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Communication

Mechanism Insights into the Iridium(III)- and $B(C_6F_5)_3$-Catalyzed Reduction of CO_2 to the Formaldehyde Level with Tertiary Silanes

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ABSTRACT: The catalytic system $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ [**1**; NSi^{Me} = (4-methylpyridin-2-yloxy)dimethylsilyl]/$B(C_6F_5)_3$ promotes the selective reduction of CO_2 with tertiary silanes to the corresponding bis(silyl)acetal. Stoichiometric and catalytic studies evidenced that species $[Ir(CF_3COO\text{-}B(C_6F_5)_3)(\kappa^2\text{-}NSi^{Me})_2]$ (**3**), $[Ir(\kappa^2\text{-}NSi^{Me})_2][HB(C_6F_5)_3]$ (**4**), and $[Ir(HCOO\text{-}B(C_6F_5)_3)(\kappa^2\text{-}NSi^{Me})_2]$ (**5**) are intermediates of the catalytic process. The structure of **3** has been determined by X-ray diffraction methods. Theoretical calculations show that the rate-limiting step for the **1**/$B(C_6F_5)_3$-catalyzed hydrosilylation of CO_2 to bis(silyl)acetal is a boron-promoted Si−H bond cleavage via an iridium silylacetal borane adduct.

The potential of CO_2 as a renewable and cheap C1 carbon source has received increasing attention over recent years.[1] The major difficulties to achieve this goal are the kinetic and thermodynamic stability of CO_2, which hampers most of its chemical transformations. In this regard, catalysis has proven to be an essential tool for transforming CO_2 into value-added chemicals. Although great advances have been made in the field of the catalytic transformation of CO_2, there are still many challenges to overcome for its utilization as a raw material on an industrial scale.[2,3]

Formic acid, formaldehyde, methanol, and methane are C1 chemicals that can be obtained from the reduction of CO_2. In this work, we focus on formaldehyde, which is obtained industrially by the partial oxidation of methanol and has an annual demand of 30 million tons.[4] The catalytic hydrogenation of CO_2 to formaldehyde has been scarcely reported.[5] However, several examples of the catalytic reduction of CO_2 to the formaldehyde level with hydrosilanes[6−14] or hydroboranes[15] have been reported. Catalytic systems based on Zr,[6] Re,[7] Ru,[8] Co,[9] Ni,[10] Pd,[11] Pt,[11] Sc,[12] Mg,[13] and Zn[13] complexes and germylene-$B(C_6F_5)_3$ adducts[14] have proven to be effective for the selective reduction of CO_2 with hydrosilanes to the corresponding bis(silyl)acetal. It is noteworthy that all of these catalytic systems require the use of a Lewis acid, such as $B(C_6F_5)_3$, to selectively achieve the formation of the corresponding bis(silyl)acetal.[16] The selectivity of these processes depends on the metal/$B(C_6F_5)_3$ ratio. Thus, with an excess of borane, the formation of methane is facilitated.[6−14] Although the effectivity of $B(C_6F_5)_3$ as a hydrosilylation catalyst is well-known,[17] $B(C_6F_5)_3$ alone cannot catalyze the hydrosilylation of CO_2.[6a,18]

It has recently been proven that bis(silyl)acetal, $H_2C(OSiPh_3)_2$, provides a means to incorporate CH_n (n = 1 or 2) moieties into organic molecules.[19] Therefore, developing catalytic systems effective for the reduction of CO_2 to the bis(silyl)acetal level using hydrosilanes is of great interest.

To date, few studies have been reported on the mechanism of these processes. Indeed, the mechanistic discussion remains open. For example, two different mechanisms have been proposed for the bis(phosphino)borylnickel hydride/$B(C_6F_5)_3$-catalyzed reduction of CO_2 to the formaldehyde level with hydrosilanes. Thus, while Rodriguez et al. proposed a boron-promoted Si−H activation mechanism,[10a,b] Ke et al. proposed a nickel-promoted Si−H mechanism.[10c]

Understanding the mechanisms that operate in different transition-metal-catalyzed processes to reduce CO_2 with hydrosiloxanes is one of our aims.[20] We have recently reported that species $[Ir(CF_3CO_2)(\kappa^2\text{-}NSi^{Me})_2]$ [**1**; NSi^{Me} = (4-methylpyridin-2-yloxy)dimethylsilyl] catalyzes the selective reduction of CO_2 with $HSiMe(OSiMe_3)_2$ to the corresponding methoxysilane, $CH_3OSiMe(OSiMe_3)_2$, or silylformate, $HCO_2SiMe(OSiMe_3)_2$, under mild reaction conditions. The selectivity of this catalytic system can be easily tuned by controlling the pressure of CO_2.[21] It is noteworthy that the two active positions of the catalytic systems based on **1** are trans located to two silyl groups; in addition, the Ir−Si bond in such species is stronger than would be expected for a traditional Ir−silyl bond.[22] Hence, the positions trans to the Ir−Si bonds in $Ir(\kappa^2\text{-}NSi^{Me})_2$ complexes are highly activated.

We now report that using **1** as a catalyst precursor in the presence of catalytic amounts of $B(C_6F_5)_3$ allow achievement of the selective formation of bis(silyl)acetals by the reaction of CO_2 with hydrosilanes (Scheme 1).

^1H NMR studies of the **1**/$B(C_6F_5)_3$ (1:1 ratio; 1.0 mol %)-catalyzed reaction of CO_2 (1 bar) with $HSiMe(OSiMe_3)_2$

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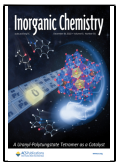

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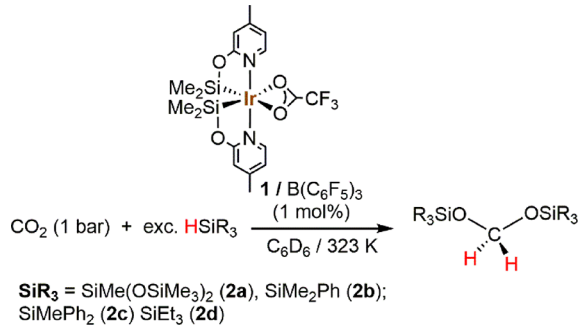
Scheme 1. 1-Catalyzed (1.0 mol %) Reactions of CO_2 with Tertiary Silanes in the Presence of $B(C_6F_5)_3$ (1.0 mol %)



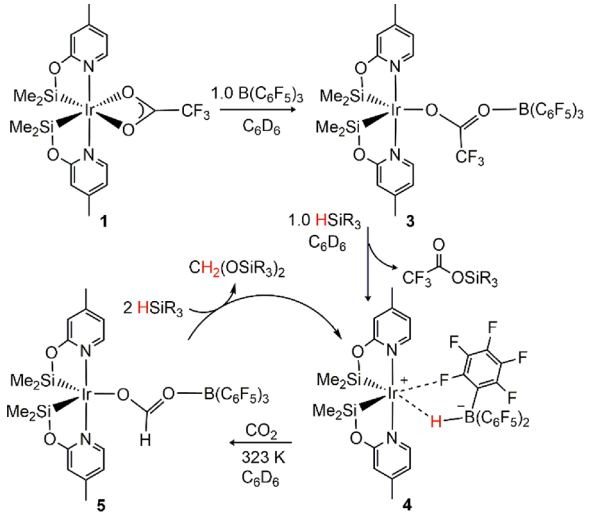
(HMTS) in C_6D_6 at 323 K show the slow and selective formation of $H_2C\{OSiMe(OSiMe_3)_2\}_2$ (**2a**; Table 1, entry 1). To explore the scope of this catalytic process, we performed the reaction of CO_2 with different silicon hydrides ($HSiMe_2Ph$, $HSiMePh_2$, $HSiEt_3$, and $HSiMe(OSiMe_3)_2$) in the presence of $\mathbf{1}/B(C_6F_5)_3$ (1:1) in C_6D_6. The best reaction conditions were found to be CO_2 (1 bar) and 323 K. The reactions are highly selective to the formation of the corresponding bis(silyl)acetal (Table 1, entries 1, 2, 4, and 5). The nature of silane influences the reaction performance. The best reaction rates were obtained using $HSiMe_2Ph$ and $HSiMePh_2$ (Table 1). The reactions with HMTS and $HSiEt_3$ were slower, which can be attributable to the higher hindrance of the Si−H bond in such compounds.

^{1}H NMR studies of the $\mathbf{1}/B(C_6F_5)_3$ (1:1; 1.0 mol %)-catalyzed reaction of CO_2 with $HSiMe_2Ph$ in C_6D_6 at 323 K demonstrate the influence of CO_2 pressure on the reaction performance; at 3 bar, the reactions are faster but less selective than those at at 1 bar (Table 1, entries 2 and 6). The stoichiometry of borane is a key factor in the selectivity of these catalytic processes. Within the range of 1−3 bar of CO_2, if the load of $B(C_6F_5)_3$ is increased from 1.0 to 2.0 mol %, the reactions are selective toward the formation of methane[23] and $O(SiMe_2Ph)_2$, albeit at a lower rate (Table 1, entry 7). While reducing the amount of $B(C_6F_5)_3$ to 0.5 mol % does not alter the activity, the selectivity is affected, resulting in the formation of silylformate (82%) and bis(silyl)acetal (18%) as secondary products (Table 1, entry 8). In the absence of additives, the catalyst precursor **1** promotes the reduction of CO_2 (1 bar) with $HSiMe_2Ph$ to give silylformate (90%) as major reaction product (Table 1, entry 9).

^{1}H NMR studies of the **1**-catalyzed (1.0 mol %) reaction of CO_2 (1 bar) with $HSiMe_2Ph$ in the presence of BPh_3 (1.0 mol %), instead of $B(C_6F_5)_3$, show a slower and less selective reaction. After 24 h, a 73% conversion of hydrosilane is reached to give a mixture of the corresponding silylformate (81%), bis(silyl)acetal (12%), and methoxysilane (7%) (Table 1, entry 3). Therefore, BPh_3 plays a role in the activity and selectivity of the process, although to a lesser degree than $B(C_6F_5)_3$, which can be correlated to its lower Lewis acidic character.[24]

^{1}H NMR studies of the reaction of **1** with $B(C_6F_5)_3$ evidenced the quantitative formation of $[Ir(CF_3COO\text{-}B(C_6F_5)_3)(\kappa^2\text{-}NSi^{Me}_2)_2]$ [**3** (CCDC 2218258); Scheme 2].

Scheme 2. NMR Monitoring of the Stepwise Stoichiometric Reaction



Contrarily, no reaction is observed between **1** and BPh_3 under the same conditions. The molecular structure of **3** has been confirmed by X-ray diffraction studies (Figure S38). The

Table 1. Results from the 1 (1.0 mol %)- and BR_3-Catalyzed Reaction of CO_2 with Hydrosilanes in C_6D_6 at 323 K

							ratio of the reaction products			
entry	silane	borane	equiv of BR_3	CO_2 (bar)	time (h)	conversion (%)[a]	OCHO (%)[b]	OCH_2O (%)[b]	CH_3O (%)[b]	CH_4 (%)
1	HMTS	$B(C_6F_5)_3$	1	1	16	28		>99	<1	
					40	74		>99	<1	
2	$HSiMe_2Ph$	$B(C_6F_5)_3$	1	1	16	93		>99	<1	
					40	>99		>99		
3	$HSiMe_2Ph$	BPh_3	1	1	24	73	81	12	7	
4	$HSiMePh_2$	$B(C_6F_5)_3$	1	1	16	78		>99	<1	
					40	>99		>99	<1	
5	$HSiEt_3$	$B(C_6F_5)_3$	1	1	16	12		>99	<1	
					40	25		>99	<1	
6	$HSiMe_2Ph$	$B(C_6F_5)_3$	1	3	8	>99	83	13	4	
7	$HSiMe_2Ph$	$B(C_6F_5)_3$	2	1	24	48				>99[c]
8	$HSiMe_2Ph$	$B(C_6F_5)_3$	0.5	1	24	93	82	18		
9	$HSiMe_2Ph$			1	24	50	90	2	8	

[a]Conversion and selectivity percentages are based on ^{1}H NMR integration using hexamethylbenzene (0.0525 mmol) as an internal standard. [b]Composition of the mixture of products. [c]On the basis of the ^{1}H NMR integral of $O(SiMe_2Ph)_2$, 12% CH_4 was formed.

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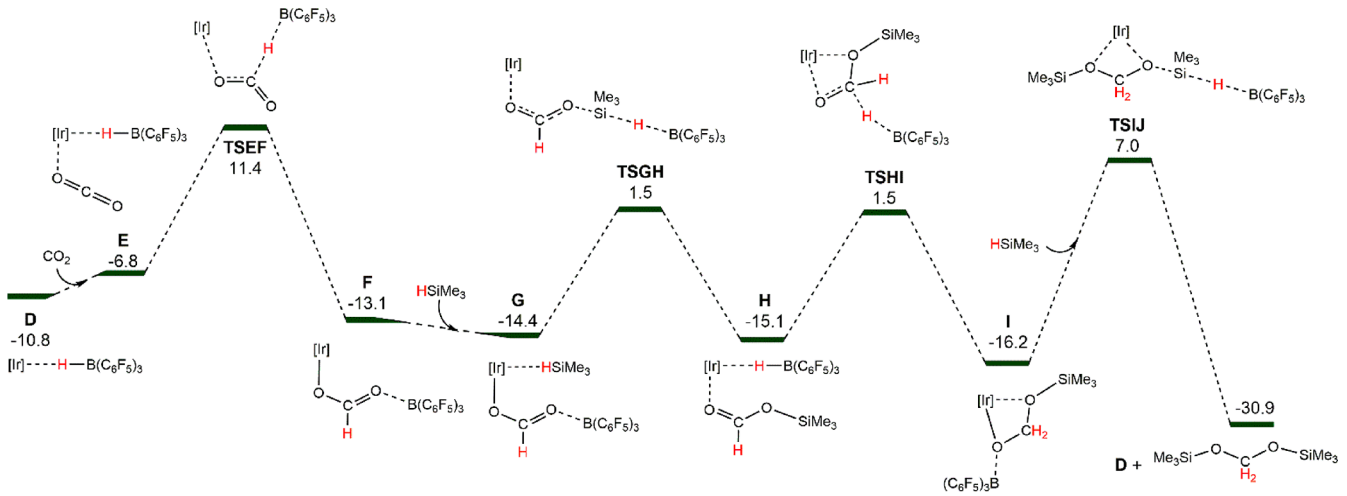

Figure 1. DFT-calculated Gibbs free energy profile for the catalytic formation of bis(silyl)acetal from **E** (kcal mol^{-1}) relative to **A**.

geometrical parameters of the [Ir(κ^2-NSi^{Me})$_2$] fragment (see the Supporting Information, SI) agree with those of **1**, with short Ir−Si bond lengths [2.2526(11) and 2.2599(11) Å]. The Ir−O bond length in **3** [2.285(3) Å] is shorter than those found in **1** [2.363(3) and 2.418(3) Å].[22a]

The ^{11}B{^{1}H} NMR spectra of **3** show a singlet at δ = −1.7 ppm (Figure S18), in agreement with what is expected for the O−B(C$_6$F$_5$)$_3$ fragment[25] (Scheme 2). The absolute value of the difference between δ_{para} and δ_{meta} of the fluorine atoms $\Delta(\delta_{m,p})$ in the ^{19}F NMR spectra of **3** is 6.3 ppm (Figure S21), which agrees with the presence of a tetracoordinated borate anion.[26,27]

The addition of 1 equiv of HSiMe(OSiMe$_3$)$_2$, at room temperature (RT), to C$_6$D$_6$ solutions of **3** gives [Ir(κ^2-NSi^{Me})$_2$][HB(C$_6$F$_5$)$_3$] (**4**) and CF$_3$CO$_2$SiR$_3$. The ^{11}B NMR spectra of **4** show a doublet resonance at δ = −15.1 ppm ($^1J_{B-H}$ = 53 Hz),[12b,15a] which in the ^{11}B{^{1}H} NMR spectra appears as a singlet (Figures S24 and S25). Moreover, the ^{19}F NMR spectra show a $\Delta(\delta_{m,p})$ value of ∼6 ppm, which is higher than the characteristic values found for noncoordinating [HB(C$_6$F$_5$)$_3$]$^-$ anions [$\Delta(\delta_{m,p})$ < 3 ppm], which indicates a certain degree of coordination of the [HB(C$_6$F$_5$)$_3$]$^-$ anion to the metallic center.[17b]

The addition of an excess of HSiMe(OSiMe$_3$)$_2$ to C$_6$D$_6$ solutions of **3** produces **4** and CF$_3$CH{OSiMe(OSiMe$_3$)$_2$}$_2$. Note that the overreduced product CF$_3$CH$_2$OSiMe(OSiMe$_3$)$_2$ is not obtained, which is reminiscent of the **1**/B(C$_6$F$_5$)$_3$ system selectivity toward the bis(silyl)acetal species. This evidences the effective entrapment of B(C$_6$F$_5$)$_3$ in the form of a hydridoborate ion pair because the free borane might promote activation of the Si−H bond toward reduction of the bis(silyl)acetal derivatives, as well as the direct participation of **4** in the catalytic reaction, because **4** not only promotes hydrosilylation of the TFA ligand or CO$_2$ but also catalyzes reduction of the R′COOSiR$_3$ species (R′ = H, CF$_3$).

The ^{1}H NMR spectra of **4** in C$_6$D$_6$ show no changes when pressurized with CO$_2$ (3 bar) at RT. However, after the reaction mixture is heated at 323 K, the formation of complex [Ir(HCOOB(C$_6$F$_5$)$_3$)(κ^2-NSi^{Me})$_2$] (**5**) is observed. The presence of a IrOC(H)OB(C$_6$F$_5$)$_3$ moiety in **5** has been demonstrated by means of ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectroscopies (Figures S32−S36). The addition of 2 equiv of HSiMe(OSiMe$_3$)$_2$ to a solution of **5**, in the absence of CO$_2$, produces the formation of **2a** and the regeneration of **4** within 1 h at RT (Scheme 2). Exposure of **5** to ^{13}CO$_2$ (2.7 bar) at 353 K for 48 h did not result in the partial substitution of [Ir]OC(H)OB(C$_6$F$_5$)$_3$ to the ^{13}C-enriched [Ir]O^{13}C(H)OB(C$_6$F$_5$)$_3$, which suggests that, different from that reported for analogous MOC(H)OB(C$_6$F$_5$)$_3$ (M = Re,[8] Ni,[10] Pd,[11] Pt[11]) species, the CO$_2$ insertion step to give **5** is irreversible under the catalytic conditions.

Density functional theory (DFT) studies at the M06L(SMD)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP level have been performed to study in detail the reaction mechanism of CO$_2$ hydrosilylation catalyzed by **3** (see the SI). HSiMe$_3$ has been selected as a model system for the silanes. The Gibbs free energy energetic profile for the catalyst activation process, from **3** (**A**) to **4** (**D**) (Figure S39), is exoergic by 10.8 kcal mol^{-1}. Si−H bond activation occurs via boron-promoted Si−H cleavage **TSBC** (9.0 kcal mol^{-1}), which corresponds to a linear S$_N$2 nucleophilic attack of the terminal oxygen of the trifluoroacetate ligand to the silicon atom in which the leaving hydride is transferred to the boron moiety. A similar type of activation mechanism has been proposed for Lewis acid PBP−Ni hydrosilylation of CO$_2$ based on DFT calculations.[10b] An alternative mechanism for the Si−H activation step based on a nickel-promoted Si−H cleavage has been proposed.[10c] In our case, the iridium-promoted Si−H cleavage is energetically disfavored (see Figures S40 and S41 for a comparison of both pathways). Intermediate **D** can be described as a hydroborate moiety and a cationic metallic complex rather than a metal hydride interacting with the Lewis acid. Inspection of the natural bond orbitals reveals a σ(B−H) bonding orbital with an electron population of 1.76 electrons (Figure S42).

The coordination of CO$_2$ to **D** leads to the beginning of the catalytic cycle. The Gibbs free energy profile for this process is reported in Figure 1. The first step corresponds to hydride transfer from HB(C$_6$F$_5$)$_3$ to CO$_2$ via **TSEF** at an energy barrier of 22.2 kcal mol^{-1} from intermediate **D**. The obtained intermediate **F** is thermodynamically favored (−13.1 kcal mol^{-1}) and corresponds to complex **5** experimentally detected by NMR. Following that, the addition of silane leads to σ^1-*H*-(HSiMe$_3$) coordination to **F**, yielding **G**. Then, activation of the Si−H bond takes place via **TSGH**, like the previously reported **TSBC**, consisting of the linear S$_N$2 nucleophilic attack of the terminal oxygen atom of the formate to the silicon atom

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and transfer of the leaving hydride to the boron atom of the Lewis acid. The activation barrier of **TSGH** is 15.9 kcal mol^{-1}, leading to intermediate **H**. The subsequent hydride transfer from the hydroborate to the carbon atom of the silylformate coordinated to the metal takes place through **TSHI**, yielding intermediate **I**. Upon reaction with another molecule of $HSiMe_3$, the silylformate develops into the final bis(silyl)acetal product via **TSIJ**, with the activation energy for this step being 23.2 kcal mol^{-1}. This activation barrier for the boron-promoted Si−H bond cleavage is higher than those of the previously related processes, **TSBC** (9.0 kcal mol^{-1}) and **TSGH** (15.9 kcal mol^{-1}). It should be noted that, for **TSIJ**, the nucleophilic attack to the silane is performed by an alkoxy group,[10,17c,28] in contrast with previous steps, where the nucleophilic attack was performed by trifluoroacetate and formate groups.

The catalytic process is strongly exergonic (−30.9 kcal mol^{-1}), and the rate-limiting step is boron-promoted Si−H cleavage by the iridium silylacetal borane adduct **I** (23.2 kcal mol^{-1}) characterized by **TSIJ**. This activation barrier agrees with the experimental finding that the reaction proceeds slowly at RT. Indeed, the reaction of **4** with CO_2 (3 bar) to give **5** requires heating at 323 K. It should be noted that the intermediates proposed in the DFT-calculated catalytic cycle match the experimentally detected species (**4** and **5**; Scheme 2).

In conclusion, this is the first example of an iridium-based catalytic system effective for the selective reduction of CO_2 to the formaldehyde level with hydrosilanes. The selectivity of this catalytic system to the formation of bis(silyl)acetals is determined by the interaction between the active species and the Lewis acid $B(C_5F_6)_3$. In fact, any factor that affects that interaction influences the selectivity of the process. Thus, using a borane with a lower Lewis acidity such as BPh_3, high temperature, or CO_2 pressure higher than 1.0 bar inhibit the selectivity toward the bis(silyl)acetal. DFT calculations support a boron-promoted Si−H cleavage mechanism, with the rate-limiting step being boron-promoted Si−H cleavage by the iridium silylacetal borane adduct **I**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c03330.

Experimental details, NMR spectra, crystallographic, and theoretical calculation data (PDF)

Accession Codes

CCDC 2218258 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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J.G., M.P., and F.J.F.-A., experimental studies; P.G.-O., X-ray diffraction; A.U. and V.P., theoretical calculations.

Notes

The authors declare no competing financial interest.

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