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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-BCF. The corresponding 2-[(diphenylsilyl)methyl]-pyridine, lacking the methyl-group on the pyridine ring, forms classic N(py)=B adduct 2H-BCF featuring an intact silane Si–H fragment. Complex 1H-BCF promotes cleavage of the C=O triple bond in carbon monoxide with double C–Csp2 bond formation, leading to complex 3 featuring a B-(diarylmethyl)-8-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). 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). In this context, also the valorization of carbon dioxide is currently attracting much attention. Partial deoxygenation strategies to convert carbon dioxide with main-group elements (e.g., hydrosilylation, hydroformylation) are investigated. 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. 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.[10] 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

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[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)

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and co-workers reported that a 2:1 mixture of tris(pentafluoro-
phenyl)borane (B(CF₃)₃ = BCF) and Pr(iBu)₃ leads to the com-
plete splitting of CO (from syngas), via a boron formyl in-
termediate, to afford A featuring one new C–C₉₂ bond, together
with cyclic product B (Scheme 1, middle). The group of
Scheshchewitz reported on the reaction between a lithium di-
lenide and CO (1:2 ratio) to generate a highly nonsymmetric
species in which three out of four CO molecules have under-
gone CO cleavage. These reports represent the only previ-
ous examples of main-group-element promoted CO 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 function-
alization (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 CO₂ and carbonyl
groups owing to the reactive B–H bond, and (ii) the well-
known ability of mixtures of silanes and B(CF₃)₃ to promote
hydroxilylation reactions of unsaturated substrates via forma-
tion of silyl cations, we sought to develop a reactive Si–B
system that would be capable of CO activation (Scheme 1, bot-
tom). Although the chemistry and catalysis with electrophilic
silylumium species is rapidly gaining attention, examples of
frustrated Lewis pair-type chemistry involving silicon are rela-
tively rare.

To address both challenges, we herein report a strategy to
stabilize a silylium species with a weak donor such as pyri-
dine, 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 CₙFₙ transfers using a simple and
novel pyridine-stabilized silylium hydroborate system. Through
a combination of experimental data and supported by DFT cal-
culations, the role of each component in this hitherto un-
known reaction sequence is detailed.

Synthesis of 2-(diphenylsilyl)methyl]-6-methylpyridine 2
from lutidine is straightforward (Scheme 2). The Si–H hydrogen
resonates at δ 5.01 ppm in the ¹H NMR spectrum (J_{SiH} =
199.9 Hz). The hydrogen atoms of the methylene bridgehead
(-CH₂-) group appear as a doublet at δ 2.91 ppm through cou-
pling with the Si–H hydrogen (J_{SiH} = 3.7 Hz). The correspond-
ing ²⁹Si[¹H] NMR signal appears as a singlet at δ ~14.6 ppm.
The analogous species ²⁹Si(2-(diphenylsilyl)methyl]pyridine)
was also prepared in this way.

Upon addition of an equimolar amount of tris(pentafluoro-
phenyl)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 ¹H and ²⁹Si NMR
spectroscopy (Scheme 2). The ¹F NMR spectrum shows 15 dif-
ferent 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 be-
tween BCF and ¹H in CDCl₃ at room temperature immediately
new a singlet at δ 23.2 ppm in the HSQC ²⁹Si-
¹H NMR spectrum, correlating with a broad singlet at δ
–25.5 ppm in the ³¹B NMR spectrum. In the correspond-
ing ¹H NMR spectrum, the -CH₂- hydrogens appear as a singlet at δ
3.43 ppm, indicating Si–H cleavage. In the ¹H NMR spec-
trum, the formation of the hydroborate H–B(CF₃)₁ is evi-
denced by a broad singlet at δ 3.57 ppm that nearly disap-
ppears in the baseline in the ¹B-coupled spectrum. Furth-
more, the para-pyridine H-atom is strongly shifted downfield
upon hydride abstraction, which suggests an intramolecular
N→Si donor–acceptor interaction in the product.

Abstraction of the hydride to generate cationic pyridine-sta-
bilized silylium fragment ¹⁺-BCF (Scheme 2) was further as-
certained 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 deriva-
tive has been described to date (featuring a five-membered
ring), whereas ¹⁺-BCF features an N→Si stabilization within
a four-membered ring. Apparently, introduction of a methyl
group ortho to the pyridine nitrogen fully suppresses the py→
B(CF₃)₁ adduct in favor of formation of the [N→Si⁺ hydrobo-
rate Lewis pair. This species can be considered isoelectron-
ically with previously described pyridine-stabilized organoboranes.

Silylum salt ¹⁺-BCF is isolated as an oil, preventing structure
elucidation by single-crystal X-ray crystallography.

Scheme 2. Synthesis of ¹H and ²⁹Si and reaction with B(CF₃)₃ (BCF) to pyri-
dine-stabilized silylium ¹⁺-BCF and pyridine-borane adduct ²⁹Si-BCF, respec-
tively.

Figure 1. Displacement ellipsoid plot (50% probability level) of ²⁹Si-BCF. Hy-
drogen atoms are omitted for clarity, except those on C1 and Si1. Selected
bond lengths (Å): N1–B1 1.6547(35); C1–Si1 1.9898(28); Si1–H1 1.3662(26).
Upon pressurizing a solution of 1\textsuperscript{+}-HBCF in CD\textsubscript{2}Cl\textsubscript{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 \textsuperscript{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 \textsuperscript{13}CO, respectively. A new signal is observed at δ 2.3 ppm in the \textsuperscript{13}B NMR spectrum, while a new singlet integrating for one hydrogen atom is observed at δ 4.75 ppm in the \textsuperscript{1}H NMR spectrum. This signal becomes a doublet (J\textsubscript{\textsuperscript{13}B-\textsuperscript{1}H} = 116.8 Hz) when the same reaction is performed with \textsuperscript{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 \textsuperscript{13}C NMR spectrum of the labeled compound displays a doublet (J\textsubscript{\textsuperscript{13}C-\textsuperscript{1}H} = 25.9 ppm) in the \textsuperscript{13}C(\textsuperscript{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 \textsuperscript{13}B nucleus. The \textsuperscript{19}F NMR spectrum displays two sets of signals with an integration ratio of 2:1, suggestive of (double) C\textsubscript{6}F\textsubscript{5} transfer from boron to the boron-bound carbon atom.

Based on multinuclear NMR spectroscopy and literature data on related organoboron compounds,\textsuperscript{[25]} we conclude that 3 contains a (C\textsubscript{6}F\textsubscript{5})\textsubscript{3}B–C(\textsuperscript{13}C)(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} 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 \textsuperscript{1}H NMR shows only broadening of the CH\textsubscript{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).\textsuperscript{[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 –C–Si-O-B-N-C– linkage (see the Supporting Information).\textsuperscript{[27]}

Liberation of the organic C(\textsuperscript{13}C)(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} 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 \textsuperscript{13}C-labeled derivative, available from \textsuperscript{13}CO) in 83% yield, confirming the generation of two new C–C\textsubscript{sp2} 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\textsubscript{sp2} 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\textsuperscript{+}-HBCF as reagent, several control experiments were carried out. Firstly, 1\textsuperscript{+}-B\textsubscript{6}Ar\textsubscript{4} as the tetrakis(pentafluorophenyl)borate analogue of 1\textsuperscript{+}-HBCF, lacking a hydridic B–H fragment, was prepared by the reaction of 1\textsuperscript{th} and (CPh\textsubscript{3})\textsubscript{2}B(C\textsubscript{6}F\textsubscript{5})\textsubscript{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\textsubscript{6}F\textsubscript{5})\textsubscript{2} 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\textsuperscript{+}-HBCF with tert-butylisocyanide at RT led to complete regeneration of the silane Si–H bond, as supported by \textsuperscript{1}H NMR spectroscopy, concomitant with formation of the tBuNC–B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} adduct 5 (Scheme 4b). This observation suggests that 1\textsuperscript{+}-HBCF is also in equilibrium with the silane and the carbonyl adduct OC–B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} under CO pressure and that intact 1\textsuperscript{th} 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\textsuperscript{+}-HBCF
and 1\textsuperscript{H}, a mixture of methylidiphenylsilane (H\textsubscript{2}SiMePh\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-(diaryl)methyl-aryl-boryloxyisilane 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 (+26.8 kcal mol\textsuperscript{-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 zwitterionic silylum-formylborate species B (the ion-separated conformer B\textsuperscript{'} 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 boranylmethoxysilane derivative D (−19.6 kcal mol\textsuperscript{-1}).\textsuperscript{[29]} The bora-epoxide conformer D\textsuperscript{'} (+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 zwitterionic 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 zwitterionic 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{pyr}−B interaction, is only 5.4 kcal mol\textsuperscript{-1} uphill relative to 3'.

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

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=O triple bond to generate 3. This sequence also results in the formation of one new C−H and two new C−C\textsubscript{aryl} 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{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.
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Conflict of interest

The authors declare no conflict of interest.

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