Boron Ligands

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Mild and Complete Carbonyl Ligand Scission on a Mononuclear Transition Metal Complex

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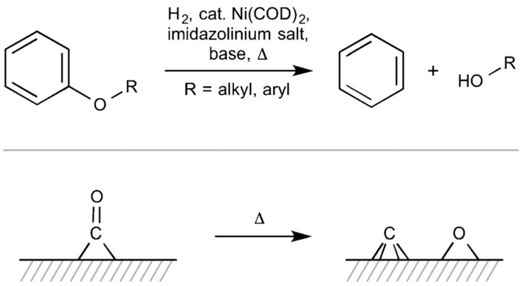
In memory of Heinrich Nöth

Abstract: *The complete scission of the carbon–oxygen bond of carbon monoxide, while frequently observed on bulk metals and with bimetallic and cluster transition metal complexes, is unknown with monometallic systems. Reaction of a zerovalent iron bis(borylene) complex with a cyclic (alkyl)-(amino)carbene revealed a highly selective intramolecular cleavage of the C–O bond of a carbonyl ligand at room temperature, leading to the formation of a highly unusual iron complex containing a base-stabilized (bora)alkylideneborane ligand. DFT investigation of the reaction mechanism suggested that the two Lewis acidic borylene boron atoms cooperate to cleave the C–O multiple bond.*

Carbon–oxygen bonds, in particular those of ethers and certain C–O bonds of esters, are particularly strong, and are challenging targets for bond cleavage reactions. There have been a number of reports of activations of usually inert C–O bonds promoted by transition-metal complexes, and more recently frustrated Lewis pairs, yet the field of C–O activation lags significantly behind those of C–H and other bond activations.[1] The hydrodeoxygenation of natural feedstocks such as oil, coal, and biomass (which necessarily relies on the cleavage of C–O bonds) has been a goal of industry for decades, and heterogeneous catalytic methods of this reaction have been applied with some success.[2] However, homogeneous catalytic methods for ester C–O cleavage (with the exception of Hartwig's nickel-catalyzed ether cleavage process; Scheme 1, top)[3] are lacking.

It might be expected that the complete scission of the multiple C–O bond of carbon monoxide would be much more difficult than that of the thermodynamically weaker C–O single bonds discussed above. However, similarly to ether C–O bonds, the C–O bond of carbon monoxide is also susceptible to cleavage by frustrated Lewis pairs.[4] Carbon monoxide C–O cleavage also appears in a few notable catalytic processes and has been extensively discussed. The Boudouard equilibrium, wherein CO disproportionates into CO_2 and graphite, promoted by a transition-metal catalyst, is a frequent nuisance in industrial catalysis.[5] Scission of the C–O bond of CO is also a key step of the Fischer–Tropsch process, where the molecule is broken into C and O atoms on a bulk metal catalyst (Scheme 1, bottom).[6] This reactivity is echoed in a molecular sense in a number of reports where binuclear or cluster complexes cleave carbonyl ligands, often to form carbido clusters.[7]



Scheme 1. Top: Hartwig's nickel-catalyzed ether hydrogenation reaction. Bottom: Representation of the carbonyl cleavage step on a metal catalyst during the Fischer–Tropsch reaction.

In marked contrast, however, is the paucity of reactions wherein a mononuclear metal complex cleaves carbonyl ligand C–O bonds. Despite extensive literature searches, we have been unable to find reports of the C–O scission of a carbonyl ligand involving a mononuclear transition-metal complex.

In a recent experiment, we found that the addition of a cyclic (alkyl)(amino)carbene (CAAC) to a zerovalent iron bis(borylene) tricarbonyl complex induced such a carbonyl scission reaction, under remarkably mild conditions, with high selectivity, and in excellent yields. The reaction leads to a highly unusual complex containing a base-stabilized (bora)alkylideneborane ligand bound to the iron center through two Fe–C bonds and in a η^6 fashion to the attached duryl (2,3,5,6-tetramethylphenyl) group. The alkylideneborane carbon atom is additionally found to be bound to the iron center with a distorted near-T-shaped geometry. This reaction, and structural, spectroscopic, and computational explorations into the properties of the product, are presented herein.

In 2012 we reported the synthesis of a mixed bis(borylene) complex of Fe^0, $[Fe(BDur)\{BN(SiMe_3)_2\}(CO)_3]$ (**1**),[8] by single borylene transfer from a group six borylene complex

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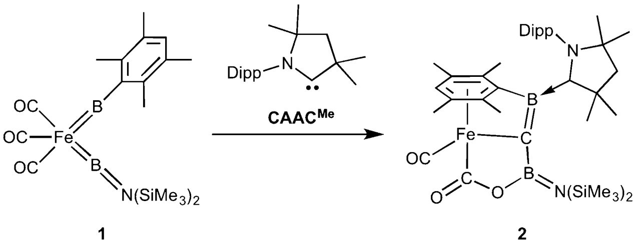
to $[Fe(BDur)(CO)_3(PMe_3)]$.[9] The two borylene ligands in **1** were found to be spatially quite close to each other (d(B–B): 1.982(3) Å) with an acute B-Fe-B angle (65.91(9)°). The B–B bonding was calculated to be significant, but with an order below unity (Wiberg bond index: 0.78). Calculations suggested that the main factor preventing the accumulation of B–B bonding character was a strong donation of electron density that would otherwise have made up the B–B σ bond to an empty orbital on the Fe center. While we were able to induce catenation of four borylene ligands by photolytic ligand loss from **1**,[8] dimerization, and CO addition, the coupling of two borylene ligands to form a π-diborene ligand, which is presumably a more simple process, continued to elude us. Consequently, we set out to populate this empty orbital to decrease the σ(BB)→Fe interaction and enforce B–B coupling by offering strong σ-donors to the metal. We instead observed that addition of trialkylphosphines to **1** resulted only in the co-catenation of :BR and CO ligands on the iron atom, leading to a complex containing a FeCBBC cycle.[10] Similarly, addition of alkynes to **1** resulted in their "diboryleneation" to form either 1,4-dibora-1,3-butadiene or 1,4-diboracyclohexa-2,5-diene complexes of iron.[11] While these reactions produced a number of fascinating products, the challenge of connecting two borylene ligands remained, and we thus turned to strongly donating persistent carbenes to fill iron-based orbitals and induce B–B coupling. Initial reactions of compound **1** with common N-heterocyclic carbenes (NHCs) IMe (1,3-dimethylimidazol-2-ylidene), IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), and IDipp (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) led only to decomposition of the iron bis(borylene) complex. Subsequently, the cyclic (alkyl)(amino)carbene[12] $CAAC^{Me}$ (Scheme 2) was selected owing to its excellent σ-donation and π-accepting properties, with which we hoped to construct a strong Fe–C bond. Treatment of **1** with $CAAC^{Me}$ in aromatic solvents resulted in an immediate color change from red to dark blue and the observation of ^{11}B NMR signals at δ 26 and 37 ppm, strongly upfield of those of precursor **1** (δ 129 and 78 ppm). When the reaction was carried out in hexane or pentane, dark blue crystals precipitated almost instantly from the solution (**2**, Scheme 2), which were isolated in 90% yield, assuming the simple combination of **1** and $CAAC^{Me}$ with no mass loss.



Scheme 2. Synthesis of complex **2**.

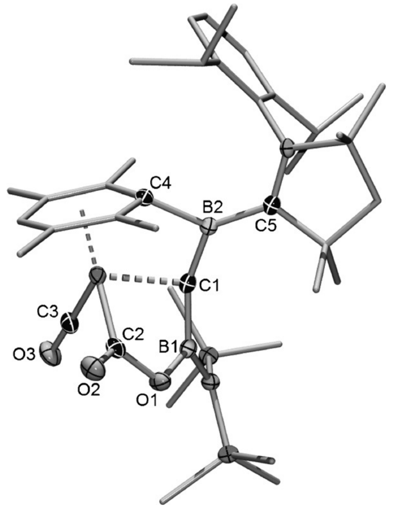


Figure 1. Crystallographically derived molecular structure of **2**.[22] Ellipsoids are set at 50% probability; for clarity, hydrogen atoms, solvent molecules, and some carbon ellipsoids have been removed. Relevant bond lengths [Å] and angles [°] for **2**: Fe–C1 2.084(3), Fe–C2 1.959(3), Fe–C3 1.750(3), C1–B1 1.512(4), C1–B2 1.456(4), B1–O1 1.425(3), C2–O1 1.387(3), C2–O2 1.208(3), C3–O3 1.154(4), B2–C4 1.627(4), B2–C5 1.540(5), Fe–(duryl centroid) 1.641; B1-C1-B2 157.6(2), Fe-C1-B1 97.1(2), Fe-C1-B2 100.2(2), (duryl centroid)-C4-B2 145.60.

The identity of **2** was not immediately apparent from its NMR data, and was instead determined by single-crystal X-ray diffraction to be complex $[(OC)Fe(\kappa^3\text{-}\sigma_C{:}\sigma_C{:}\eta_C{}^6\text{-} C\{O\}OB\{N(SiMe_3)_2\}CB\{CAAC^{Me}\}\{C_6HMe_4\text{-}2,3,5,6\})]$ (Scheme 2 and Figure 1). The complex comprises an unprecedented chelating structure anchored by an η^6-bound duryl group, a σ_C-bound carboxyl moiety and an unusual distorted coordination of the carbon atom of an alkylideneborane unit. The structure implies complete cleavage of one CO ligand, with the oxygen atom now part of the carboxyl group and the carbon atom spanning the two boron atoms with a near-T-shaped geometry (Fe-C1-B1 97.1(2)°; Fe-C1-B2 100.2(2)°; B1-C1-B2 157.6(2)°; sum of angles around C1: 354.9°). The three (non-aryl) Fe–C bonds in the complex ($Fe{-}C^{BCB}$ 2.084(2); $Fe{-}C^{carboxyl}$ 1.959(3); $Fe{-}C^{carbonyl}$ 1.751(3) Å) provide an instructive comparison of the different bonds involved, from the significantly multiple $Fe{-}C^{carbonyl}$ bond, to the conventional $Fe{-}C^{carboxyl}$ σ bond, to the more loosely-bound $Fe{-}C^{BCB}$ alkylideneborane interaction. The $Fe{-}C^{BCB}$ distance of 2.084(2) Å is relatively long for a Fe–C(sp^2) single bond, but is in fact shorter than many complexes containing bulky σ-aryl ligands or σ-aryl ligands in conjunction with sterically congested or strained ligand sets. Examples include the Fe–C bonds of the tetranaphthyliron dianion (2.104(6), 2.147(7) Å)[13] and the Fe^{II} σ-phenyl complex *cis,trans*-$[FeBr(CO)_2(C_6H_5)(PMe_3)_2]$ (2.093(4) Å).[14] Thus, while the geometry of the C1 atom is certainly unusual, this may be merely a result of the strained and sterically congested ligand environment. The Fe–C interaction is thus best described as as a long σ bond, an assertion also supported by DFT calculations (see below). The C–B distances involving the Fe-bound carbon atom correspond to single (1.512(4) Å) and double (1.456(4) Å) bonds, the latter being in the range of those of known borataalkene compounds.[15] The $CAAC^{Me}$ unit, although nearly coplanar with its attached boron atom (torsion angle N-C5-B2-C1 171.8°), forms a B–C bond (B2–C5 1.540(5) Å) that is somewhat longer than B-CAAC bonds observed recently wherein multiple bonding was inferred, for example, $[B_2(CAAC^{Me})_2]$ (1.459(2), 1.458(2) Å)[16] and $[B_2(CAAC^{Me})_2(CNtBu)_2]$ (1.499(4), 1.498(4) Å).[17]

The IR spectrum shows one carbonyl band (1907 cm^{-1}) at lower frequency than those of precursor **1** (2000 cm^{-1}, 1923 cm^{-1}), thus indicating a higher degree of $M\rightarrow CO$ π back-bonding character. The position of the band approaches that of the half-sandwich boryl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMe_3)\{B(NCy_2)Cl\}]$ (1890 cm^{-1}) and is very close to that of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{B(NCy_2)Cl\}]$ (1901 cm^{-1}), both prepared by Aldridge and co-workers.[18] As mentioned above, the ^{11}B NMR signals of **2** were observed at δ 26 and 37 ppm, the latter presumably corresponding to the alkylideneborane boron center, given its resemblance to the ^{11}B NMR signals of previously reported alkylideneborates (δ 35, 40 ppm).[15] The ^1H NMR shift of the duryl *para* hydrogen nucleus of **2** (δ 4.70 ppm) is shifted greatly to high field compared to that of the precursor **1** (δ 7.00 ppm),[8] reflective of its η^6-coordination in the latter complex. Due to the presence of restricted rotation around the B=N bond, two singlets (δ 0.36 and 0.50 ppm) were observed for the trimethylsilyl groups, along with two singlets in the ^{29}Si NMR spectrum (δ 2.63, 4.01 ppm). Four singlets (δ 1.02, 1.42, 1.87, and 2.11 ppm) were detected for the methyl groups of the duryl group owing to the planar chirality at the η^6-bound ring. Singlet ^{13}C NMR signals at δ 182.9, 202.6, and 218.7 ppm are tentatively assigned to the iron-bound BCB, carbonyl, and carboxyl carbon nuclei, respectively. The UV/Vis spectrum of **2** shows a broad band at 377 and two overlapping bands at 573 nm and 619 nm. The depression between the peaks at 377 and 573 nm (centered at ca. 470 nm) provides a rationalization for the dark blue color of the complex (see the Supporting Information for the spectrum).

Geometry optimization of **2** was undertaken using the hybrid *meta*-GGA functional M05-2X[19] in conjunction with the def2-SVP[20] basis set (Figure 2). The geometry of **2** was reproduced relatively well by calculation, with only small deviations from those observed experimentally (Fe−C: exptl. 2.084(3) Å, calcd 2.036 Å; C1−B1: exptl. 1.512(4) Å, calcd 1.532 Å; C1−B2: exptl. 1.456(4) Å, calcd 1.460 Å). The calculated frontier orbitals of **2** associated with the iron–alkylideneborane moiety are displayed in Figure 3. The HOMO is effectively a delocalized π bond spanning the alkylideneborane B−C bond and the $B-CAAC^{Me}$ bond, while HOMO−1 shows Fe−C σ-bonding character. HOMO−6 suggests significant Fe−C π bonding character, presumably a Fe-to-C π back-bonding interaction.

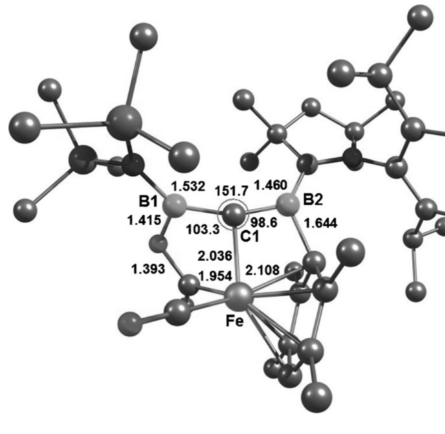


Figure 2. Optimized geometry of **2** at the M05-2X/def2-SVP level.

The frontier molecular orbitals of **2** (Figure 3) suggested the possibility of reactivity at $FeCB_2$ unit with both nucleophiles and electrophiles. Owing to the instability of compound **2** in solution at ambient conditions all reactivity studies had to be carried out between −30 °C and 0 °C. Preliminary results showed that it is not possible to either populate the LUMO with common Lewis bases (no reaction with PMe_3, IMe, IMes, IDipp, or MeNC) or to induce selective reaction of the complex with Lewis acids (decomposition with $GaCl_3$ and CuCl). The complex also shows no reaction with methyl iodide. Further studies showed a remarkable stability of **2** towards air and moisture as long as the temperature does not exceed 0 °C, which can be attributed to kinetic stabilization of the reactive Fe−C=B unit by the bulky $CAAC^{Me}$, $BN(SiMe_3)_2$, and Dur groups.

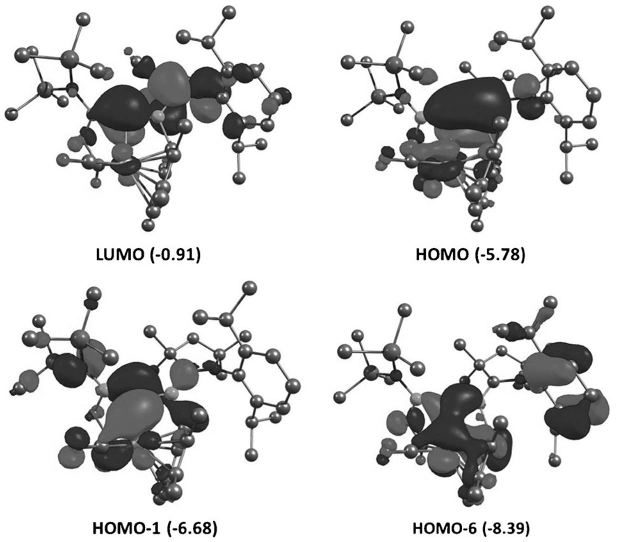


Figure 3. Plot of the frontier molecular orbitals of **2** associated with the $FeCB_2$ unit (energies in eV) at the M05-2X/def2-SVP level.

To elucidate the reaction mechanism of the unusual CO bond-cleavage reaction, DFT calculations were carried out at the PCM-M05-2X/def2-SVP level. The calculated reaction profile is shown in Figure 4 and begins with **I1**, the simple adduct of **1** with $CAAC^{Me}$ which binds at the BDur boron atom (Figure 4; the Supporting Information, Figure S2 shows the geometries and key bond distances of the intermediates and transition states). The calculated free energy of **I1** is 12.1 kcal mol^{-1}, which should be accessible at room temperature. The coupling of the base-stabilized borylene ligand of **I1** with one CO ligand forms **I2**, analogous to a number of recently-isolated complexes containing side-on-bound base-stabilized boraketenes (O=C=BRL) and boraketenimines (RN=C=BRL).[21] Unfortunately, attempts to locate a transition state between **I1** and **I2** failed. A systematic scan of the potential energy surface of the $B-C_{carbonyl}$ bond cleavage in **I2** showed that the energy increases in that direction (Supporting

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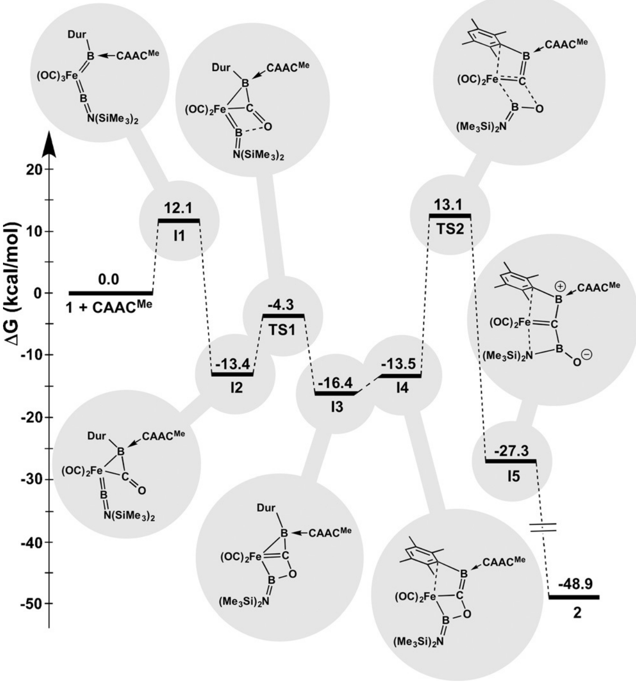

Figure 4. The calculated Gibbs energy profile of the CO bond cleavage reaction calculated at the PCM-M05-2X/def2-SVP level.

Information, Figure S3), which means the carbonyl-bridging reaction from **I1** to **I2** is a barrierless process. Intermediate **I2** is $25.5\ \text{kcal mol}^{-1}$ more stable than **I1** in terms of free energy (Figures 4; Supporting Information, Figure S2). The reaction proceeds from **I2** to **I3** by connection of the aminoborylene boron atom to the boraketene CO oxygen atom via the early transition state **TS1**, which resembles **I2** (Figures 4; Supporting Information, Figure S2), with a free energy of activation of $9.1\ \text{kcal mol}^{-1}$. The rearrangement of the four-membered-metallocycle **I3** by the elongation of Fe–B bond forms **I4**. The free energy of **I4** is only $2.9\ \text{kcal mol}^{-1}$ higher in energy than that of **I3**. The reaction proceeds with C–O and Fe–B(N) bond activation of the four-membered ring of **I4** via **TS2** to form **I5**, which contains another four-membered ring. The free energy of activation of this process is $26.6\ \text{kcal mol}^{-1}$ with respect to **I4**. The attack of the oxygen atom at a remaining CO ligand by the rotation around a B–C bond forms the product **2**. All attempts to locate such a transition state between **I5** and **2** failed. A systematic scan of the potential energy surface of the C–O bond cleavage in **2** showed that the energy monotonically increases in that direction (Supporting Information, Figure S4), which means the attack of the oxygen atom at the CO group is a barrierless process.

The cleavage of a C–O bond of carbon monoxide observed herein leads to a highly unusual complex with a two-boron-containing ligand bound at three points to the iron center, and a nearly T-shaped central carbon atom. The calculated mechanism of the reaction suggests that the two Lewis acidic borylene boron atoms cooperate to cleave the C–O multiple bond with minimal influence from the metal center, a feature reminiscent of the C–O cleavage reported by Stephan in 2013.[4] The mechanism also hinges on the partial transfer of a CO ligand from the metal to an arylborylene ligand, a phenomenon that also forms the basis of our recent work on borylene–CO coupling and the liberation of monovalent boron species from metal scaffolds, including our recent syntheses of boraketenes, boraketenimines, and a borylene dicarbonyl.[21]

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Keywords: boryl complexes · borylene complexes · carbon monoxide · small-molecule activation · transition metals

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[22] CCDC 1421498 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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