0$ Hz; Cat = catechol).[6b] The methylene ^{1}H and ^{13}C signals of compound **10** in the NMR spectra ($\delta_H = 5.49$ ppm, $^1J_{HC} = 167.2$ Hz and $\delta_C = 85.4$ ppm) compare well to those reported for the related silicon product $CH_2(OSiEt_3)_2$ ($\delta_H =$ 5.01 ppm, $^1J_{HC} = 161.4$ Hz and $\delta_C = 84.2$ ppm).[7c]
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