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Cyclization with CO

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Cyclization of a 1,4-Diborabutadiene Ligand with Both Atoms of CO**

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Abstract: *A 1,4-dibora-1,3-butadiene iron complex was successfully synthesized through the stoichiometric reaction of an iron bis(borylene) complex with diphenylacetylene. This complex was treated with CO and PMe_3, which led to the formation of an unusual six-membered B_2C_3O ylidic ring bound to both the PMe_3 group and zerovalent iron center. The reaction is a very rare example of the incorporation of both atoms of CO into a ring system.*

The reactive HOMO of carbon monoxide,[1] comprised predominantly of a lone pair of electrons at the carbon atom, means that its characteristic reactivity is largely centered at the carbon atom.[2] Cyclization reactions involving CO are a popular synthetic strategy, particularly in conjunction with transition metals, but they overwhelmingly favor the incorporation of just the carbon atom of CO into the ring system, that is, cycloadditions of the form $[n+m+1]$. This is nicely demonstrated by the Pauson–Khand reaction, a [2+2+1] cyclization of an alkyne, an alkene, and CO to form a cyclopentenone,[3] as well as the related synthesis of cyclopentadienone ligands on a metal scaffold.[4]

By contrast, simultaneous reactivity of CO at both atoms is exceedingly rare. Side-on binding of both atoms of a CO ligand to transition metals is not uncommon in organometallic chemistry, however this is observed only in multimetallic complexes as an auxiliary mode in conjunction with conventional end-on OC−M binding.[5] Cyclization reactions in which the C and O atoms are both incorporated into the resulting ring are rarer still. Reported examples are the cyclization of unsaturated chromium alkylidene complexes with alkynes to form cyclopenta[*b*]pyrans (Figure 1 a),[6] the hydroboration and capture of a CO molecule by a frustrated Lewis pair/hydroborane system reported by the Erker group (Figure 1 b),[7] and our previous construction of a doubly base-stabilized bis(boralactone) through treatment of a diboryne[8] compound with CO (Figure 1 c).[9] Herein, we report a highly unusual incorporation of CO into a six-membered-ring ligand through treatment of a 1,4-dibora-1,3-butadiene complex of iron with CO and trimethylphosphine. The reaction is a very rare example of a cyclization that incorporates both atoms of CO and is reminiscent of the frustrated Lewis pair chemistry demonstrated by Erker and co-workers.

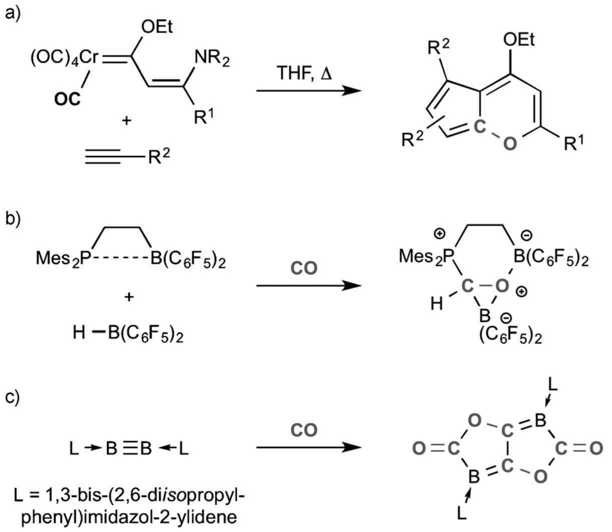

Figure 1. Known cyclization reactions involving incorporation of both atoms of carbon monoxide into the resulting ring systems.

In 2012, we reported the synthesis of the 1,4-dibora-1,3-butadiene complex **2c** through insertion of bis(trimethylsilyl)-ethyne into the weak B···B interaction of the iron bis(borylene) complex **1**[10] (Figure 2). Alternatively, with the less sterically encumbered reagents dimethyl- and diphenylethyne, two-fold incorporation of alkynes to form 1,4-diboracyclohexadiene ligands was observed, thus leading to the complexes **3a**,**b**.[11] These reactions presumably proceed via the 1,4-dibora-1,3-butadiene complexes **2a**,**b**, which we were at the time unable to isolate. However, the possibility of cyclization reactions of the complexes **2** prompted us to explore their reactions with other reagents. Given that complex **2c** was found to be relatively unreactive, we set out to prepare and isolate the presumably more reactive 1,4-dibora-1-3-butadiene complex **2b**.

Since the photolytic reaction of diphenylethyne with iron bis(borylene) complex **1** (Figure 2) was uncontrollable and gave exclusively the two-fold addition product **3b**, we reasoned that the reaction might be better controlled by using heat rather than photolysis. Complex **1** was thus stirred with one equivalent of diphenylethyne in hexane at 80 °C overnight. Remarkably, a nearly selective conversion of **1** into the monoinsertion product **2b** was indicated by the ^{11}B NMR spectrum (signals at $\delta_B = 90$ and 61 ppm). After workup, **2b** was isolated as orange crystals in 31 % yield. Multinuclear NMR spectra for **2b** displayed all relevant signals in the

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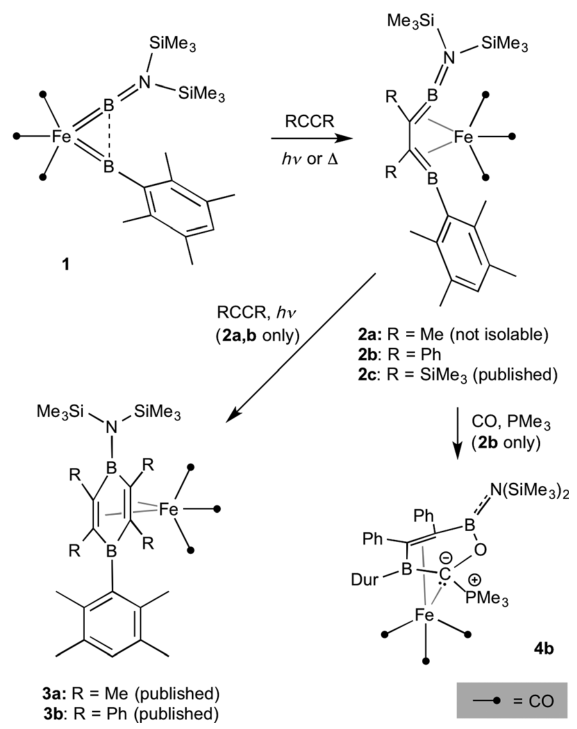


Figure 2. Synthesis of 1,4-diboracyclohexadiene complexes **3** (previously published) and formation of a B_2C_3O ring in the synthesis of **4b** (this work).

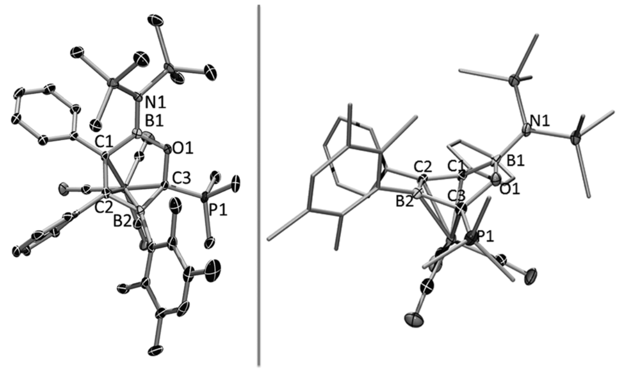


Figure 3. Molecular structure of **4b** shown from two different angles. Thermal ellipsoids depicted at the 50% probability level. For clarity, hydrogen atoms, solvent molecules, and some carbon ellipsoids in the view on the right have been removed. Selected bond lengths [Å] and angles [°]: B1–C1 1.584(4), C1–C2 1.460(4), C2–B2 1.526(4), B2–C3 1.566(4), C3–O1 1.452(3), O1–B1 1.378(4), C3–P1 1.778(3), B1–N1 1.449(4), Fe–C1 2.173(3), Fe–C2 2.139(3), Fe–B2 2.262(3), Fe–C3 2.073(3); $\Sigma C1^{CCB}$ 356.24, $\Sigma C3^{OPB}$ 347.14, $\Sigma B1^{CON}$ 359.99, $\Sigma C2^{CBC}$ 359.89, $\Sigma B2^{CCC}$ 359.55.

expected ranges (see the Supporting Information). Notably, the ^1H NMR spectrum displayed two singlets ($\delta_H = 2.06$ and 2.01 ppm) and two broad singlets ($\delta_H = 0.4$ and 0.1 ppm) for the methyl groups of the 2,3,5,6-tetramethylphenyl (Dur) and trimethylsilyl substituents, respectively. This suggests the presence of a higher rotational barrier around the B–N bond compared to the B–Dur bond, which could be explained by the presence of π donation from the nitrogen lone pair electrons to the boron atom.

Given the presumed Lewis acidity of the boron atoms of **2b**, particularly the Dur-bound boron atom, and the steric bulk of the complex, we predicted that the complex may react with small Lewis bases. With this in mind, we treated a C_6D_6 solution of **2b** with trimethylphosphine at room temperature. In a separate experiment, **2b** was placed under an atmosphere of CO. In neither sample was any reaction observed. By contrast, when a stoichiometric mixture of **2b** and PMe_3 in C_6D_6 was exposed to a CO atmosphere, the color of the benzene solution changed immediately from orange to light yellow. Multinuclear NMR spectra for the reaction mixture revealed the selective formation of a new boron- and phosphorus-containing compound (**4b**), as indicated by new signals ($\delta_B = 37$, 20; $\delta_P = 28.44$ ppm). The significant upfield shifts of the ^{11}B resonances suggest an increase in coordination number at both boron centers.

After workup, complex **4b** could be isolated as yellow crystals in 53% yield. Single crystals of **4b** suitable for X-ray crystallography were obtained upon cooling a hexane solution of the complex to −30 °C. The results of X-ray structural analysis (Figure 3) revealed a six-membered B_2C_3O ring, bound in a near-planar η^4(CBCC) fashion to the zerovalent $\{Fe(CO)_3\}$ fragment (torsion angle C1-C2-B2-C3 = 11.76°). The CO unit had been incorporated into the ring, with the carbon atom binding to the more acidic B(Dur) atom and the oxygen atom binding to the amino-bound boron atom. Additionally, the PMe_3 group is bound to the carbon atom of the former CO unit as a phosphonium unit, thus forming an ylide. This addition of boron and phosphorus atoms to the carbon atom of CO is reminiscent of a phosphaboration of a CS ligand reported by Hill and coworkers in 2007.[12] The synthesis of **4b** presumably comes about through nucleophilic attack of PMe_3 at the carbon atom of one CO ligand, and thus the CO unit incorporated into the ring is presumably one of the three originally attached to the iron atom. However, the mechanism of the subsequent cyclization is unclear at this point. An alternative picture of the bonding in **4b** could be that of a B=C borataalkene moiety, however the B2–C3 distance (1.566 Å) is far too long to fit with the corresponding distances in known borataalkenes.[13] The ylide description is supported by the relatively short Fe–C3 (2.073 Å) and relatively long Fe–B2 (2.262 Å) distances compared to those in conventional π-olefinic coordination of the C1–C2 unit (Fe–C: 2.173, 2.139 Å). These distances and the slight tilting of B2 out of the plane suggest that the Fe–B interaction is weaker than the three Fe–C interactions. The $OB(NR_2)$ section of the ring is tilted away from the iron center and does not obviously participate in the π bonding (torsion angle: B2-C3-C1-B1 133.82°, C2-C1-C3-O1 142.03°). The $N(SiMe_3)_2$ unit is twisted significantly (angle between NSiSi and BCO planes: 38.74°) from the ring boron atom, thus indicating significant disruption of the N→B dative π bonding.

Compound **4b** was characterized by multinuclear NMR spectroscopy in solution. The ^1H NMR spectrum displays four singlets ($\delta_H = 2.50$, 2.40, 2.19 and 1.97 ppm) and two singlets ($\delta_H = 0.44$ and 0.07 ppm) for the methyl groups of the Dur and $N(SiMe_3)_2$ groups, respectively, thus indicating a considerable rotational barrier around the exocyclic B–N and B–C bonds, which is presumably imposed by the high degree of steric congestion around the ring. Most remarkably, the signal for the C3 nucleus (derived from carbon monoxide) was detected at $\delta_C = 82.2$ ppm in an HMBC NMR experiment and shows an ^{1}H-^{13}C long-range correlation to the protons of $P(CH_3)_3$.

To provide further insight into the electronic structure of compound **4b**, DFT calculations were performed. The optimized geometry of the complex at the M05-2X/def2-SVP level is shown in Figure 4. The calculated bond lengths agree well with the experimentally measured bond lengths.

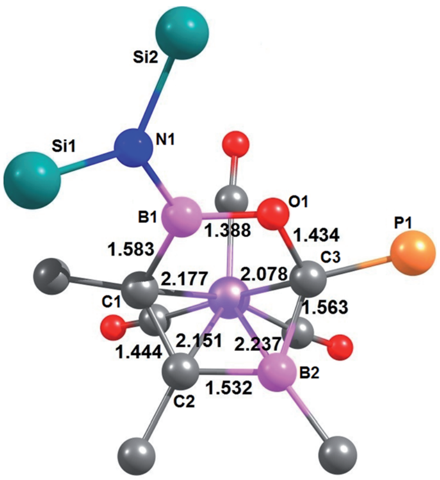
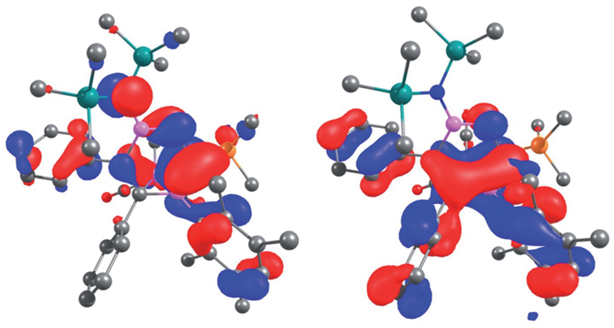


Figure 4. Optimized geometry of the core structure of compound **4b** at the M05-2X/def2-SVP level.

Analysis of the Kohn–Sham molecular orbitals of **4b** revealed that the HOMO−1 corresponds to a π-type orbital mainly located on the C3 atom, with a small contribution from the p(π) orbital of the B2 atom (Figure 5). The HOMO−3 corresponds to a π-type bonding orbital, which is delocalized through the C3-B2-C2-C1 unit but located mainly on C2 and C1 atoms. These two orbitals of the cyclic ligand, HOMO−1 and HOMO−3, both form donor–acceptor bonds to the Fe atom such that, together with the other three CO ligands on Fe, the 18-electron rule is fulfilled. The HOMO−1 and HOMO−3 of **4b** correspond to the HOMO and HOMO−1 of the free heterocyclic ligand (Table S2 in the Supporting Information), respectively, and are essentially analogous. It should also be noted that calculations show the central C_3B_2O ring of this free heterocycle to be almost completely planar.



HOMO−1 HOMO−3

Figure 5. Plot of the HOMO−1 and HOMO−3 of compound **4b** at the M05-2X/def2-SVP level.

In summary, a very rare example of incorporation of both atoms of carbon monoxide into a ring system was observed in the reaction of a 1,4-dibora-1,3-butadiene iron complex with CO and trimethylphosphine. The solid-state structure of **4b** suggests that the main bonding interactions of the ring with the $[Fe(CO)_3]$ fragment are donation of the lone pair electrons of the ylidic carbon atom (C3) and a conventional π-olefinic $C_2 \rightarrow Fe$ bond from the C1=C2 unit. These interactions are supported by inspection of the frontier orbitals of the complex, and comprise the HOMO−1 and HOMO−3, respectively.

Keywords: boracycles · boron · carbon monoxide · cyclization reactions · iron

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