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 1H, 2-[diphenylsilyl]methyl]-6-methylpyridine, reacts with tris(pentafluorophenyl)borane (BCF) to form the intramolecular pyridine-stabilized silylium 1H-HBCF. The corresponding 2-[diphenylsilyl]methyl]-pyridine, lacking the methyl-group on the pyridine ring, forms classic N(pyz)–B adduct 2H-BCF featuring an intact silane Si–H fragment. Complex 1H-HBCF promotes cleavage of the C=O triple bond in carbon monoxide with double C–Cp2 bond formation, leading to complex 3 featuring a B-(diarylmethyl)-aryl-boryloxy silane 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 homogeneous 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, hydroboration) 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 azaborinidines[8ab] or the M–C bond of alanes[8c,d] and gallanes[9a] 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 C2O 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)(C6F3)2) with intramolecular phosphine–borane FLP systems, generating a new C–H bond (Scheme 1, top).[14] Stephan

---

[a] Dr. M. Devillard, Prof. Dr. B. de Bruin, Dr. 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, Weinheim.


Wiley Online Library
and co-workers reported that a 2:1 mixture of tris(pentafluorophenyl)borane (B(CF₃)₃) = BCF) and Ph(tBu)₂ leads to the complete splitting of CO (from syngas), via a boron formyl intermediate, to afford A featuring one new C–C₉₂ bond, together with cyclic product B (Scheme 1, middle).¹³⁴ 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=O cleavage.¹³⁵ These reports represent the only previous examples of main-group-element promoted C=O cleavage and concurrent C–C₉₂ 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 tris(pentafluorophenyl)boranes to activate CO₂ and carbonyl groups owing to the reactive B–H bond,¹⁵¹ and (ii) the well-known ability of mixtures of silanes and B(CF₃)₃ to promote hydrosilylation reactions of unsaturated substrates via formation of silyl cations,¹⁵² 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,¹⁵³ 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–C₉₂ bond formation by two C₉₃ transfers using a simple and novel pyridine-stabilized silylium hydrosilaborate 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 ¹Η from lutidine is straightforward (Scheme 2). The Si–H hydrogen resonates at δ 5.01 ppm in the ¹Η NMR spectrum (δSiH = 199.9 Hz). The hydrogen atoms of the methylene bridgehead (–CH₂–) group appear as a doublet at δ 2.91 ppm through coupling with the Si–H hydrogen (δJSiH = 3.7 Hz). The corresponding ²⁹Si[¹H] NMR signal appears as a singlet at δ –14.6 ppm. The analogous species ²⁹Si{(2-$\text{diphenylsilyl}$)methyl}pyridine was also prepared in this way.

Upon addition of an equimolar amount of tris(pentafluorophenyl)borane (BCF) to a solution of ²⁹Si, selective formation of species ²⁹Si-BCF, featuring a direct N→B adduct, is observed with an intact hydrosilane unit, according to ¹Η and ²⁹Si NMR spectroscopy (Scheme 2). The ¹⁹F 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 ¹⁴N in CD₂Cl₂ at room temperature immediately generates a new singlet at δ 23.2 ppm in the HSQC ²⁹Si-¹Η NMR spectrum, correlating with a broad singlet at δ –25.5 ppm in the ¹⁴N NMR spectrum. In the corresponding ¹Η NMR spectrum, the –CH₂-hydrogens appear as a singlet at δ 3.43 ppm, indicating Si–H cleavage. In the ¹⁴N (¹⁹F) NMR spectrum, the formation of the hydroborate H–B(CF₃)₃ is evidenced by a broad singlet at δ 3.57 ppm that nearly disappears in the baseline in the ¹⁹F-coupled spectrum. Furthermore, the para-pyridine H-atom is strongly shifted downfield upon hydride abstraction, which suggests an intramolecular N→Si donor–acceptor interaction in the product.²²

Abstraction of the hydride to generate cationic pyridine-stabilized silylium fragment ¹⁴N-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 ¹⁴N-HBCF features an N→Si stabilization within a four-membered ring.²³ Apparently, introduction of a methyl group ortho to the pyridine nitrogen fully suppresses the py→B(CF₃)₃ adduct in favor of formation of the [N→Si⁺] hydroborate Lewis pair. This species can be considered isoelectronic with previously described pyridine-stabilized organoboranes.²⁴ Silanyle salt ¹⁴N-HBCF is isolated as an oil, preventing structure elucidation by single-crystal X-ray crystallography.

---

**Figure 1.** Displacement ellipsoid plot (50% probability level) of ²⁹Si-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 1.3662(26).
Upon pressurizing a solution of $^{1+}$-HBCF in CD$_2$Cl$_2$ with 5 bar of CO for two hours at 50 °C, a single new resonance at δ = −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 incorporation of one molecule of CO or $^{13}$CO, respectively. A new signal is observed at δ = 2.3 ppm in the $^{13}$B NMR spectrum, while a new singlet integrating for one hydrogen atom is observed at δ = 4.75 ppm in the $^1$H NMR spectrum. This signal becomes a doublet (J$_{CH}$ = 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 $^{11}$C NMR spectrum of the labeled compound displays a doublet (J$_{CH}$ = 116.8 Hz) at δ = 25.9 ppm. In the $^{13}$C($^1$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 $^1$B nucleus. The $^{19}$F NMR spectrum displays two signals with an integration ratio of 2:1, suggestive of (double) $^{13}$C$_2$F$_7$ 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 (C$_4$F$_5$)BF(C$_2$H)$_2$ 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 is noted that the hydrogens of the methane bridge in 3 do not display a diastereotopic effect (low temperature $^1$H NMR shows only broadening of the CH 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 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 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 C3-Si-O-B-N-C linkage (see the Supporting Information).[27]

Liberation of the organic C(H)(C$_2$H)$_2$ 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 $^{13}$CO) in 83% yield, confirming the generation of two new C–C$_{sp}$ 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–C$_{sp}$ 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 silylum species $^{1+}$-HBCF as reagent, several control experiments were carried out. Firstly, $^{1+}$-BAr$_7^+$, the tetrakis(pentafluorophenyl)borate analogue of $^{1+}$-HBCF, lacking a hydridic B–H fragment, was prepared by the reaction of $^{1}$H and (CPh$_3$)B(C$_2$F$_7$)$_3$ 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 LiBH(C$_2$F$_7$)$_3$ also gives no reaction under the same reaction conditions, thus showing that the pyridine–silylum fragment is also crucial for the reaction to proceed.

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 $^1$H NMR spectroscopy, concomitant with formation of the tBuNC–B(C$_2$F$_7$)$_3$ adduct 5 (Scheme 4b). This observation suggests that $^{1+}$-HBCF is also in equilibrium with the silane and the carbonyl adduct OC–B(C$_2$F$_7$)$_3$[28] under CO pressure and that intact $^{1+}$ rather than the silylum 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 hydridicity of the silane would be enhanced through intramolecular stabilization of the corresponding silylum fragment by the nearby pyridine group. In agreement with this proposed equilibrium between $^{1+}$-HBCF
and 1\textsuperscript{H}, a mixture of methylidiphenylsilane (HSiMePh\textsubscript{3}), lacking the internal stabilizing pyridine ring, and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{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 \( B - (\text{diarylmethyl}) - B \)-aryl-boroxylsilane system, we performed DFT calculations (BP86, def2-TZVP, disp3, m4 grid). The complete pathway from 1\textsuperscript{H} to 3 is displayed in Figure 2. The separated Lewis acid–base pair (1\textsuperscript{H} + BCF; set at 0 kcal mol\textsuperscript{-1} with free CO; starting point) and 1\textsuperscript{H} -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 OC --B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and 1\textsuperscript{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 kcal mol\textsuperscript{-1} relative to 1\textsuperscript{H} + BCF, to form zwiterionic silylum-formylborate species B (the ion-separated conformer B’ is 2.4 kcal mol\textsuperscript{-1} higher in energy than B). Intermediate C (−11.8 kcal mol\textsuperscript{-1}) is formed upon interaction of the silyl cation with the oxygen atom of the formyl group. Subsequent facile transfer of a C\textsubscript{6}F\textsubscript{5} group from boron to carbon via transition state TS2 (+5.6 kcal mol\textsuperscript{-1} relative to 1\textsuperscript{H} + BCF) generates the open form of the neutral boronimethoxysilane derivative D (−19.6 kcal mol\textsuperscript{-1}).\textsuperscript{[28]} The bora-epoxide conformer D’ (+0.8 kcal mol\textsuperscript{-1} relative to D) undergoes a 1,2-oxo-shift via TS3 (+11.9 kcal mol\textsuperscript{-1} compared to D’) to form the open zwiterionic 3\textsuperscript{H}-boranyloxysilane E with a formal cationic carbon fragment (−9.6 kcal mol\textsuperscript{-1}). Interestingly, bora-epoxides have been proposed as intermediates in alkyl transfer from boron to carbon.\textsuperscript{[30]} This reactive species E can undergo direct transfer of a second C\textsubscript{6}F\textsubscript{5} group from boron to form G over transition state TS4 (+1.9 kcal mol\textsuperscript{-1} relative to E). Alternatively, formation of the closed zwiterionic pyridinium intermediate F (−26.3 kcal mol\textsuperscript{-1} relative to E) followed by transfer of a second C\textsubscript{6}F\textsubscript{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 kcal mol\textsuperscript{-1}) representing the rate-limiting step of the reaction. The closed form 3, featuring an additional N\textsubscript{Py} --B interaction, is only 5.4 kcal mol\textsuperscript{-1} uphill relative to 3’.

In summary, we have prepared silylum species 1\textsuperscript{H} -HBCF using the pyridine-appended tertiary silane 1\textsuperscript{H} and Lewis acid tris(pentafluorophenyl)borane. This FLP-like compound is able to induce full cleavage of the C\textsubbox{O} triple bond to generate 3. This sequence also results in the formation of one new C–H and two new C–C 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\textsubscript{Py} 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 JvdV. We thank Ed Zudinga 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

[4] We prefer the RSiP notation over RSi–P for reasons of relative electronegativity of N vs. Si. DFT-calculated natural bond order (NBO) values support this assignment: Si—N = 1.77; N—Si = 0.54.
[9] Despite multiple attempts to selectively oxidize 3 to generate 30 in a targeted manner, this compound was not obtained in pure form again.

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.