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Authors: Marc Devillard, Bas de Bruin, Maxime Siegler, and Jarl Ivar van der Vlugt

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## **Transition Metal-Free Cleavage of CO**

Marc Devillard,<sup>[a]</sup> Bas de Bruin,<sup>[a]</sup> Maxime A. Siegler,<sup>[b]</sup> and J. I. van der Vlugt\*<sup>[a]</sup>

Abstract: Tertiary silane 1<sup>H</sup>. 2-((diphenylsilyl)methyl)-6methylpyridine, reacts with tris(pentafluorophenyl)borane (BCF) to form the intramolecular pyridine-stabilized silylium 1+HBCF. The corresponding 2-((diphenylsilyl)methyl)-pyridine, lacking the methylgroup on the pyridine ring, forms classic N(py) $\rightarrow$ B adduct 2<sup>H</sup>-BCF featuring an intact silane Si-H fragment. Complex 1\*-HBCF promotes cleavage of the C=O triple bond in carbon monoxide with double C-C<sub>sp2</sub> bond formation, leading to complex 3 featuring a B-(diarylmethyl)-B-aryl-boryloxysilane fragment. Reaction with pinacol generates bis(pentafluorophenyl)methane 4 as isolable product, proving the transition metal-free deoxygenation of carbon monoxide by this main-group system. Experimental data and DFT calculations support the existence of an equilibrium between the silyliumhydroborate ion pair and the silane-borane mixture that is responsible for the observed reactivity.

The coordination chemistry and subsequent reactivity of carbon monoxide with transition metal complexes is well-developed and forms the platform for current-day applications of CO as  $C_1$ building block, including large-scale industrial processes (e.g. acetic acid production, hydroformylation).<sup>[1]</sup> However, the C-O linkage is typically preserved in these applications. This is in stark contrast to heterogeneous Fischer-Tropsch catalysis, where CO (with  $H_2$ ) is utilized as a true  $C_1$  building block to make new C-C bonds concomitant with full deoxygenation of CO.<sup>[2]</sup> Valorization of carbon dioxide is currently attracting much attention.<sup>[3]</sup> Partial deoxygenation strategies to convert carbon dioxide with main group elements (e.g. hydrosilylation, hydroboration) are investigated.<sup>[4]</sup> Since the pioneering work of Brown on the carbonylation of alkylboranes,<sup>[5]</sup> the transition metal-free chemistry of carbon monoxide with main group compounds is also rapidly developing. To generate stable or observable adducts of CO, mainly boron-based compounds<sup>[6]</sup> and diaminocarbenes are utilized,<sup>[7]</sup> but only a handful of compounds have proven capable of activating CO to the extent that new C-X bonds (X = O, N, C, H) can be formed. Insertion of CO in the B-B single bond of azaboriridines,<sup>[8a,b]</sup> or the M-C bond of alanes<sup>[8c,d]</sup> and gallanes<sup>[8e]</sup> is known, and reductive coupling of CO has recently been achieved.<sup>[9]</sup> However, transition metal-free full deoxygenation of CO is elusive.

Well-defined homogeneous transition metal complexes that are capable of CO triple bond scission normally require highly reactive co-reagents and/or strongly reducing conditions in order to enforce (stepwise) C-O cleavage.<sup>[10]</sup> Recently, a mononuclear

[b] Dr. M. A. Siegler

Small Molecule X-ray Crystallography, John Hopkins University 3400 N Charles St, Baltimore MD, 21218 USA

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Mo platform was shown to generate  $C_2O_1$  species by stoichiometric CO triple bond scission combined with C-C bond formation, aided by the use of silyl chlorides as co-reagents, which inadvertedly generates siloxanes as by-product.<sup>[11]</sup>



**Scheme 1.** Top: Rare example of CO activation using main-group (FLP) systems, including C-H and single  $C-C_{sp2}$  bond formation, respectively. Bottom: Unique CO triple bond activation of intramolecularly stabilized silylium hydroborate system with double  $C-C_{sp2}$  bond formation.

Combinations of an electrophilic borane and a phosphine-based donor, examples of FLPs (Frustrated Lewis Pairs),<sup>[12]</sup> have been used to activate CO. The group of Erker described the trapping of the CO adduct of Piers borane<sup>[13]</sup> (OC $\rightarrow$ B(H)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>) with intramolecular phosphine-borane FLP systems, generating a new C-H bond (Scheme 1, top).[14] Stephan and co-workers reported that a 2:1 mixture of tris(pentafluorophenyl)borane  $(B(C_6F_5)_3 = BCF)$  and  $P(tBu)_3$  leads to the complete splitting of CO (from syngas), via a boron formyl intermediate, to afford A featuring one new C-C<sub>sp2</sub> bond, together with cyclic product B (Scheme 1,middle).<sup>[15]</sup> This report represents the only previous example of main-group element promoted C-C<sub>sp2</sub> bond formation from CO, to the best of our knowledge. No mechanistic information is available to shed light on the formation to A. Also, more extensive CO functionalization (i.e. additional C-C bond formation) would be very interesting.

Inspired by these recent advances and realizing (i) the ability of triphenylboron hydrides to activate  $CO_2$  and carbonyl groups owing to the reactive B-H bond,<sup>[16]</sup> and (ii) the well-known ability of mixtures of silanes and  $B(C_6F_5)_3$  to promote hydrosilylation reactions of unsaturated substrates via formation of silyl cations,<sup>[17],[18]</sup> we sought to develop a reactive Si---B system that would be susceptible to CO activation (Scheme 1, bottom).

<sup>[</sup>a] Dr. M. Devillard, Prof.Dr. B. de Bruin, Dr.Ir. J.I. van der Vlugt van 't Hoff Institute for Molecular Sciences, University of Amsterdam Science Park 904, 1098 XH Amsterdam, the Netherlands E-mail: j.i.vandervlugt@uva.nl

While the chemistry and catalysis with electrophilic silylium species is rapidly gaining attention,<sup>[19]</sup> examples of frustrated Lewis pair-type chemistry involving silicon are relatively rare.<sup>[20]</sup>

To address both challenges, we herein report a strategy to stabilize a silylium species with a weak donor such as pyridine.<sup>[21]</sup> whilst retaining the inherent reactivity of the Si center. This strategy has enabled transition metal-free rupture of the triple bond in carbon monoxide and subsequent *double*  $C-C_{sp2}$  bond formation by  $C_6F_5$  transfer using a simple and novel pyridine-stabilized silylium hydroborate system. Through a combination of experimental data and supported by DFT calculations, the role of each component in this hitherto unknown reaction sequence is detailed.

Synthesis of 2-((diphenylsilyl)methyl)-6-methylpyridine **1**<sup>H</sup> from lutidine is straightforward (Scheme 2). The Si-H hydrogen resonates at  $\delta$  5.01 in the <sup>1</sup>H NMR spectrum (<sup>1</sup>*J*<sub>SiH</sub> = 199.9 Hz). The hydrogen atoms of the methylene bridgehead (–CH<sub>2</sub>–) group appear as a doublet at  $\delta$  2.91 through coupling with the Si-H hydrogen (<sup>3</sup>*J*<sub>HH</sub> = 3.7 Hz). The corresponding <sup>29</sup>Si{<sup>1</sup>H} NMR signal appears as a singlet at  $\delta$  -14.6. The analogous species **2**<sup>H</sup> (2-((diphenylsilyl)methyl)pyridine) was also prepared in this way.



**Scheme 2.** Synthesis of 1<sup>H</sup> and 2<sup>H</sup> and reaction with  $B(C_6F_5)_3$  to pyridine-stabilized silylium 1<sup>+</sup>-HBCF and pyridine-borane adduct 2<sup>H</sup>-BCF, respectively.

Upon addition of an equimolar amount of tris(pentafluorophenyl)borane (BCF) to a solution of 2<sup>H</sup>, selective formation of species  $2^{H}$ -BCF, featuring a direct N $\rightarrow$ B adduct, is observed with an intact hydrosilane unit, according to <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy (Scheme 2). The <sup>19</sup>F NMR spectrum shows 15 different resonance signals due to hindered rotation around the N-B and B-C linkages, resulting in low overall symmetry. Single crystal X-ray diffraction analysis confirms the molecular structure of species 2 (Figure 1). The analogous reaction between BCF and 1<sup>H</sup> in CD<sub>2</sub>Cl<sub>2</sub> at room temperature immediately generates a new singlet at  $\delta$  23.2 in the HSQC <sup>29</sup>Si-<sup>1</sup>H NMR spectrum, correlating with a broad singlet at  $\delta$  -25.5 in the <sup>11</sup>B NMR spectrum. In the corresponding <sup>1</sup>H NMR spectrum, the  $-CH_2$ - hydrogens appear as a singlet at  $\delta$  3.43, indicating complete Si-H cleavage. In the <sup>1</sup>H{<sup>11</sup>B} NMR spectrum, the formation of the hydroborate H-B(C6F5)3 is evidenced by a broad singlet at  $\delta$  3.57 that nearly disappears in the baseline in the <sup>11</sup>B-coupled spectrum. Furthermore, the para-pyridine Hatom is strongly shifted downfield upon hydride abstraction,

which suggests an intramolecular  $N{\rightarrow}Si$  donor-acceptor interaction in the product.  $^{[22]}$ 



Figure 1. Displacement ellipsoid plot (50% probability level) of 2<sup>H</sup>-BCF. Hydrogen atoms are omitted for clarity, except those on C1 and Si1. Selected bond lengths (Å): N1-B1 1.6547(35); C1-Si1 1.8983(28); Si1-H1 1.366(26).

Abstraction of the hydride to generate cationic pyridine-stabilized silylium fragment **1<sup>+</sup>-HBCF** (Scheme 2) was further ascertained by high resolution mass spectrometry (HR-MS; see ESI). To the best of our knowledge, only one other example of a pyridine-stabilized silylium derivative has been described to date (featuring a 5-membered ring), whereas **1<sup>+</sup>-HBCF** features an N→Si stabilization within a 4-membered ring.<sup>[23]</sup> Apparently, introduction of a methyl group *ortho* to the pyridine nitrogen fully suppresses the  $py \rightarrow B(C_6F_5)_3$  adduct in favor of formation of the  $[N\rightarrow Si]^+$  hydroborate Lewis pair. This species can be considered isoelectronic with previously described pyridine-stabilized organoboranes.<sup>[24]</sup> Silylium salt **1<sup>+</sup>-HBCF** is isolated as an oil, preventing structure elucidation by single crystal X-ray crystallography.



Scheme 3. Reaction of 1\*-HBCF with CO to generate 3 and follow-up hydrolysis with pinacol to release bis(pentafluorophenyl)methane.

Upon pressurizing a solution of **1<sup>+</sup>-HBCF** in CD<sub>2</sub>Cl<sub>2</sub> with 5 bar of CO for two hours at 50 °C, a single new resonance at  $\delta$  -8.6 is observed in the <sup>29</sup>Si DEPT NMR spectrum, revealing a reaction to a new species **3** featuring a saturated tetracoordinated silicon (Scheme 3). High resolution mass spectrometry reveals the incorporation of one molecule of CO or <sup>13</sup>CO, respectively. A new signal is observed at  $\delta$  2.3 in the <sup>11</sup>B NMR spectrum, while a new singlet integrating for one hydrogen atom is observed at  $\delta$  4.75 in the <sup>1</sup>H NMR spectrum. This signal becomes a doublet (<sup>1</sup>J<sub>CH</sub> = 116.8 Hz) when the same reaction is performed with <sup>13</sup>C-labeled CO, supporting the formation of a direct C-H bond, with the hydrogen atom most likely stemming from the silane. In agreement with this observation, the proton-coupled <sup>13</sup>C NMR

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spectrum of the labeled compound displays a doublet ( ${}^{1}J_{CH}$  = 116.8 Hz) at  $\delta$  25.9. In the  ${}^{13}C{}^{1}H{}$  NMR spectrum, this signal is very broad (full-width at half-maximum = 20.3 Hz) and nearly disappears in the baseline in the non-labeled product, which suggests a direct scalar coupling with the  ${}^{11}B$  nucleus. The  ${}^{19}F{}$  NMR spectrum displays two sets of signals with an integration ratio of 2:1, suggestive of (double)  $C_6F_5$  transfer from boron to the boron-bound carbon atom.

Based on multinuclear NMR spectroscopy and literature data on related organoboron compounds,<sup>[25]</sup> we conclude that **3** contains a  $(C_6F_5)B-C(H)(C_6F_5)_2$  fragment as well as a siloxyborate linkage. DFT calculated and benchmarked NMR chemical shifts support the presence of a four-coordinated B-nucleus with an additional pyridine—boron interaction, as in **3** (Scheme 3 and ESI). It can be noted that the hydrogens of the methylene bridge in **3** do not display a diastereotopic effect (low temperature <sup>1</sup>H NMR shows only broadening of the CH<sub>2</sub> resonance at -70 °C). This suggests that **3** is probably in equilibrium with its open form **3'** featuring a three-coordinated B-nucleus, as supported by DFT calculations (see ESI for details).<sup>[26]</sup>

As a result, the C=O triple bond in carbon monoxide is completely cleaved, with the formation of one new C-H and two new C-C bonds. Although complex **3** proved high air-sensitive and the oily nature of **3** prohibited direct elucidation of the structure by single crystal X-ray crystallography, a crystallization attempt at -20 °C furnished crystals of moderate quality of the oxidized derivative **30**, which confirms the proposed connectivity with a six-membered ~C-Si-O-B-N-C~ linkage (see ESI).<sup>[27]</sup>

Liberation of the organic  $C(H)(C_6F_5)_2$  fragment from 3 was achieved via alcoholysis with an equimolar amount of pinacol in dichloromethane (Scheme 3). Gratifyingly, this results in clean formation and isolation of bis(pentafluorophenyl)methane 4 (as well as the <sup>13</sup>C-labeled derivative, available from <sup>13</sup>CO) in 83% yield, confirming the generation of two new C-C(sp<sup>2</sup>) bonds from CO in 3. Compound 4 is fully characterized by multinuclear NMR spectroscopy, high resolution mass spectrometry, micro-analysis and single crystal X-ray diffraction (see ESI for details). The skeletal composition and protocol for formation and reactivity of 3 is unique, to the best of our knowledge, as it represents the first example of double C-Csp<sup>2</sup> bond formation from C-O cleavage by CO activation promoted by a main-group derivative. To get additional insights in the reaction mechanism and the requirement for silylium species 1<sup>+</sup>-HBCF as reagent, several control experiments were carried out. Firstly, 1<sup>+</sup>-BAr<sup>F</sup><sub>4</sub>, the tetrakis(pentafluorophenyl)borate analogue of 1<sup>+</sup>-HBCF, lacking a hydridic B-H fragment, was prepared by the reaction of 1<sup>H</sup> and (CPh<sub>3</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> in 76% yield and characterized by multinuclear NMR spectroscopy and HR-MS analysis (see ESI for details). This compound is completely unreactive toward CO, which suggests that a borohydride moiety is necessary for carbon monoxide activation to occur (Scheme 4, a). Furthermore, the lithium hydroborate salt LiBH( $C_6F_5$ )<sub>3</sub> also gives no reaction under the same reaction conditions, thus showing that the pyridinesilylium fragment is also crucial for the reaction to proceed.





**Scheme 4.** a) Control experiments to highlight the need for silicon, pyridine and hydroborate in Lewis pair 1\*-**HBCF** to cleave CO. b) Reaction with isocyanide to give **5**, demonstrating equilibrium between 1\*-**HBCF** and 1<sup>H</sup>+**BCF**. c) proposed hydride transfer from 1<sup>H</sup> to  $OC \rightarrow B(C_6F_5)_3$ .

Next, we attempted to translate the observed reactivity with CO to the electronically related isocyanide moiety. Surprisingly, reaction of 1<sup>+</sup>-HBCF with tert-butylisocyanide at r.t. led to complete regeneration of the silane Si-H bond, as supported by <sup>1</sup>H NMR spectroscopy, concomitant with formation of the  $tBuNC \rightarrow B(C_6F_5)_3$  adduct 5 (Scheme 4, b). This observation suggests that 1<sup>+</sup>-HBCF is also in equilibrium with the silane and the carbonyl adduct  $OC \rightarrow B(C_6F_5)_3^{[28]}$  under CO pressure and that intact 1<sup>H</sup> rather than the silvlium derivative is responsible for the observed reactivity. At this stage we hypothesized that the reaction could be initiated by a hydride transfer from the silane to the activated CO carbon of the boron-adduct (Scheme 4, c). The hydridicity of the silane would be enhanced through intramolecular stabilization of the corresponding silylium fragment by the nearby pyridine group. In agreement with this proposed equilibrium between 1<sup>+</sup>-HBCF and 1<sup>H</sup>, a mixture of methyldiphenylsilane (HSiMePh<sub>2</sub>), lacking the internal stabilizing pyridine ring, and  $B(C_6F_5)_3$  do not react with CO.

To provide a qualitative picture of the plausible mechanism of CO triple bond rupture and formation of 3. featuring the highly unsual six-membered B-(diarylmethyl)-B-aryl-boryloxysilane system, we performed DFT calculations (BP86, def2-TZVP, disp3, m4 grid). The complete pathway from 1<sup>H</sup> to 3 is displayed in Figure 2. The separated Lewis acid-base pair (1<sup>H</sup> + BCF: set at 0 kcal mol<sup>-1</sup> with free CO; starting point) and 1<sup>+</sup>-HBCF (+2.6 kcal mol<sup>-1</sup>) are likely in equilibrium under the experimental reaction conditions. Activation of CO to give A most likely proceeds via the separated Lewis acid-base pair. The entropy penalty associated with formation of a van der Waals adduct of OC-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and  $1^{H}$  is largely compensated by relatively strong  $\pi$ - $\pi$  stacking interactions. This pre-organization facilitates hydride transfer, via a low TS1 barrier of +4.5 kcal mol<sup>-1</sup> relative to 1<sup>H</sup> + BCF, to form zwitterionic silvlium-formylborate species B (the ion-separated conformer **B**' is 2.4 kcal·mol<sup>-1</sup> higher than **B**). Intermediate C (-11.8 kcal·mol<sup>-1</sup>), is formed upon interaction of the silyl cation with the oxygen atom of the formyl group. Subsequent facile transfer of a C<sub>6</sub>F<sub>5</sub>-group from boron to carbon via transition state TS2 (+5.6 kcal mol<sup>-1</sup> relative to 1<sup>H</sup> + BCF) generates the open form of the neutral boranylmethoxysilane derivative **D** (-19.6 kcal·mol<sup>-1</sup>).<sup>[29]</sup> The boraepoxide conformer **D**' (+0.8 kcal·mol<sup>-1</sup> relative to  $\mathbf{D}$ ) undergoes a 1,2-oxo-shift via **TS3** (+11.9 kcal·mol<sup>-1</sup> compared to **D**') to form the open zwitterionic

 $\lambda^4$ -boranyloxysilane **E** with a formal cationic carbon fragment (-9.6 kcal·mol<sup>-1</sup>). Interestingly, boraepoxides have been proposed as intermediates in alkyl transfer from boron to carbon.<sup>[30]</sup> This reactive species **E** can undergo direct transfer of a second C<sub>6</sub>F<sub>5</sub>group from boron to form **G** over transition state **TS4** (+1.9 kcal mol<sup>-1</sup> relative to **E**). Alternatively, formation of the closed zwitterionic pyridinium intermediate **F** (-26.3 kcal mol<sup>-1</sup> relative to **E**) followed by transfer of a second C<sub>6</sub>F<sub>5</sub>-group from boron would form the open form **3'** over transition state **TS5**. Given the strong driving force for formation of intermediate **F**, this path is deemed most probable, with the barrier to **TS5** (+20.8 kcal mol<sup>-1</sup>) representing the rate-limiting step of the reaction. The closed from **3**, featuring an additional N<sub>Py</sub>→B interaction, is only 5.4 kcal mol<sup>-1</sup> uphill relative to **3'**. transition metal-free deoxygenation of CO. This study shows that pyridine-appended silanes in combination with B-based Lewis acids may provide suitable platforms to deoxygenate CO and to form new C-C bonds. Follow-up research on the scope of Lewis acids available for this TM-free transformation is ongoing.

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Figure 2. DFT calculated (BP86, def2-TZVP, disp3, m4 grid) pathway for the conversion of  $1^{H}+BCF$  to 3. For details, see also the Supporting Information.

In summary, we have prepared silvlium species  $1^+$ -HBCF using the pyridine-appended tertiary silane  $1^H$  and Lewis acid tris(pentafluorophenyl)borane. This FLP-like compound is able to induce full cleavage of the C=O triple bond to generate **3**. This sequence also results in the formation of one new C-H and two new C-C<sub>sp2</sub> bonds, as supported by multinuclear NMR spectroscopy and solid state characterization of the oxidized derivative. Alcoholysis of complex **3** with pinacol provides bis(pentafluorophenyl)methane as the organic C<sub>1</sub> product from Keywords: CO • silicon • small molecule activation • boron • C-C bond formation

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# COMMUNICATION

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Marc Devillard, Bas de Bruin, Maxime A. Siegler, and J. I. van der Vlugt \*

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Transition Metal-Free Cleavage of CO

The transition metal-free complete deoxygenation of CO is achieved using a combination of tertiary silane 1<sup>H</sup>, 2-((diphenylsilyI)methyl)-6-methylpyridine and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (BCF), which generates the intramolecular pyridine-stabilized silylium 1<sup>+</sup>-**HBCF**. In the process of CO activation, one new C-H and two new C-C<sub>sp2</sub> bonds are formed. Hydrolysis with pinacol gives H<sub>2</sub>C(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> as isolable product. DFT has provided insight in the plausible pathway for this remarkable transformation.



one new C-H and two new C-C(sp2) bonds after CO triple bond cleavage!!!

- [a] Dr. M. Devillard, Prof.Dr. B. de Bruin, Dr.Ir. J.I. van der Vlugt van 't Hoff Institute for Molecular Sciences, University of Amsterdam Science Park 904, 1098 XH Amsterdam, the Netherlands E-mail: j.i.vandervlugt@uva.nl
- [b] Dr. M. A. Siegler

Small Molecule X-ray Crystallography, John Hopkins University 3400 N Charles St, Baltimore MD, 21218 USA

Supporting information for this article is given via a link at the end of the document.