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Ruthenium-Catalyzed Reduction of Carbon Dioxide to Formaldehyde

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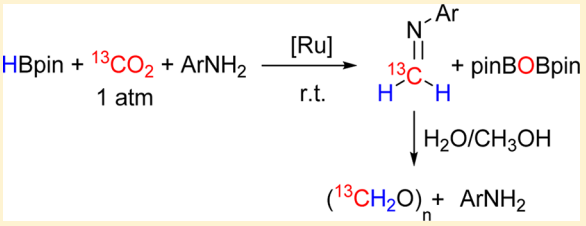
Supporting Information

ABSTRACT: Functionalization of CO_2 is a challenging goal and precedents exist for the generation of HCOOH, CO, CH_3OH, and CH_4 in mild conditions. In this series, CH_2O, a very reactive molecule, remains an elementary C_1 building block to be observed. Herein we report the direct observation of free formaldehyde from the borane reduction of CO_2 catalyzed by a polyhydride ruthenium complex. Guided by mechanistic studies, we disclose the selective trapping of formaldehyde by in situ condensation with a primary amine into the corresponding imine in very mild conditions. Subsequent hydrolysis into amine and a formalin solution demonstrates for the first time that CO_2 can be used as a C_1 feedstock to produce formaldehyde.



INTRODUCTION

CO_2 is an attractive alternative to fossil resources for the synthesis of common C_1 sources.[1] Beyond the CO_2 reduction into formic acid, it has been demonstrated that organometallic and organic catalytic systems can afford CO, CH_3OH, and CH_4 under 1 atm of CO_2 at room temperature using, in most cases, boranes or silanes as reductant and oxygen scavenger (Chart 1).[2] With dihydrogen as the sole reductant, CH_3OH can also be produced through a cascade reaction involving three different catalysts,[3] or by using a tridentate phosphine ruthenium catalyst precursor under harsher conditions.[4] To our knowledge CH_2O is a missing elementary building block that has never been observed in the catalytic reduction of CO_2.[5] To account for the formation of CH_3OH, transient formaldehyde has been postulated and supported by theoretical calculations.[6] It is noteworthy that at the industrial level, CH_2O is a major reactive C1 source, since more than 20 million tons per year are produced mainly from methanol oxidation.[7] In this context the synthesis of this versatile molecule would not only be of fundamental interest but could also expand the scope of products accessible from the reduction of CO_2. For instance, reduction into formaldehyde and subsequent reaction with a N−H bond would produce an imine, an important functional group in chemistry. Related multicomponent strategies were recently developed for the formylation[8] and methylation[9] of N−H bonds.

Chart 1. Mild Catalytic Reduction of CO_2 (1 atm) into C_1 Building Blocks (*corresponding author*, resulting oxygen acceptor product, and year of publication. Reactions mainly performed at r.t.)

CH_4
Matsuo, Kawaguchi, SiOSi, 2006
Piers, SiOSi, 2010
Brookhart, SiOSi, 2012
Turculet, SiOSi, 2012
Piers, Maron, Eisenstein, SiOSi, 2013

CH_3OH
Zhang, SiOSi, 2009
O'Hare, BOB, 2009
Guan, BOB, 2010
Bontemps, Sabo-Etienne, BOB, 2012
Stephan, BOB, 2012
Maron, Fontaine, BOB, 2013

CO
Sadighi, BOB, 2005
Zhang, RCOOH, 2009
Kleeberg, BOSi, 2011
Stephan, R_3PO, 2013

CH_2O
This work, pinBOBpin

Recently, we launched a program aimed at studying the ability of polyhydride ruthenium complexes to catalyze the reduction of CO_2. We first focused on a system based on the bis(tricyclohexylphosphine) complex $[RuH_2(H_2)_2(PCy_3)_2]$ ($\mathbf{1}_{Cy}$) for which borane coordination studies had been conducted previously in the group.[10]

Using pinacolborane as reducing agent and oxygen scavenger, we reported the fast reduction of CO_2 into five boron compounds, including an original C_2 compound resulting from the unprecedented reductive coupling of two molecules of CO_2.[11] An important step in proving the involvement of formaldehyde was reached when we demonstrated that this C_2 compound, $pinBOCH_2OCHO$ (**11**), was formed from the reaction of pinBOCHO (**9**) with transient CH_2O.[12]

By using the analogous bis(tricyclopentylphosphine) complex $[RuH_2(H_2)_2(PCyp_3)_2]$ ($\mathbf{1}_{Cyp}$),[13] we have shown that a small modification in the phosphine substituents had a major impact in catalytic nitrile reduction,[14] H/D exchange,[15] and dehydrogenation processes.[16] We now disclose the use of $\mathbf{1}_{Cyp}$ as catalyst precursor for the reduction of carbon dioxide leading

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to the direct observation of free formaldehyde. Mechanistic considerations on the nature of the active species and on the role of the C_1 and C_2 compounds are discussed. Through *in situ* condensation of formaldehyde with a primary amine, and subsequent hydrolysis of the resulting imine into a formalin solution, we demonstrate the concept of using CO_2 as a C_1 feedstock to produce formaldehyde—the process being selective under very mild conditions.

RESULTS AND DISCUSSION

Catalytic Experiments Using $\mathbf{1}_{Cyp}$ as Catalyst Precursor. Generation of Free Formaldehyde. The dihydride bis(dihydrogen) complex $[RuH_2(H_2)_2(PCyp_3)_2]$ ($\mathbf{1}_{Cyp}$) bearing two tricyclopentylphosphines acts as a catalyst precursor for the reduction of CO_2 mediated by pinacolborane in the same standard conditions previously reported for complex $\mathbf{1}_{Cy}$ (10 mol %, 1 atm of $^{13}CO_2$, 30 min, r.t. in a closed NMR tube).[11] HBpin is readily consumed, and the different organic compounds **6**–**11** are shown in Scheme 1. The relative ratios

Scheme 1. Direct Observation of Free Formaldehyde Using $\mathbf{1}_{Cyp}$ as a Catalyst (see Table 1 for relative ratios)

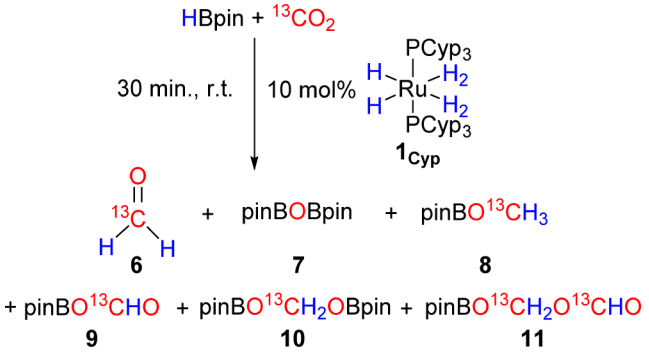

Table 1. Relative Ratios of Compounds 6–11, under Various Conditions (catalyst precursor, CO_2 pressure and solvent)

	catalyst	P CO_2, (atm)	solvent	relative ratios (%) **6/7/8/9/10/11**
1	$\mathbf{1}_{Cy}$	1	C_6D_6	0/49/12/13/5/21
2	$\mathbf{1}_{Cyp}$	1	C_6D_6	22/49/11/0/6/12
3	$\mathbf{1}_{Cyp}$	0.5	C_6D_6	18/49/15/0/7/11
4	$\mathbf{1}_{Cyp}$	1.5	C_6D_6	0/50/9/6/9/26
5	$\mathbf{1}_{Cyp}$	4	C_6D_6	0/52/5/13/4/26
6	$\mathbf{1}_{Cyp}$	1	THF-d_8	0/47/6/10/4/33
7	$\mathbf{2}_{Cyp}$	1	C_6D_6	1/63/35/0/1/0
8	$\mathbf{3}_{Cyp}$	1	C_6D_6	1/52/44/0/3/0
9	$\mathbf{4}_{Cyp}$	1	C_6D_6	1/55/41/0/3/0

obtained in different conditions are reported in Table 1. One striking difference between the two systems is in the present case the absence of the formoxyborane compound **9** (Table 1, entry 2 vs 1) and the formation in rather large proportions of a new compound characterized by a resonance at 8.74 ppm in the ^1H NMR spectrum, and assigned to formaldehyde **6**. This signal appears as a doublet when $^{13}CO_2$ is used ($^1J_{H-C}$ = 176.6 Hz)—providing evidence for its formation from carbon dioxide—and is associated with a carbon NMR signal at 193.0 ppm, indicative of free formaldehyde. We had shown that the C_2 compound **11** could be obtained by direct reaction of **9** with CH_2O.[12] Here, as a large ratio of formaldehyde is formed, complete conversion of **9** is achieved. This proves to be the first direct observation of free formaldehyde from a homogeneously catalyzed reduction of CO_2. Monitoring the mixture over a longer period shows that final conversion into **7** and **8** is obtained in a much shorter time, 48 h, by comparison to the 22 days necessary when using $\mathbf{1}_{Cy}$ as catalyst precursor. Additionally, the new C_2 compound $pinBOCH_2OCH_3$ (**12**) was detected as a minor product after 24h (Figure 1).

In an attempt to isolate formaldehyde, we conducted the standard reaction, and after 30 min, the volatile products were transferred upon vacuum. NMR spectra of the volatiles showed formaldehyde as the major compound along with $pinBOCH_3$ (**8**) and new signals resulting from multiple insertion of formaldehyde into **8**. Among them, $pinBOCH_2OCH_3$ (**12**) and the new C_3 compound $pinBOCH_2OCH_2OCH_3$ (**13**) were characterized. These compounds could also be independently generated from the reaction of $pinBOCH_3$ and formaldehyde in the absence of any ruthenium catalyst (Scheme 2).

To explore further the reduction of CO_2, various experimental conditions have been applied, and the relative ratios of compounds **6**–**11** are reported in Table 1. It appears that selectivity is significantly influenced by the nature of the catalyst precursor, as well as by the CO_2 pressure and the nature of the solvent. In C_6D_6 and with a low CO_2 pressure (Table 1, entries 2 and 3), formaldehyde is favored over **9**. On the contrary, in THF or using a higher pressure of CO_2 (Table 1, entries 4–6) compound **9** is favored over **6**.

Mechanistic Studies and Characterization of Complexes $\mathbf{2}_{Cyp}$–$\mathbf{4}_{Cyp}$. To better understand the differences between the PCy_3 and $PCyp_3$ systems leading to the observation of formaldehyde, we evaluated the fate of the catalyst precursor. In the cyclohexyl system, we had identified three organometallic species that played a major role in the catalysis: two monocarbonyl complexes coexisting all along the catalysis, $RuH(CO_2H)(CO)(PCy_3)_2$ ($\mathbf{2}_{Cy}$), and $RuH(H_2Bpin)(CO)(PCy_3)_2$ ($\mathbf{4}_{Cy}$), prior to deactivation into the dicarbonyl $RuH_2(CO)_2(PCy_3)_2$ ($\mathbf{5}_{Cy}$).[11] In the cyclopentyl system, the corresponding monocarbonyl complex $\mathbf{2}_{Cyp}$ is readily formed with traces of the inactive dicarbonyl $\mathbf{5}_{Cyp}$.[17] After 24 h, a new carbonate complex $RuH(O_2COMe)(CO)(PCyp_3)_2$ ($\mathbf{3}_{Cyp}$) is observed, whereas the dihydroborate complex $\mathbf{4}_{Cyp}$ was never detected during the catalysis. The new $PCyp_3$ complexes $\mathbf{2}_{Cyp}$–$\mathbf{4}_{Cyp}$ have been independently synthesized and characterized (Chart 2). $\mathbf{2}_{Cyp}$ and $\mathbf{4}_{Cyp}$ present NMR data similar to the corresponding PCy_3 complexes. Complex $\mathbf{3}_{Cyp}$ displays a set of NMR signals presenting strong similarities with complex $\mathbf{2}_{Cyp}$ for the phosphine ($\delta^{31}P$ = 45.6 Hz, $^2J_{P-C}$ = 14.0 Hz), carbonyl ($\delta^{13}C$ = 208, t, $^2J_{C-P}$ = 14.0 Hz) and hydride (δ^1H = −17.71, td, $^2J_{H-P}$ = 19.8 Hz, $^2J_{H-C}$ = 11.3 Hz) ligands, but lacking any signature for a formate ligand. Instead, a set of signals (δ^1H = 3.52, dd, $^1J_{HC}$ = 145.2 Hz, $^3J_{H-C}$ = 4.0 Hz; $\delta^{13}C$ = 158.7 and 52.7) is indicative of a carbonate ligand featuring two ^{13}C-labeled carbon atoms when $^{13}CO_2$ is used. X-ray diffraction analyses have been conducted on complexes $\mathbf{2}_{Cyp}$, $\mathbf{3}_{Cyp}$, and $\mathbf{4}_{Cyp}$ (see Supporting Information [SI]). The three compounds present octahedral arrangements with the two phosphines in axial position, a hydride (in the case of $\mathbf{3}_{Cyp}$, statistical disorder issues prevented hydride location) and a carbonyl in cis position in the equatorial plane. The carbonyl ligands are further characterized by IR spectroscopy at 1899, 1894, and 1935 cm^{-1}, respectively. To complete the equatorial plane, the formate ($\mathbf{2}_{Cyp}$), carbonate ($\mathbf{3}_{Cyp}$), and dihydroborate ($\mathbf{4}_{Cyp}$)

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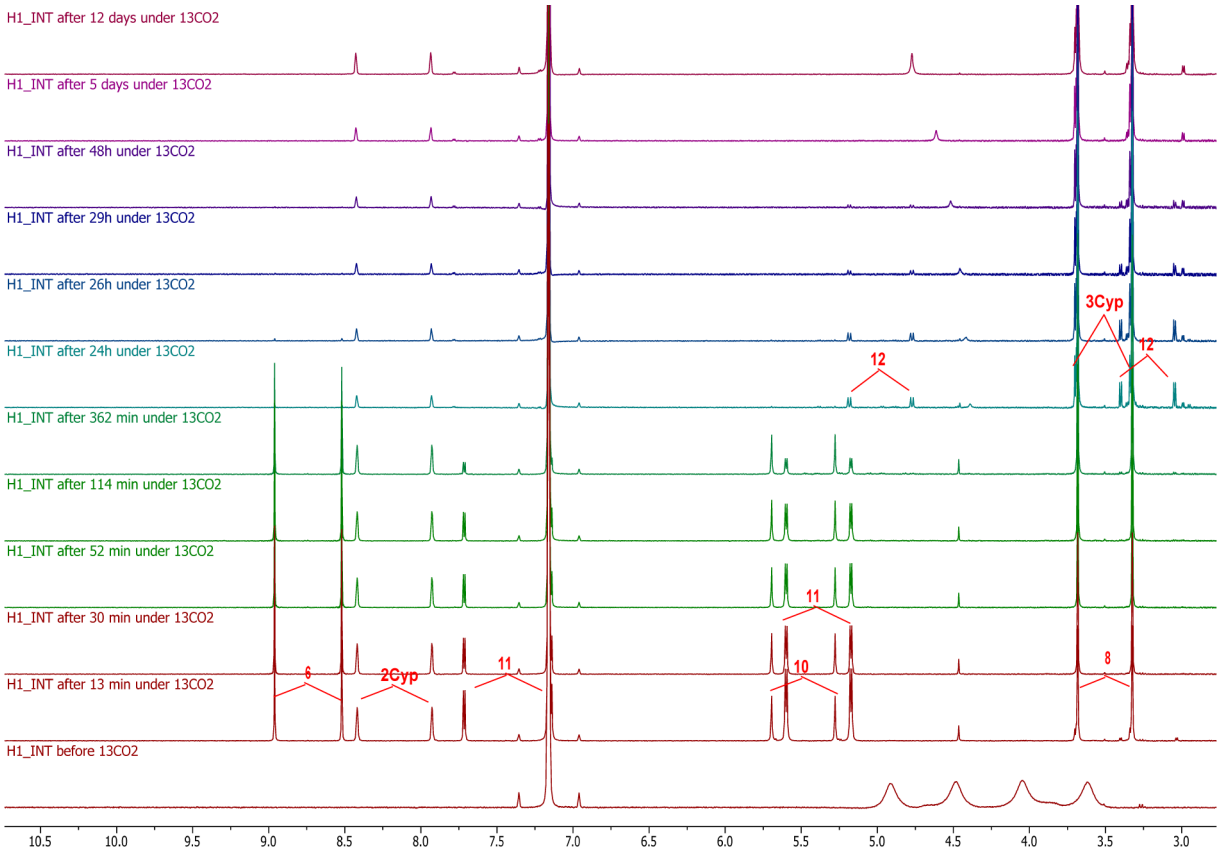


Figure 1. ^{1}H NMR stack spectra of the standard reaction with catalyst precursor $\mathbf{1}_{Cyp}$ at various times; 10.5−3.0 ppm region.

Scheme 2. Reaction of Formaldehyde with Compounds 8 and 9

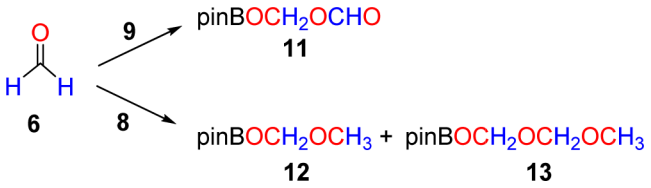
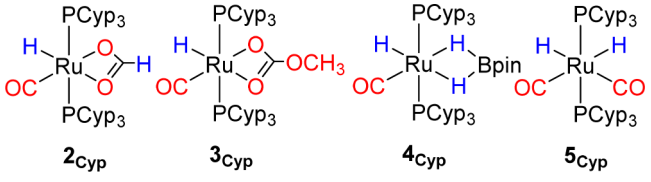


Chart 2. Ruthenium Bis(tricyclopentyl) Complexes $\mathbf{2}-\mathbf{5}_{Cyp}$



ligands are coordinated in a bidentate fashion further substantiated by stretching frequencies in the case of $\mathbf{2}_{Cyp}$ (νO_2C = 1555 cm^{-1}) and $\mathbf{3}_{Cyp}$ (νO_2CO = 1578 cm^{-1}).[11,18]

Complex $\mathbf{1}_{Cyp}$ exhibits a higher activity than $\mathbf{1}_{Cy}$; at room temperature, complete transformation of HBpin and CO_2 into **7** and **8** is achieved within 48 h instead of 22 days for $\mathbf{1}_{Cy}$. Remarkably, when the standard reaction was conducted with the isolated complexes $\mathbf{2}-\mathbf{4}_{Cyp}$, compounds **7** and **8** were obtained in 30 min with only traces amount of **6** and **10** (Table 1, entries 7−9). To explain this enhanced activity, the differences in the fate of the catalyst precursor were examined when starting from $\mathbf{1}_{Cyp}$ or from $\mathbf{2}-\mathbf{4}_{Cyp}$. As already mentioned, when using $\mathbf{1}_{Cyp}$, complex $\mathbf{2}_{Cyp}$ is readily formed with traces of $\mathbf{5}_{Cyp}$. Complex $\mathbf{3}_{Cyp}$ only appeared in small amount after 24h (Figure 1) and complex $\mathbf{4}_{Cyp}$ was never detected. We have independently shown that $\mathbf{3}_{Cyp}$ can be slowly produced from $\mathbf{2}_{Cyp}$ and formaldehyde (Sup. Info. Figure S3). It thus appears that in the catalytic mixture *i.e.* in the presence of HBpin *and* CO_2, complex $\mathbf{2}_{Cyp}$ does not afford complex $\mathbf{4}_{Cyp}$. However, when starting from complexes $\mathbf{2}_{Cyp}$ or $\mathbf{3}_{Cyp}$, introduction of HBpin readily generates complex $\mathbf{4}_{Cyp}$. It is thus not surprising to observe similar catalytic activities when starting from complexes $\mathbf{2}-\mathbf{4}_{Cyp}$, since $\mathbf{4}_{Cyp}$ is the only complex present in the system when CO_2 is introduced. When the catalysis begins, complex $\mathbf{4}_{Cyp}$ is readily converted into $\mathbf{2}_{Cyp}$ and $\mathbf{3}_{Cyp}$ in less than 10 min. When starting from $\mathbf{4}_{Cyp}$, the observation of complex $\mathbf{3}_{Cyp}$ at the early stage of catalysis is in marked contrast with the standard reaction conducted with $\mathbf{1}_{Cyp}$ ($\mathbf{3}_{Cyp}$ observed after 24 h). There is thus a link between the presence of $\mathbf{3}_{Cyp}$ and the enhanced catalytic activity. Moreover we observed that CO_2 addition to isolated $\mathbf{4}_{Cyp}$ resulted in the fast formation of $\mathbf{2}_{Cyp}$ and $\mathbf{3}_{Cyp}$ in a 1:0.15 ratio and reduction of CO_2 into **7** and **8** (SI).

On the basis of the data gained by conducting the CO_2 reduction with the PCy_3 and $PCyp_3$ systems, we propose the following mechanism featuring three main catalytic cycles to account for the accumulation of the different compounds (Scheme 3). The first step consists in the classical CO_2 insertion into a Ru−H bond in competition with HBpin coordination. This coordination appears to have no impact on the outcome of the catalysis in the PCy_3 system. Guan et al. also mentioned an innocent behavior of an [Ni]-H·HBCat adduct in a related CO_2 reduction process.[2f] However, in the $PCyp_3$ system, the dihydroborate complex $\mathbf{4}_{Cyp}$ may generate

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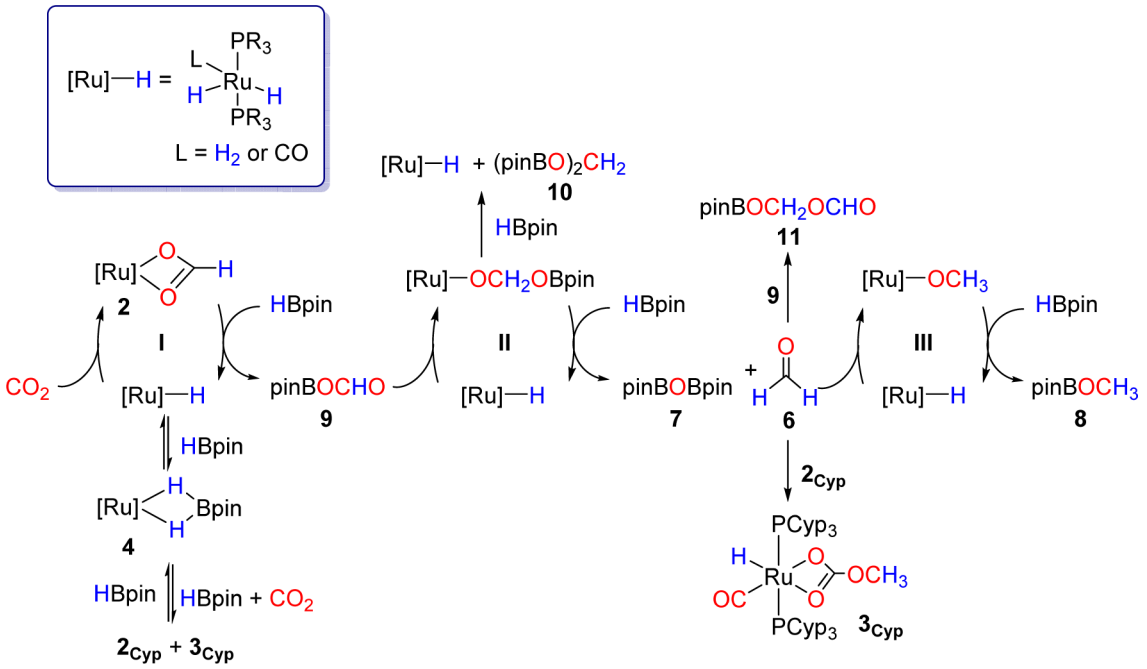
Scheme 3. Proposed mechanism based on the detection of compounds 2−11



the more active carbonate complex $\mathbf{3}_{Cyp}$. The formate complex **2** then reacts with a first equivalent of HBpin to afford compound **9**, which can further react with the regenerated catalyst to give rise to an acetal species {[Ru]OCH_2OBpin}. The observation of the acetal compound **10** substantiates the occurrence of such an intermediate, previously postulated in borane-based reductive processes.[2f,o,6b] The reaction of the acetal complex with a second equivalent of HBpin results in formal oxygen abstraction and formation of pinBOBpin (**7**) along with the release of formaldehyde. Formaldehyde is able to enter the last cycle to afford a methoxy complex that reacts with the third equivalent of HBpin and finally releases the methoxyborane **8**. To confirm that the last step is metal-catalyzed, we conducted two additional experiments; treatment of HBpin with formaldehyde produced compound **8** in less than 10 min in the presence of $\mathbf{1}_{Cyp}$, whereas 8 days were necessary when no metal catalyst was introduced. In addition, we have shown that formaldehyde can react in the catalytic conditions with $\mathbf{2}_{Cyp}$, **8**, and **9** to afford $\mathbf{3}_{Cyp}$, **12**, and **11**, respectively. A similar mechanism involving three cycles for the reduction of CO_2 with HBCat has been proposed by Guan et al., and further substantiated by Wang et al. calculations.[2f,i,o,6b] Our in-depth studies provide conclusive proofs for various steps of this complex mechanism. Key findings are (i) the direct observation of formaldehyde and the variation of the compound relative ratios depending on the conditions, (ii) the observation of compounds **9**, **10**, and **11** and their direct link with formaldehyde,[12] (iii) the validation that the reaction of formaldehyde with HBpin is metal-catalyzed. Moreover, as observed in previous studies,[13,14,16] it is interesting to note the differences resulting from the use of $\mathbf{1}_{Cyp}$ or $\mathbf{1}_{Cy}$; conformational changes in the cycloalkyl rings and solubility properties being important factors.[19]

From CO_2 Reduction to Formalin: Generation of the Imine 14. Many efforts have been devoted to better control selectivity issues in this ruthenium CO_2 reduction process. We have observed that the relative ratios of compounds **6**−**11** are sensitive to various conditions. The $PCyp_3$ system appears to change the relative rates of the three proposed catalytic cycles, allowing the accumulation and thus the detection of free formaldehyde. *In situ* trapping of formaldehyde sounded like an attractive way to obtain this target molecule and solve selectivity issues by preventing side reactions occurring at early stages. The formation of formaldehyde **6** and compound **11** are proofs that trapping is possible. We had shown earlier that formaldehyde could be recovered from the reaction of CH_3OH with compounds **10** and **11**.[12] However, when methanol was added at the beginning of the reaction, it reacted with HBpin. The more hindered 2,6-bis(diisopropyl)phenol gave also side reactions before the introduction of CO_2. We then turned our attention to amine functions. Condensation of ketones or aldehydes with amines is indeed the most common way to generate imines.[20] In addition, these reactions are reversible, an important requirement to recover and use formaldehyde. 2,6-Bis(diisopropyl)aniline was chosen for its protected amine function; it affords the only known stable monomeric methylene aniline compound upon reaction with formaldehyde.[21] When 2,6-bis(diisopropyl)aniline was introduced in the catalytic system, NMR control prior to CO_2 introduction showed that no reaction had occurred. By applying 1 atm of CO_2, we were then pleased to observe the complete disappearance of HBpin within 1 h and the appearance of NMR signals associated with methylene aniline (**14**) (Scheme 4).[21] The methylene moiety presents a characteristic deshielded AB resonance in ^{1}H NMR at 7.25 ppm (dd, $^1J_{H-C}$ = 179.4 Hz, $^2J_{H-H}$ = 18.5 Hz, 1H, CH_2) and 6.88 ppm (dd, $^1J_{H-C}$ = 160.5 Hz, $^2J_{H-H}$ = 18.5 Hz, 1H, CH_2) with a large $^1J_{H-C}$ coupling constant when using labeled $^{13}CO_2$, correlating to a carbon signal at 155.2 ppm (Figure S6 of SI). HRMS analysis on the crude material confirmed the presence of ^{12}C or ^{13}C labeled-methyleneaniline when $^{12}CO_2$ and $^{13}CO_2$ were employed, respectively. To our delight, this reaction is very selective: HBpin is totally consumed and the ^{13}C NMR spectrum shows only the signals associated with labeled compound **14** along with complex $\mathbf{2}_{Cyp}$ (Figure S7 of SI). Subsequent hydrolysis of the methyleneaniline **14**, regenerated

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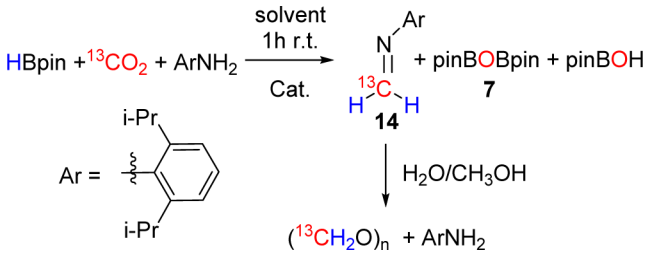
Scheme 4. From CO_2 Reduction to Formalin: Generation of the Imine 14 and Subsequent Hydrolysis to Formalin and Amine



aniline and afforded a formalin solution (Figures S8 and S9 of SI), thus demonstrating the concept of using CO_2 as a C_1 feedstock to produce formaldehyde.

The yield in methylene aniline **14**, based on 2 equiv of HBpin for the transformation of CO_2 into CH_2O, was determined by ^1H NMR and reported in Table 2. One can

Table 2. Variation of Catalytic Conditions and Corresponding Yields in Compound 14

entry[a]	catalyst loading %	P (CO_2) (atm)	solvents	T (°C)	yield in **14** (%)
1	$\mathbf{1}_{Cyp}$ (10)	1	C_6D_6	25	47
2[b]	$\mathbf{1}_{Cyp}$ (7)	1	C_6D_6	25	74
3	$\mathbf{1}_{Cyp}$ (10)	1	THF-D_8	25	42
4[c]	$\mathbf{1}_{Cyp}$ (1)	1	C_6D_6	10	49
5	$\mathbf{1}_{Cyp}$ (10)	1	C_6D_6	70	32
6[c]	$\mathbf{1}_{Cyp}$ (1)	1	C_6D_6	70	43
7	$\mathbf{1}_{Cyp}$ (10)	3	C_6D_6	25	36
8	$\mathbf{1}_{Cy}$ (10)	1	C_6D_6	25	29
9	$\mathbf{4}_{Cyp}$ (2)	1	C_6D_6	25	51
10[c]	$\mathbf{4}_{Cyp}$ (1)	1	C_6D_6	25	50
11[b]	$\mathbf{4}_{Cyp}$ (7)	1	C_6D_6	25	74
12	$\mathbf{1}_{Cyp}$ (5)	1	C_6D_6	25	47
13[c]	$\mathbf{1}_{Cyp}$ (1)	1	C_6D_6	25	50
14[d]	$\mathbf{1}_{Cyp}$ (0.5)	1	C_6D_6	25	54

[a]Catalyst loading and yield based on HBpin, unless otherwise stated. [b]Catalyst loading and yield based on CO_2. [c]3 h of reaction. [d]5 h of reaction.

be surprised by the observed 47% yield as **14** was the only compound detected (Table 2, entry 1). A rather simple explanation is that HBpin is involved not only as a reductant of carbon dioxide but also as a dehydrating agent, driving the reaction toward the formation of the imine by trapping water formed during the condensation of aniline with formaldehyde. Indeed, 1−2 equiv of HBpin reacted with water to generate pinBOBpin, pinBOH, and H_2 as observed by NMR. Thus, the maximum yield based on our calculation ranges formally between 50 and 66%.

To account for the selectivity observed by NMR spectroscopy and calculate a yield based on CO_2, we conducted the catalysis by transferring a known amount of CO_2 to an excess of HBpin and aniline with 7 mol % catalyst (Table 2, entry 2). If 2 equiv of CO_2 reacted with $\mathbf{1}_{Cyp}$ to generate $\mathbf{2}_{Cyp}$, thus limiting the yield at a 86% maximum, the measured 74% yield after 1 h corroborates that **14** and complex $\mathbf{2}_{Cyp}$ were solely detected in the $^{13}C\{^1H\}$ NMR spectrum with no trace of free $^{13}CO_2$. We then applied various catalytic conditions and observed minor differences, as opposed to the catalytic system without aniline. Varying the solvent (Table 2, entry 3), temperature (Table 2, entries 4−6), and CO_2 pressure (Table 2, entry 7) conditions have little impact. Moreover, when using complex $\mathbf{1}_{Cy}$ or $\mathbf{4}_{Cyp}$ as catalyst precursors, compound **14** was also obtained in moderate to good yield based on HBpin (Table 2, entries 8−11). Finally, one major drawback of the reduction process in the absence of aniline was the catalyst deactivation that prevented us from decreasing the catalyst loading. Trapping formaldehyde appears to suppress the deactivation process since the catalyst loading can be decreased down to 0.5 mol % with 54% yield after 5 h (Table 2, entries 12−14), the active catalyst $\mathbf{2}_{Cyp}$ being the only complex detected at the end of the reaction. As a summary, by preventing competitive reactions in this intricate system, trapping formaldehyde *in situ* successfully allowed the establishment of a catalyzed CO_2 functionalization process exhibiting high selectivity with low catalyst loading.

CONCLUSION

Formaldehyde was an elementary C_1 building block that had never been observed in the homogeneous reduction of CO_2. By using the bis(dihydrogen) complex $[RuH_2(H_2)_2(PCyp_3)_2]$ ($\mathbf{1}_{Cyp}$) we describe the catalyzed reduction of CO_2 into various organic compounds including free formaldehyde. Guided by in-depth mechanistic studies, we were able to selectively trap formaldehyde by in situ condensation to a primary amine affording the corresponding imine under very mild conditions. Subsequent hydrolysis provided a formalin solution and regenerated the amine, thus demonstrating for the first time that CO_2 can be used as a C_1 feedstock to produce formaldehyde. Further research to optimize this concept is currently underway in our group.

EXPERIMENTAL SECTION

General Methods. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk or glovebox techniques. Solvents were dried using an MBraun SPS column. Deuterated benzene, toluene, and THF were freeze−pump−thaw degassed and stored under Ar over 4 Å molecular sieves. Quick pressure valve NMR tubes were used for reactions with CO_2. ^1H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded on Bruker AV 400 or 500 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, relative to residual ^1H and ^{13}C solvent signals, and external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4. Complexes $\mathbf{1}_{Cyp}$ and $\mathbf{5}_{Cyp}$ were synthesized according to literature procedures.[13,17]

Synthesis and Characterization of $\mathbf{2}$−$\mathbf{4}_{Cyp}$. $\mathbf{2}_{Cyp}$: A solution of $Ru(H)_2(\eta^2\text{-}H_2)(CO)(PCyp_3)_2$ (50 mg, 0.08 mmol) in Et_2O (2 mL) was exposed to 1 atm of CO_2 for 15 min at ambient temperature. The solvent was removed by filtration, and the residue was washed twice with pentane (0.5 mL) at −30 °C, affording the expected complex $Ru(H)(O_2CH)(CO)(PCyp_3)_2$ as an orange solid in 53% yield. Crystals suitable for X-ray analysis were grown from the slow evaporation of a pentane solution at room temperature. Mp = 163−165 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 8.20 (s, 1H, O_2CH), 2.25−1.45 (m, 54H, Cyp), −17.83 (t, $^2J_{H-P}$ = 19.6 Hz, 1H, Ru−H); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 207.9 (t, $^2J_{C-P}$ = 13.9 Hz, CO), 172.9 (s, O_2CH), 37.4 (t, J_{C-P} = 11.5 Hz, Cyp), 30.3 (s, Cyp), 29.9 (s, Cyp), 26.5 (t, J_{C-P} = 4.0 Hz, Cyp), 26.3 (t, J_{C-P} = 4.0 Hz, Cyp); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 298 K): δ 45.8. IR (solid, cm^{-1}): 2040 (weak, νRuH), 1899

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(very strong, νCO), 1555 (strong, νO_2C). Anal. Cald. for $C_{32}H_{57}O_3P_2Ru$: C, 58.88; H, 8.80. Found: C, 59.12; H, 8.48.

$Ru(H)(O_2{}^{13}CH)(^{13}CO)(PCyp_3)_2$ has been characterized in situ in the standard reaction. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 8.20 (d, $^1J_{H-C}$ = 195.5 Hz, 1H, O_2CH), 2.25−1.45 (m, 54H, Cyp), −17.84 (td, $^2J_{H-P}$ = 19.6 Hz, $^2J_{H-C}$ = 11.4 Hz, 1H, Ru−H); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 298 K): δ 45.8 (d, $^2J_{P-C}$ = 13.9 Hz)

3_{Cyp}: A solution of $Ru(H)(O_2CH)(CO)(PCyp_3)_2$ (150 mg, 0.20 mmol) in toluene/methanol (2 mL/2 mL) was stirred at 70 °C for 6 h. The solvents were removed by vacuum, and the residue was washed with methanol (3*2 mL), affording $Ru(H)(O_2COCH_3)(CO)(PCyp_3)_2$ in 74% yield. Monocrystals suitable for X-ray analysis were obtained from a concentrated solution of diethylether or toluene/methanol at room temperature. In each case, poor definition resulting from statistical disorder did not allow any discussion about angles and bond distances (see SI). Mp = 142−144 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 3.53 (s, 3H, CH_3), 2.25−1.44 (m, 54H, Cyp), −17.68 (t, $^2J_{H-P}$ = 19.6 Hz, 1H, Ru−H); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 208.0 (t, $^2J_{C-P}$ = 14.0 Hz, CO), 158.7 (s, O_2COCH_3), 52.7 (s, CH_3), 37.3 (t, J_{C-P} = 11.3 Hz, Cyp), 30.2 (s, Cyp), 29.8 (s, Cyp), 26.5 (t, J_{C-P} = 4.2 Hz, Cyp), 26.4 (t, J_{C-P} = 4.2 Hz, Cyp); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 298 K): δ 45.6. IR (solid, cm^{-1}): 1894 (very strong, νCO), 1578 (strong, νO_2C). Anal. Cald. for $C_{33}H_{59}O_4P_2Ru$: C,58.05; H,8.71. Found: C,57.45; H,8.64

$Ru(H)(O_2{}^{13}CO{}^{13}CH_3)(^{13}CO)(PCyp_3)_2$ has been characterized in situ in the standard reaction. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 3.52 (dd, $^1J_{H-C}$ = 145.2 Hz, $^3J_{H-C}$ = 4.0 Hz, 3H, CH_3), 2.25−1.44 (m, 54H, Cyp), −17.71 (td, $^2J_{H-P}$ = 19.8 Hz, $^2J_{H-C}$ = 11.3 Hz, 1H, Ru−H); $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 298 K): δ 45.6 (d, $^2J_{P-C}$ = 14.0 Hz).

4_{Cyp}: HBpin (50 mg, 0.39 mmol) was added in excess to a solution of $Ru(H)_2(H_2)(CO)(PCyp_3)_2$ (89 mg, 0.15 mmol) in pentane (5 mL) and stirred for 3 h. The solvent and excess HBpin were then removed by vacuum, and the residue was washed with cold pentane, affording complex **4_{Cyp}** in a 48% yield. Monocrystals suitable for X-ray analysis were obtained from a concentrated solution of pentane at room temperature. Mp = 76−78 °C. ^1H NMR (C_6D_6, 298 K, 500.3 MHz) δ = 2.46−2.38 (m, 6H, Cyp), 2.05−1.98 (m, 12H, Cyp), 1.93−1.83 (m, 12H, Cyp), 1.77−1.69 (m, 12H, Cyp), 1.61−1.48 (m, 12H, Cyp), 1.16 (s, 12H, CH_3(pin)), −6.90 (br, 1H, Ru−H), −8.81 (br, 1H, Ru−H), −9.76 (br, 1H, Ru−H); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 125.8 MHz) δ = 208.7 (t, $^2J_{C-P}$ = 12.0 Hz, CO), 81.5 (s, C(pin)), 39.7 (pseudo-t, J_{C-P} = 12.6 Hz, Cipso (Cyp)), 30.1 (s, Cyp), 30.0 (s, Cyp), 26.4 (s, 2C, Cyp), 24.5 (s, CH3(pin)); $^{11}B\{^1H\}$ NMR (C_6D_6, 298 K, 128.4 MHz) δ = 29.9 (br w1/2 = 265 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 162.0 MHz) δ = 56.2. IR (solid, cm^{-1}): 1935 (strong, νCO). Any attempt to characterize the compound by elemental analysis or mass spectrometry failed, presumably because of the poor stability of the complex observed upon storage in the glovebox at room temperature.

In situ characterization of 12−14. **12**: ^1H NMR (400.1 MHz, C_6D_6, 298 K) δ = 4.99 (dd, $^1J_{H-C}$ = 164.6, $^3J_{H-C}$ = 7.0, 2H), 3.23 (dd, $^1J_{H-C}$ = 141.9, $^3J_{H-C}$ = 4.9, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ = 91.7 (d, $^2J_{C-C}$ = 2.7, CH_2), 55.6 (d, $^2J_{C-C}$ = 2.7, CH_3).

13: ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 5.19 (dd, $^1J_{H-C}$ = 169.9 Hz, $^3J_{H-C}$ = 6.1 Hz, 2H, CH_2), 4.68 (pseudo-td, $^1J_{H-C}$ = 163.6 Hz, $^3J_{H-C}$ = 6.0 Hz, 2H, CH_2), 3.12 (dd, $^1J_{H-C}$ = 141.3 Hz, $^3J_{H-C}$ = 4.8 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 94.0 (pseudo-t, $^2J_{C-C}$ = 2.3 Hz, CH_2), 87.2 (d, $^2J_{C-C}$ = 2.2 Hz, CH_2), 55.2 (d, $^2J_{C-C}$ = 2.3 Hz, CH_3).

14: ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.25 (dd, $^1J_{H-C}$ = 179.4 Hz, $^2J_{H-H}$ = 18.5 Hz, 1H, CH_2), 7.13 − 7.02 (m, 3H, CH(arom)), 6.88 (dd, $^1J_{H-C}$ = 160.5 Hz, $^2J_{H-H}$ = 18.5 Hz, 1H, CH_2), 2.97 (hept, $^3J_{H-H}$ = 6.9 Hz, 2H, CH(i-Pr), 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH_3(i-Pr)); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 155.2 (s, $^{13}CH_2$).

^1H NMR (400.1 MHz, Tol-d_8, 298 K): δ 7.30 (dd, $^1J_{H-C}$ = 179.5 Hz, $^2J_{H-H}$ = 18.6 Hz, 1H, CH_2), 7.16−7.02 (m, 3H, CH(arom)), 6.92 (dd, $^1J_{H-C}$ = 160.5 Hz, $^2J_{H-H}$ = 18.5 Hz, 1H, CH_2), 3.38 (hept, $^3J_{H-H}$ = 6.9 Hz, 2H, CH(i-Pr), 1.23 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH_3(i-Pr)); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 155.4 (s, $^{13}CH_2$); HRMS (DCI-CH4): m/z (M^+: $^{12}C_{13}H_{19}N$): calculated: 189.1517, found: 189.1522; m/z (M^+: $^{12}C_{12}{}^{13}CH_{19}N$): calculated: 190.1566, found: 190.1551.

^1H NMR (400.1 MHz, THF-d_8, 298 K): δ 7.73 (dd, $^1J_{H-C}$ = 179.5 Hz, $^2J_{H-H}$ = 18.4 Hz, 1H, CH_2), 7.37 (dd, $^1J_{H-C}$ = 160.5 Hz, $^2J_{H-H}$ = 18.4 Hz, 1H, CH2), 7.13 − 6.97 (m, 3H, CH(arom)), 2.91 (hept, $^3J_{H-H}$ = 6.9 Hz, 2H, CH(i-Pr), 1.16 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH_3(i-Pr)); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 156.5 (s, $^{13}CH_2$).

Catalytic Experiments. *Generation of Compounds **6**−**11**.* In a pressurizable NMR tube, a solution of a ruthenium complex (0.013 mmol) and HBpin (17 mg, 0.130 mmol) was degassed and placed under a pressure of $^{13}CO_2$ at room temperature. NMR characterization was conducted after 30 min showing the formation of **6**−**11**.[11] For $^{13}CH_2O$: ^1H NMR (400.1 MHz, C_6D_6, 298 K) δ = 8.74 (d, $^1J_{H-C}$ = 176.6 Hz, 1H); $^{13}C\{^1H\}$, NMR (100.6 MHz, C_6D_6, 298 K): δ = 193.0 (s).

*Generation of Compound **14**.* In a pressurizable NMR tube, a solution of a ruthenium complex, HBpin (17 mg, 0.13 mmol), and 2,6-bis(diisopropyl)aniline (18 mg, 0.10 mmol) was degassed and placed under a pressure of $^{13}CO_2$. Catalyst loading and yields given in Table 2 were based on HBpin, considering that 2 equiv of HBpin were necessary to reduce CO_2 to CH_2O, except otherwise stated. For entries 2 and 11, a known quantity of $^{13}CO_2$ (0.19 mmol) was vacuum transferred to a J-Young tube containing HBpin (99 mg, 0.77 mmol), 2,6-bis(diisopropyl)aniline (60 mg, 0.34 mmol) and a ruthenium catalyst (0.013 mmol) in C_6D_6 solution; the yields were then calculated based on CO_2. The yields were determined by NMR by using a known quantity of 4-methyl-anisole as a standard, added to the tube at the end of the reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental spectroscopic and X-ray crystallographic data for **2**−**4_{Cyp}**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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