

C–O Activation

Transition-Metal-Free Cleavage of CO

Marc Devillard,^[a] Bas de Bruin,^[a] Maxime A. Siegler,^[b] and J. I. van der Vlugt^{*[a]}

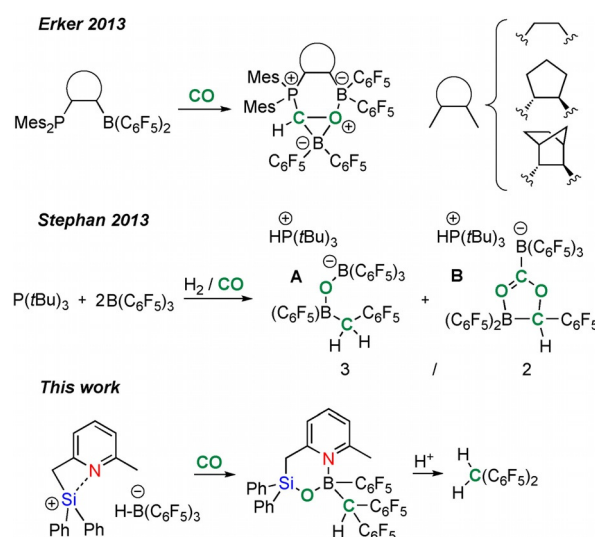
Abstract: Tertiary silane **1**^H, 2-[(diphenylsilyl)methyl]-6-methylpyridine, reacts with tris(pentafluorophenyl)borane (BCF) to form the intramolecular pyridine-stabilized silylium **1**⁺-HBCF. The corresponding 2-[(diphenylsilyl)methyl]pyridine, lacking the methyl-group on the pyridine ring, forms classic N(py)→B adduct **2**^H-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_{sp2} 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 silylium–hydroborate 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 C₁ building block, including large-scale industrial processes (e.g., acetic acid production, hydroformylation).^[1] However, the C–O linkage is typically preserved in these applications. This is in stark contrast to heterogeneous Fischer–Tropsch catalysis, where CO (with H₂) is utilized as a true C₁ building block to make new C–C bonds concomitant with deoxygenation of CO (i.e., C≡O cleavage).^[2] In this context, also the valorization of carbon dioxide is currently attracting much attention.^[3] Partial deoxygenation strategies to convert carbon dioxide with main-group elements (e.g., hydrosilylation, hydro-

boration) are investigated.^[4] Since the pioneering work of Brown on the carbonylation of alkylboranes,^[5] 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^[6] and diaminocarbenes are utilized,^[7] 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,^[8a,b] or the M–C bond of alanes^[8c,d] and gallanes^[8e] is known, and reductive coupling of CO has recently been achieved.^[9]

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.^[10] Recently, a mononuclear Mo platform was shown to generate C₂O₁ species by stoichiometric CO triple-bond scission combined with C–C bond formation, aided by the use of silyl chlorides as co-reagents, which inadvertently generates siloxanes as by-product.^[11] In contrast, however, selective transition-metal-free deoxygenation of CO is virtually unknown.

Combinations of an electrophilic borane and a phosphine-based donor, (referred to as FLPs (Frustrated Lewis Pairs),^[12] have been used to activate CO. The group of Erker described the trapping of the CO adduct of Piers borane^[13] (OC→B(H)(C₆F₅)₂) with intramolecular phosphine–borane FLP systems, generating a new C–H bond (Scheme 1, top).^[14] Stephan



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: CO triple-bond activation of intramolecularly stabilized silylium hydroborate system with double C–C_{sp2} bond formation.

[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 and the ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/chem.201703798>.

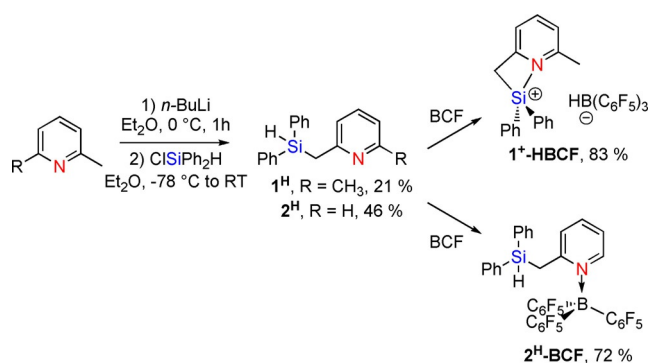
© 2017 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of Creative Commons Attribution NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

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 $C-C_{sp2}$ bond, together with cyclic product **B** (Scheme 1, middle).^[15a] The group of Scheschkewitz reported on the reaction between a lithium disilene and CO (1:2 ratio) to generate a highly nonsymmetric species in which three out of four CO molecules have undergone $C\equiv O$ cleavage.^[15b] These reports represent the only previous examples of main-group-element promoted $C\equiv O$ cleavage and concurrent $C-C_{sp2}$ bond formation, 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,^[16] 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,^[17,18] we sought to develop a reactive $Si-B$ system that would be capable of CO activation (Scheme 1, bottom). Although the chemistry and catalysis with electrophilic silylium species is rapidly gaining attention,^[19] examples of frustrated Lewis pair-type chemistry involving silicon are relatively rare.^[20]

To address both challenges, we herein report a strategy to stabilize a silylium species with a weak donor such as pyridine,^[21] 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 two C_6F_5 transfers 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^H** from lutidine is straightforward (Scheme 2). The $Si-H$ hydrogen resonates at δ 5.01 ppm in the 1H NMR spectrum ($^1J_{SiH} = 199.9$ Hz). The hydrogen atoms of the methylene bridgehead ($-CH_2-$) group appear as a doublet at δ 2.91 ppm through coupling with the $Si-H$ hydrogen ($^3J_{HH} = 3.7$ Hz). The correspond-



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

ing $^{29}Si\{^1H\}$ NMR signal appears as a singlet at δ -14.6 ppm. The analogous species **2^H** (2-[(diphenylsilyl)methyl]pyridine) was also prepared in this way.

Upon addition of an equimolar amount of tris(pentafluorophenyl)borane (BCF) to a solution of **2^H**, selective formation of species **2^H-BCF**, featuring a direct $N\rightarrow B$ adduct, is observed with an intact hydrosilane unit, according to 1H and ^{29}Si NMR spectroscopy (Scheme 2). The ^{19}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^H** in CD_2Cl_2 at room temperature immediately generates a new singlet at δ 23.2 ppm in the HSQC $^{29}Si-^1H$ NMR spectrum, correlating with a broad singlet at δ -25.5 ppm in the ^{11}B NMR spectrum. In the corresponding 1H NMR spectrum, the $-CH_2-$ hydrogens appear as a singlet at δ 3.43 ppm, indicating $Si-H$ cleavage. In the $^1H\{^{11}B\}$ NMR spectrum, the formation of the hydroborate $H-B(C_6F_5)_3^-$ is evidenced by a broad singlet at δ 3.57 ppm that nearly disappears in the baseline in the ^{11}B -coupled spectrum. Furthermore, the *para*-pyridine H-atom is strongly shifted downfield upon hydride abstraction, which suggests an intramolecular $N\rightarrow Si$ donor-acceptor interaction in the product.^[22]

Abstraction of the hydride to generate cationic pyridine-stabilized silylium fragment **1⁺-HBCF** (Scheme 2) was further ascertained by high resolution mass spectrometry (HR-MS; see the Supporting Information). To the best of our knowledge, only one other example of a pyridine-stabilized silylium derivative has been described to date (featuring a five-membered ring), whereas **1⁺-HBCF** features an $N\rightarrow Si$ stabilization within a four-membered ring.^[23] 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.^[24] Silylium salt **1⁺-HBCF** is isolated as an oil, preventing structure elucidation by single-crystal X-ray crystallography.

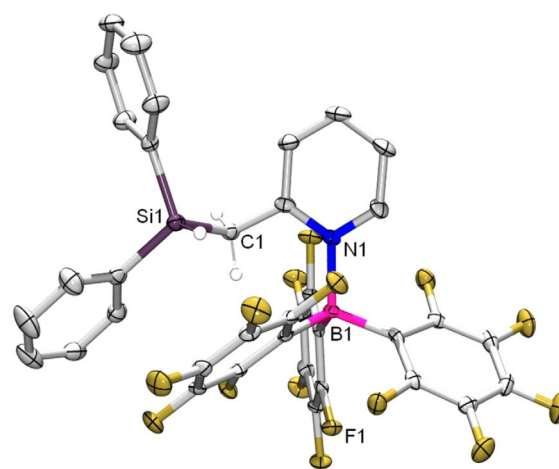
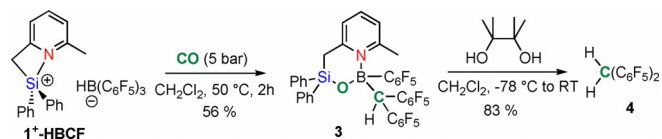


Figure 1. Displacement ellipsoid plot (50% probability level) of **2^H-BCF**. Hydrogen atoms are omitted for clarity, except those on C1 and Si1. Selected bond lengths (Å): N1-B1 1.6547(35); C1-Si1 1.8983(28); Si1-H1 1.366(26).

Upon pressurizing a solution of 1^+ -HBCF in CD_2Cl_2 with 5 bar of CO for two hours at 50°C , a single new resonance at $\delta -8.6$ ppm is observed in the ^{29}Si DEPT NMR spectrum, revealing a reaction to a new species **3** featuring a saturated tetra-coordinated silicon (Scheme 3). HR-MS reveals the incorpora-



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

tion of one molecule of CO or ^{13}C , respectively. A new signal is observed at $\delta 2.3$ ppm in the ^{11}B NMR spectrum, while a new singlet integrating for one hydrogen atom is observed at $\delta 4.75$ ppm in the ^1H NMR spectrum. This signal becomes a doublet ($J_{\text{CH}} = 116.8$ Hz) when the same reaction is performed with ^{13}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 ^{13}C NMR spectrum of the labeled compound displays a doublet ($J_{\text{CH}} = 116.8$ Hz) at $\delta 25.9$ ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, this signal is 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.

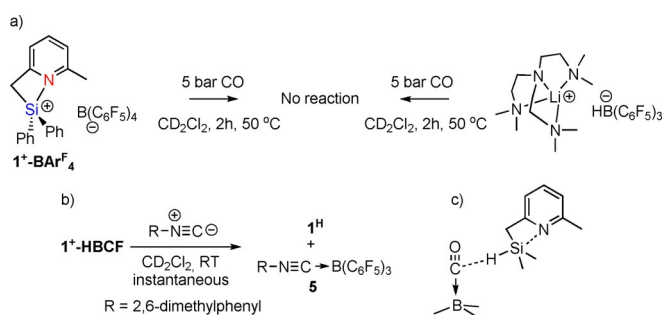
Based on multinuclear NMR spectroscopy and literature data on related organoboron compounds,^[25] we conclude that **3** contains a $(\text{C}_6\text{F}_5)_2\text{B}-\text{C}(\text{H})(\text{C}_6\text{F}_5)_2$ fragment as well as a siloxyborate linkage. DFT calculated and benchmarked NMR chemical shifts support the presence of a four-coordinated B-nucleus with an additional pyridine→boron interaction, as in **3** (Scheme 3 and the Supporting Information). It can be noted that the hydrogens of the methylene bridge in **3** do not display a diastereotopic effect (low temperature ^1H NMR shows only broadening of the CH_2 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 the Supporting Information for details).^[26]

As a result, the $\text{C}\equiv\text{O}$ 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 highly 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 **3O**, which confirms the proposed connectivity with a six-membered $\sim\text{C}-\text{Si}-\text{O}-\text{B}-\text{N}-\text{C}\sim$ linkage (see the Supporting Information).^[27]

Liberation of the organic $\text{C}(\text{H})(\text{C}_6\text{F}_5)_2$ fragment from **3** was achieved through 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 ^{13}C -labeled derivative, available from ^{13}C) in 83% yield, confirming the generation of two new C– $\text{C}_{\text{sp}2}$ 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 the Supporting Information for details). The skeletal composition, the protocol for its formation and the subsequent reactivity of **3** are unique, to the best of our knowledge, as it represents the first example of double C– $\text{C}_{\text{sp}2}$ 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^+ -HBCF as reagent, several control experiments were carried out. Firstly, 1^+ -BAR $^{\text{F}}_4$, the tetrakis(pentafluorophenyl)borate analogue of 1^+ -HBCF, lacking a hydridic B–H fragment, was prepared by the reaction of 1^{H} and $(\text{C}_6\text{F}_5)_4\text{B}$ in 76% yield and characterized by multinuclear NMR spectroscopy and HR-MS analysis (see the Supporting Information for details). This compound is completely unreactive toward CO, which suggests that a borohydride moiety is necessary for carbon monoxide activation to occur (Scheme 4a). Furthermore, the lithium hydroborate salt $\text{LiBH}(\text{C}_6\text{F}_5)_3$ also gives no reaction under the same reaction conditions, thus showing that the pyridine–silylium 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 $1^{\text{H}} + \text{BCF}$. c) Proposed hydride transfer from 1^{H} to $\text{OC}\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$.

Next, we attempted to translate the observed reactivity with CO to the electronically related isocyanide moiety. Surprisingly, reaction of 1^+ -HBCF with *tert*-butylisocyanide at RT led to complete regeneration of the silane Si–H bond, as supported by ^1H NMR spectroscopy, concomitant with formation of the $\text{tBuNC}\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ adduct **5** (Scheme 4b). This observation suggests that 1^+ -HBCF is also in equilibrium with the silane and the carbonyl adduct $\text{OC}\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ ^[28] under CO pressure and that intact 1^{H} rather than the silylium derivative may be 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 4c). The hydricity 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^+ -HBCF

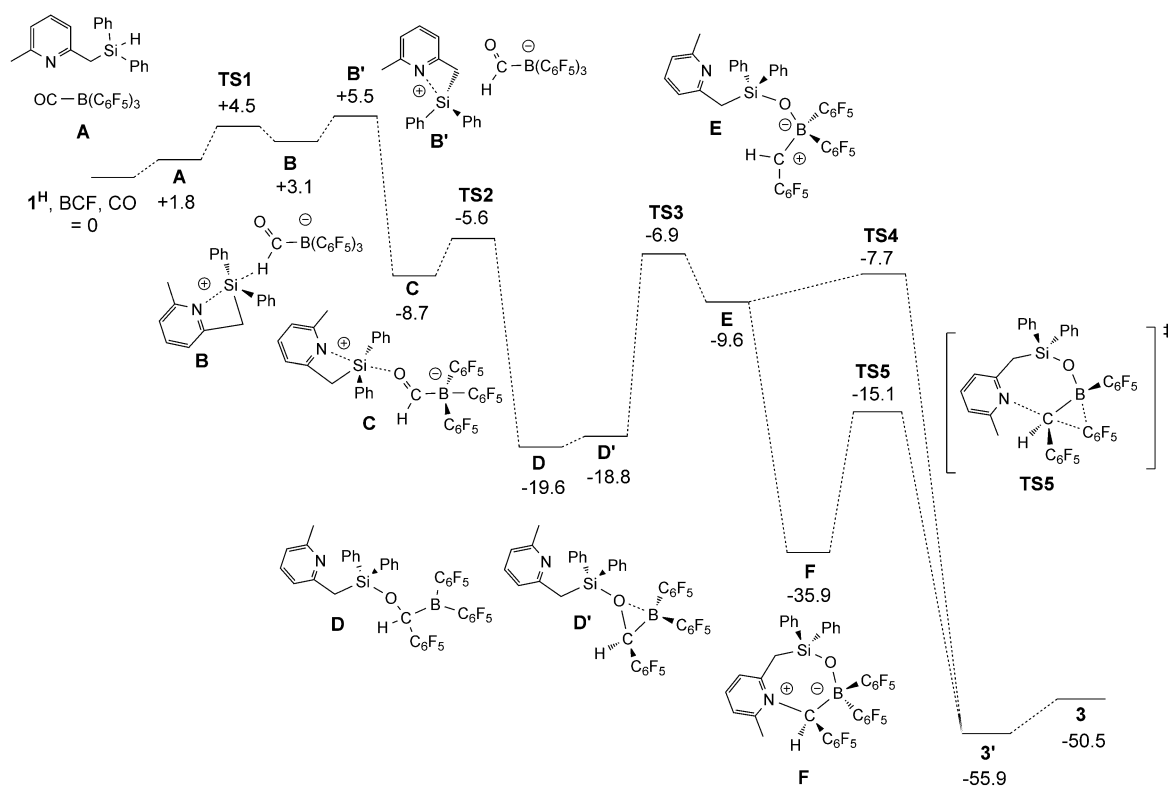


Figure 2. DFT-calculated (BP86, def2-TZVP, disp3, m4 grid) pathway for the conversion of $1^{\text{H}} + \text{BCF}$ to **3**. For details, see also the Supporting Information.

and 1^{H} , a mixture of methyldiphenylsilane (HSiMePh_2), lacking the internal stabilizing pyridine ring, and $\text{B}(\text{C}_6\text{F}_5)_3$ do not react with CO.

To provide a qualitative picture of the plausible mechanism of CO triple-bond scission and formation of **3**, featuring the highly unusual six-membered *B*-(diarylmethyl)-*B*-aryl-boryloxysilane system, we performed DFT calculations (BP86, def2-TZVP, disp3, m4 grid). The complete pathway from 1^{H} to **3** is displayed in Figure 2. The separated Lewis acid–base pair ($1^{\text{H}} + \text{BCF}$; set at 0 kcal mol^{-1} with free CO; starting point) and 1^+ -HBCF ($+2.6 \text{ kcal mol}^{-1}$) 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 $\text{OC}-\text{B}(\text{C}_6\text{F}_5)_3$ and 1^{H} is largely compensated by relatively strong π - π stacking interactions. This pre-organization facilitates hydride transfer, via a low **TS1** barrier of $+4.5 \text{ kcal mol}^{-1}$ relative to $1^{\text{H}} + \text{BCF}$, to form zwitterionic silylium-formylborate species **B** (the ion-separated conformer **B'** is $2.4 \text{ kcal mol}^{-1}$ higher in energy than **B**). Intermediate **C** ($-11.8 \text{ kcal mol}^{-1}$), is formed upon interaction of the silyl cation with the oxygen atom of the formyl group. Subsequent facile transfer of a C_6F_5 -group from boron to carbon via transition state **TS2** ($+5.6 \text{ kcal mol}^{-1}$ relative to $1^{\text{H}} + \text{BCF}$) generates the open form of the neutral boranylmethoxysilane derivative **D** ($-19.6 \text{ kcal mol}^{-1}$).^[29] The bora-epoxide conformer **D'** ($+0.8 \text{ kcal mol}^{-1}$ relative to **D**) undergoes a 1,2-oxo-shift via **TS3** ($+11.9 \text{ kcal mol}^{-1}$ compared to **D'**) to form the open zwitterionic λ^4 -boranyloxysilane **E** with a formal cationic carbon frag-

ment ($-9.6 \text{ kcal mol}^{-1}$). Interestingly, bora-epoxides have been proposed as intermediates in alkyl transfer from boron to carbon.^[30] This reactive species **E** can undergo direct transfer of a second C_6F_5 -group from boron to form **G** over transition state **TS4** ($+1.9 \text{ kcal mol}^{-1}$ relative to **E**). Alternatively, formation of the closed zwitterionic pyridinium intermediate **F** ($-26.3 \text{ kcal mol}^{-1}$ relative to **E**) followed by transfer of a second C_6F_5 -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** ($+20.8 \text{ kcal mol}^{-1}$) representing the rate-limiting step of the reaction. The closed form **3**, featuring an additional $\text{N}_{\text{py}} \rightarrow \text{B}$ interaction, is only $5.4 \text{ kcal mol}^{-1}$ uphill relative to **3'**.

In summary, we have prepared silylium 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 $\text{C}\equiv\text{O}$ triple bond to generate **3**. This sequence also results in the formation of one new C–H and two new C– $\text{C}_{\text{sp}2}$ 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_1 product from 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 to explore the scope of Lewis acids available for this TM-free transformation is ongoing.

Acknowledgements

This research is funded by the European Research Council through ERC Starting Grant *EuReCat* 279097 to JlvdV. We thank Ed Zuidinga for MS analysis and Dr. Andreas Ehlers and Jan-Meine Ernsting for assistance with NMR spectroscopy.

Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · C–C bond formation · CO · silicon · small molecule activation

- [1] a) M. Beller, X.-F. Wu, *Transition Metal Catalyzed Carbonylation Processes*, Springer, **2013**; b) S. T. Gadge, B. M. Bhanage, *RSC Adv.* **2014**, *4*, 10367–10389.
- [2] a) P. M. Maitlis, V. Zanotti, *Chem. Commun.* **2009**, 1619–1634; b) C. K. Rofer-DePoorter, *Chem. Rev.* **1981**, *81*, 447–474.
- [3] a) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* **2016**, *55*, 7296–7343; *Angew. Chem.* **2016**, *128*, 7416–7467; b) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1749; c) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.* **2013**, *113*, 6621–6658; d) W. Wang, S. Wang, X. Ma, J. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703–3727.
- [4] a) C. Chauvier, T. Cantat, *ACS Catal.* **2017**, *7*, 2107–2115; b) S. Bontemps, *Coord. Chem. Rev.* **2016**, *308*, 117–130; c) A. Maity, T. S. Teets, *Chem. Rev.* **2016**, *116*, 8873–8911; d) M. Aresta, *CO₂ as Chemical Feedstock*, Wiley, Weinheim, **2010**.
- [5] H. C. Brown, *Acc. Chem. Res.* **1969**, *2*, 65–72.
- [6] a) M. Finze, E. Bernhardt, A. Terheiden, M. Berkei, H. Willner, D. Christen, H. Oberhammer, F. Aubke, *J. Am. Chem. Soc.* **2002**, *124*, 15385–15398; b) A. Fukazawa, J. L. Dutton, C. Fan, L. G. Mercier, A. Y. Houghton, Q. Wu, W. E. Piers, M. Parvez, *Chem. Sci.* **2012**, *3*, 1814–1818; c) H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature* **2015**, *522*, 327–330.
- [7] a) D. Martin, C. E. Moore, A. L. Rheingold, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 7014–7017; *Angew. Chem.* **2013**, *125*, 7152–7155; b) U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke, G. Frenking, *Chem. Sci.* **2010**, *1*, 697–704.
- [8] a) P. Paetzold, B. Redenz-Stormanns, R. Boese, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 900–902; *Angew. Chem.* **1990**, *102*, 910–911; b) J. Teichmann, H. Stock, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 459–453; c) M. R. Mason, B. Song, K. Kirschbaum, *J. Am. Chem. Soc.* **2004**, *126*, 11812–11813; d) X. Li, C. Ni, H. Song, C. Cui, *Chem. Commun.* **2006**, 1763–1765; e) M. R. Mason, B. Song, Y. Han, X. Hu, *Inorg. Chim. Acta* **2008**, *361*, 3332–3337.
- [9] a) H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan, A. Vargas, *Nat. Chem.* **2013**, *5*, 1025–1028; b) X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettingler, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 6912–6913; c) Z. D. Brown, P. P. Power, *Inorg. Chem.* **2013**, *52*, 6248–6259.
- [10] N. M. West, A. J. M. Miller, J. A. Labinger, J. E. Bercaw, *Coord. Chem. Rev.* **2011**, *255*, 881–898.
- [11] a) J. A. Buss, T. Agapie, *Nature* **2016**, *529*, 72–75; b) J. A. Buss, T. Agapie, *J. Am. Chem. Soc.* **2016**, *138*, 16466–16477.
- [12] D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032.
- [13] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492–5503.
- [14] M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2013**, *52*, 2243–2246; *Angew. Chem.* **2013**, *125*, 2299–2302.
- [15] a) R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 4974–4977; b) M. Majumdar, I. Omlor, C. B. Yildiz, A. Azizoglu, V. Huch, D. Scheschke, *Angew. Chem. Int. Ed.* **2015**, *54*, 8746–8750; *Angew. Chem.* **2015**, *127*, 8870–8874.
- [16] D. Mukherjee, H. Osseili, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2016**, *138*, 10790–10793.
- [17] Recent review: M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202–2220.
- [18] A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983–988.
- [19] a) M. C. Lipke, A. L. Liberman-Martin, T. D. Tilley, *Angew. Chem. Int. Ed.* **2017**, *56*, 2260–2294; *Angew. Chem.* **2017**, *129*, 2298–2335; b) H. F. T. Klare, M. Oestreich, *Dalton Trans.* **2010**, *39*, 9176–9184; see also: c) M. Khandelwal, R. J. Wehmschulte, *Angew. Chem. Int. Ed.* **2012**, *51*, 7323–7326; *Angew. Chem.* **2012**, *124*, 7435–7439.
- [20] a) A. Schäfer, M. Reissmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 12636–12638; *Angew. Chem.* **2011**, *123*, 12845–12848; b) B. Waerder, M. Pieper, L. A. Körte, T. A. Kinder, A. Mix, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2015**, *54*, 13416–13419; *Angew. Chem.* **2015**, *127*, 13614–13617; c) Z. Mo, T. Szilvási, Y.-P. Zhou, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 3699–3702; *Angew. Chem.* **2017**, *129*, 3753–3756; d) W. Nie, H. F. T. Klare, M. Oestreich, R. Fröhlich, G. Kehr, G. Erker, *Z. Naturforsch. B* **2012**, *67*, 987–994.
- [21] We prefer the R₂Si⁺-Py notation over R₂Si-Py⁺ for reasons of relative electronegativity of N vs. Si. DFT-calculated natural bond order (NBO) values support this assignment: Si = +1.77; N = –0.54.
- [22] a) J. Vergnaud, T. Ayed, K. Hussein, L. Vendier, M. Grellier, G. Bouhadir, J.-C. Barthelat, S. Sabo-Etienne, D. Bourissou, *Dalton Trans.* **2007**, 2370–2372; b) E. R. Clark, A. Del Grosso, M. J. Ingleson, *Chem. Eur. J.* **2013**, *19*, 2462–2466; c) L. A. Körte, R. Warner, V. Y. Vishnevskiy, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Dalton Trans.* **2015**, *44*, 9992–10002; d) J. Zheng, Y.-J. Lin, H. Wang, *Dalton Trans.* **2016**, *45*, 6088–6093; e) M. Devillard, C. Alvarez Lamsfus, V. Vreeken, L. Maron, J. I. van der Vlugt, *Dalton Trans.* **2016**, *45*, 10989–10998.
- [23] a) T. Nokami, R. Soma, Y. Yamamoto, T. Kamei, K. Itami, J.-I. Yoshida, *Beilstein J. Org. Chem.* **2007**, *3*, 7. b) For stabilization of hypervalent Si^{IV} in a 4-membered ring, see: T. R. van den Ancker, C. L. Raston, B. W. Skelton, A. H. White, *Organometallics* **2000**, *19*, 4437–4444.
- [24] See ref. [18e] and: U. Gellrich, Y. Diskin-Posner, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2016**, *138*, 13307–13313.
- [25] R. C. Neu, C. Jiang, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 726–736.
- [26] For lutidine-boron N→B equilibrated adducts and ¹¹B NMR data, see: a) S. J. Geier, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477; b) G. Ferguson, J. F. G. D. Murphy, J. P. Sheehan, T. R. Spalding, *Polyhedron* **1993**, *12*, 859–864. c) See also: *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds* (Eds.: H. Niith, B. Wrackmeyer), Springer, Berlin, **1978**.
- [27] Despite multiple attempts to selectively oxidize **3** to generate **30** in a targeted manner, this compound was not obtained in pure form again.
- [28] This adduct decomposes above –120 °C, see ref. [5a]. For DFT calculations, see: a) H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1999**, *18*, 1724–1735; b) for a structurally related adduct OC→B(H)(C₆F₅)₂, see: M. Sajid, G. Kehr, C. G. Daniliuc, G. Kehr, *Angew. Chem. Int. Ed.* **2014**, *53*, 1118–1121; *Angew. Chem.* **2014**, *126*, 1136–1139.
- [29] Akin to 1,1-carboboration reactions, see: a) B. Wrackmeyer, E. Khan, *Eur. J. Inorg. Chem.* **2016**, 300–312; b) G. Kehr, G. Erker, *Chem. Commun.* **2012**, *48*, 1839–1850.
- [30] See ref. [4] and: A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron, O. Eisenstein, *J. Am. Chem. Soc.* **2012**, *134*, 10843–10851.

Manuscript received: August 14, 2017

Accepted manuscript online: August 17, 2017

Version of record online: September 7, 2017

Please note: Minor changes have been made to this manuscript since its publication in *Chemistry—A European Journal* Early View. The Editor.