

Main-Group Metallomimetics: Transition Metal-like Photolytic CO Substitution at Boron

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S Supporting Information

ABSTRACT: The carbon monoxide adduct of an unhindered and highly reactive CAAC-bound arylborylene, [(CAAC)B(CO)Ar] (CAAC = cyclic (alkyl) (amino)-carbene), has been prepared using a transfer reaction from the linear iron borylene complex [(PMe₃)₃(CO)Fe=BAR]. [(CAAC)B(CO)Ar] is a source of the dicoordinate [(CAAC)ArB:] borylene that can be liberated by selective photolytic CO extrusion and that, although highly reactive, is sufficiently long-lived to react intermolecularly. Through trapping of the borylene generated in this manner, we present, among others, the first metal-free borylene(I) species containing a nitrogen-based donor, as well as a new boron-containing radical.

The unique place of transition metal (TM) complexes in the fundamental and synthetic sciences is owed, in no small part, to their distinctive electron configuration that puts *d*-orbitals to the forefront.¹ As such, a large part of the properties and reactivity of transition metal compounds come from the combination of filled and empty, spatially proximate frontier orbitals that are localized around the metal center. This characteristic of transition metals explains their ability to bind ligands such as carbon monoxide, which is an essential and fascinating contributor to organometallic chemistry. Possessing, in addition to an available electron pair, an antibonding orbital that is a suitable π -backbonding acceptor, the carbonyl ligand strongly stabilizes a wide range of important metal complexes, especially when the metal is in a low oxidation state. Equally important is the ability of carbonyl ligands to liberate selectively a coordination site by photodissociation from a metal center in a process that is a crucial step of many catalytic reactions.² By contrast, few CO adducts of the main group elements are known, and π -backbonding is not significant in many of them.^{3–9} CO photodissociation has also found limited applications in main group chemistry, notably to generate nitrenes and phosphinidenes from isocyanates and phosphaketenes.^{10–12} More recently, associative CO substitution at a phosphaketene by different Lewis bases was demonstrated.¹³

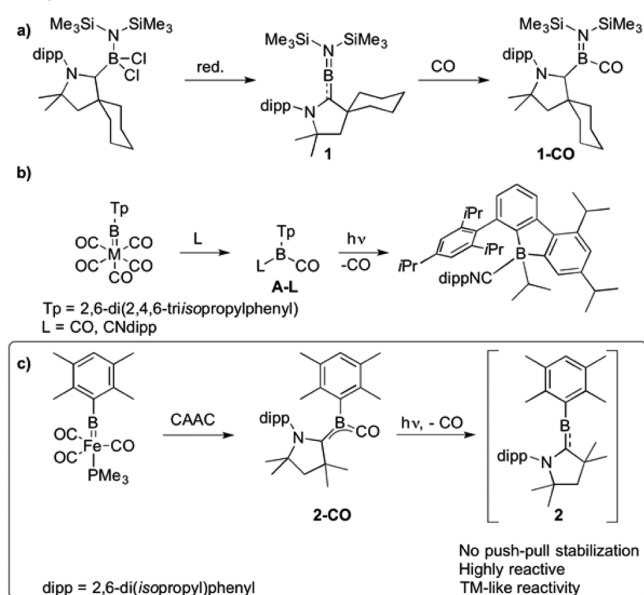
The last few decades have seen the emergence of a growing number of complexes of the main group elements that emulate the frontier orbitals of transition metals and possess the ability to react in the same way.^{14–22} In catalysis, for example strategies that use frustrated Lewis pairs mimic TMs by

involving simultaneously the orbitals of different main group elements to mediate important synthetic processes such as reduction, functionalization and small-molecule activation that were hitherto unique to transition metals.^{22–24} The development of novel, atypical and transition metal-inspired reactivity for the main group elements thus represents a challenging and promising possibility for the discovery of synthetic applications of earth-abundant elements. In this context, we are interested in the chemistry of complexes of the borylene fragment (RB:) as an insight into the unique reactivity of boron in a low oxidation state.^{25,26} Although the isolation of borylenes was, until recently, limited to their respective transition metal complexes, recent advances have led to the isolation of several metal-free tricoordinate [L₂BR] borylenes (L = Lewis base)^{27–30} that display significant nucleophilicity at the boron atom.^{27–30} On the other hand, monocoordinate, as well as most dicoordinate, B(I) species remain elusive compounds that can only be transiently generated under harsh reducing conditions.^{31–33} In this research field, Bertrand and co-workers have recently reported the first example of a linear metal-free borylene (Scheme 1a).^{8,34} This compound, [(^{Cy}CAAC)BN(SiMe₃)₂] (**1**, see Scheme 1), was found to cleave molecular hydrogen and bind carbon monoxide in a manner reminiscent of transition metals, but featured reduced reactivity because of its push–pull π -electronic stabilization. Our group has also reported the coordination of two equivalents of CO to an arylborylene fragment in a way that is unequivocally analogous to the chemistry of transition metals (Scheme 1b).⁷ Interestingly, exposure of one borylene–CO complex to UV irradiation led to intramolecular C–C bond activation, presumably through a metal carbonyl-like CO extrusion. To develop the full reactivity potential of linear borylenes that are not stabilized by steric or push–pull π -electronic effects, we now demonstrate that CO extrusion from CO-bound borylenes is a selective and productive reactivity pattern that may be used to generate a free coordination site in highly reactive borylene complexes. This led us to isolate and characterize a family of novel CAAC-bound arylborylenes by photolytic exchange of a carbonyl ligand in an unprecedented reaction for the group 13 elements.

As a starting point to this chemistry, we turned to the iron borylene [(PMe₃)₃Fe(CO)₃(BDur)] (Dur = 2,3,5,6-tetrame-

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Scheme 1. CO Chemistry of Metal-Bound and Metal-Free Borylenes^a

^a(a) Direct coordination of CO to a linear borylene; (b) coordination of CO to an arylborylene generated from a metal complex; (c) unique preparation of a transient dicoordinate borylene by CO-extrusion (this works).

thylphenyl) that was previously reported by our group.³⁵ Although the borylene transfer chemistry (i.e., the ability of the transition metal complex to transfer the borylene fragment to a substrate) of this compound remains limited to the synthesis of bis-isocyanide complexes of the durylborylene,^{7,36} we hypothesized that strong ligands such as CAAC could be suitable to receive the borylene fragment. Indeed, we find that CAAC (1 equiv) reacts readily with the [(PMe₃)Fe(CO)₃(BDur)] to generate the CO-bound CAAC-durylborylene **2-CO** (Scheme 1c) as the only boron-containing species, as judged by ¹¹B NMR spectroscopy. The boron NMR shift of **2-CO** ($\delta = -13.4$) is highly upfield shifted when compared to the corresponding aminoborylene adduct **1-CO** ($\delta = -3.4$), which is indicative of significantly different electronic properties of the two borylene fragments. After purification, **2-CO** was isolated as bright red crystals that were suitable for X-ray diffraction measurements (Figure 1, left). The generation of compound **2-CO** through this method is particularly noteworthy as, contrary to the CO complex of the CAAC-aminoborylene **1**, there are currently no known ways to generate it. Indeed, although **1-CO** can be synthesized by the reaction of the particularly stable **1** and gaseous carbon monoxide, free **2** remains an elusive species. The reduction of [(CAAC)B(Dur)Br₂] is known not to afford **2**, but rather the persistent, captodatively stabilized radical [(CAAC)B(Dur)Br].³⁷ The use of iron borylene precursors thus appears to be a suitable tool for the generation of CO-bound metal-free borylenes that are not stabilized by push–pull effects. These species, in their free form, are expected to display significantly increased reactivity when compared to their amino-substituted analogs. This hypothesis is supported by a structural analysis of **2-CO**, which reveals a very short B–CO bond (1.469(2) Å) and an elongated C–O bond (1.158(2) Å), which indicates a high degree of π -backbonding between the borylene fragment and CO. By contrast, the corresponding bond distances in **1-**

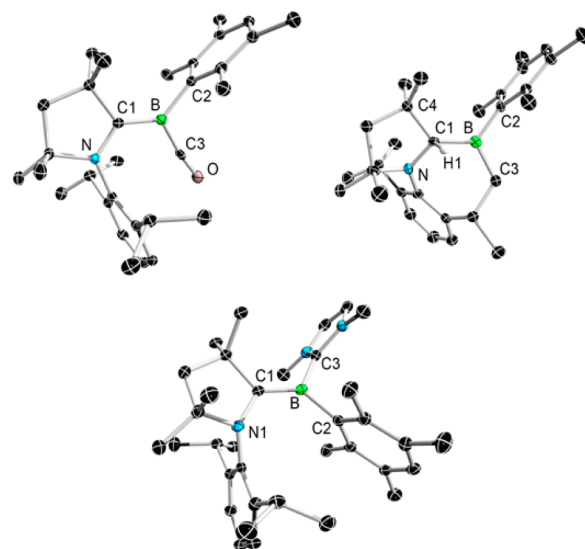


Figure 1. Solid-state structures of **2-CO** (left), **3** (main diastereoisomer in crystal, right) and **2-Ime** (bottom). Hydrogen atoms are omitted for clarity. Interatomic distances [Å] and angles [deg]. **2-CO**: B–C1 1.499(2), B–C2 1.613(2), B–C3 1.469(2), C3–O 1.158(2), C1–B–C2 130.4(1), C1–B–C3 110.0(1), C2–B–C3 119.6(1), B–C3–O 171.3(1). **3**: B1–C1 1.546(2), B–C2 1.583(2), B–C3 1.579(2), C1–N 1.445(2), B–C1–H1 83.8(9), N–C1–H1 110.3(9), C4–C1–H1 104.1(9), C1–B–C2 124.8(1), C1–B–C3 117.3(1), C2–B–C3 117.0(1). **2-Ime**: B–C1 1.458(2), B–C2 1.623(2), B–C3 1.605(2), C1–B–C2 128.8(1), C1–B–C3 119.4(1), C2–B–C3 111.81(9).

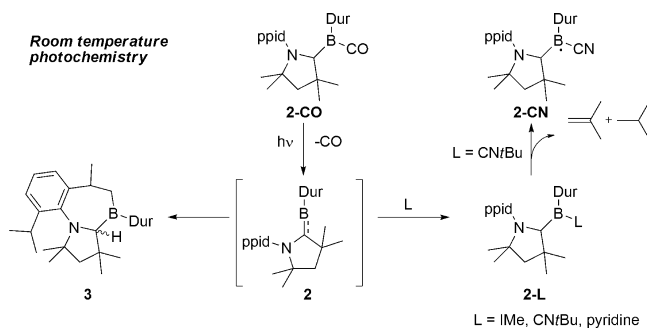
CO (1.529(5) Å, 1.091(3) Å, respectively) are closer to those of borane-carbonyl complexes ($R_3B \leftarrow CO$; typical B–C distances are 1.6–1.7 Å) that do not feature such transition metal-like boron-to-carbon electron sharing.³⁸ In fact, the B–CO bonding in **2-CO** is not significantly different to that of **A-CNdipp** (Scheme 1b) in which backbonding was thoroughly studied (B–CO 1.464(4) Å, C–O 1.161(3) Å) and found to be the strongest yet reported for boron and CO.⁷ Infrared spectroscopy also indicates significant π -backbonding with a CO stretching band at 1942 cm⁻¹, which is once again comparable to that of **A-CNdipp** (1930).

To probe the reactivity of this novel metal-free borylene-CO adduct, we began to explore the possibility of selectively photodissociating the carbonyl ligand to promote reactivity at the boron center. As an initial experiment, a borosilicate glass J. Young NMR tube containing a C₆D₆ solution of **2-CO** in benzene was irradiated by a mercury vapor UV lamp. After 4 h of this treatment, NMR analysis of the solution showed the disappearance of the signals associated with **2-CO**, along with the appearance of two new signals in the ¹¹B NMR spectrum ($\delta = 73, 92$, broad signals). Except in some key characteristic regions, the ¹H NMR spectrum of this reaction solution was found to be quite complex (see ESI). We were, however, able to identify two diastereoisomers of **3** as the main products of the photolysis (ratio ca. 42:58), which arise from the intramolecular C–H activation of one isopropyl group of the CAAC ligand, following a seemingly selective photodissociation of CO. This assignment is supported by X-ray diffraction analysis of crystals of **3** (Figure 1) that indeed revealed that the two diastereoisomers crystallized together, although in a different ratio than the reaction mixture (ca. 80:20) (Figure 1, right). HRMS also confirmed the composition of **3**. Interestingly, the

two diastereoisomers are very different in structure, which also gives them different ^{11}B NMR chemical shifts ($\delta = 73, 92$), which were found consistent with density functional theory-based NMR simulations. On the one hand, this C–H activation process has literature precedent as a reaction of highly reactive free borylenes, which supports the idea that, unlike **1**, **2** appears to be a species that cannot be isolated.³² On the other hand, the reported reaction is unique in its regioselectivity. Indeed, the reaction selectively forms a seven-membered ring instead of the more predictable six-membered cycle.^{26,39} Also interesting is the transfer of a hydrogen atom to the CAAC ligand, which is known to occur in some cases with CAAC-borane adducts.^{8,40,41} However, in a unique manner, this hydrogen transfer seems to be only partial as some interaction seems to remain between the boron center and this hydrogen atom as evidenced by a $\text{B}-\text{C}_{\text{CAAC}}-\text{H}$ angle of $83.8(9)^\circ$ (hydrogen atom localized on the Fourier map). This angle is the lowest to have been structurally identified for a B–C–H motif in tricoordinate boron compounds and thus appears to be the first example of a CH-to-B agostic interaction, which reinforces the similarity of durylborylenes to transition metals. Unfortunately, contrary to transition metals, the agostic interaction could not be characterized by ^{13}C NMR spectroscopy because of the strong boron-induced broadening of the C_{CAAC} signal.

Although free **2** does not seem to be isolable, we decided to investigate whether it could be trapped, following its in situ photolytic generation. To this end, we photolyzed **2-CO** in the presence of a range of Lewis bases. The results of this study are summarized in Scheme 2. In typical experiments, solutions of **2-**

Scheme 2. Photolytic Reactivity of **2-CO**



CO with a slight excess of L (L = *N,N*-dimethylimidazolyliene (IMe), *tert*-butylisocyanide and pyridine (pyr)) in benzene or hexane were prepared. Although no reaction took place when such solutions were left standing at room temperature for several hours, drastic color changes were observed in all cases within 15 min of irradiation. After 8 h, complete consumption of **2-CO** was confirmed by ^{11}B NMR and we were pleased to witness in the cases of L = IMe and pyridine, complete and selective conversion to new deeply colored species ($\delta^{11}\text{B} = 12$ and 23, red and dark green, respectively). Single-crystal X-ray diffraction allowed us to identify the products as **2-IMe** and **2-pyr**, respectively (Figure 2). This trapping of **1** by Lewis bases is consistent with the generation of a highly reactive dicoordinate borylene that is sufficiently long-lived to undergo intermolecular, productive reactivity under mild conditions. As such, compound **2-CO** can be seen as a conveniently protected source of free **2**, which is crucial in order to study the chemistry of free borylenes under mild conditions. On the one hand, **2-IMe** is reminiscent of mixed-carbene hydroboron(I) complexes

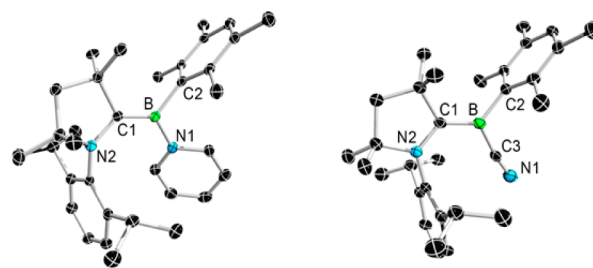


Figure 2. Solid-state structures of **2-pyr** (left) and **2-CN** (right). Hydrogen atoms are omitted for clarity. Interatomic distances [Å] and angles [deg]. **2-pyr**: B–C1 1.490(3), B1–C2 1.610(3), B–N1 1.516(2), C1–N2 1.417(2), C1–B–C2 124.0(2), C1–B–N1 127.3(2), C2–B–N1 108.7(1). **2-CN**: C1–B 1.519(3), B1–C2 1.596(3), B1–C3 1.551(3), C3–N1 1.158(3), C1–N2 1.450(3), C1–B–C2 124.8(2), C1–B–C3 123.5(2), C2–B–C3 111.6(2), B–C3–N1 171.9(2).

that were previously reported by Bertrand and co-workers.²⁸ It is, however, particularly encumbered around the boron atom, which leads to hindered rotation of the ligands. Consequently, the ^1H NMR spectrum of **2-IMe** at room temperature shows inequivalent and broad signals for most positions of the compound. Variable temperature NMR spectroscopy, however, gives sharper signals at low temperature and confirmed the assignment of the resonance peaks. On the other hand, **2-pyr** is the first borylene complex of a comparatively weaker nitrogen-based ligand and has no literature precedent. Its crystal structure shows that the pyridine ligand is not coplanar with the sp^2 boron atom, which precludes boron-to-pyridine back-bonding. As a matter of fact, the lengths of the C–C bonds in the pyridine ring do not suggest that any dearomatization has taken place.

When CNtBu is used as a ligand, the substitution is also facile. However, **2-CNtBu** is only observed as an intermediate species ($\delta^{11}\text{B} = -3.4$). The final product observed in this case is instead the radical **2-CN**, which is isolated as dark green crystals. **2-CN** was characterized by electron paramagnetic resonance (EPR) spectroscopy and X-ray diffraction (Figure 2, right). The formation of **2-CN** proceeds through elimination of isobutene and isobutane, as these products are observed in the reaction mixture by ^1H NMR spectroscopy. Similar elimination processes have previously been reported for the respective reactions of a disilyne⁴² and a [CAAC = B]₂ diboracumulene⁴³ with *tert*-butyl isocyanide. However, these reactions led to the formation of diamagnetic dicyano products. EPR spectroscopy of **2-CN** revealed a multiple-line spectrum with $g_{\text{iso}} = 2.0029$, indicative of hyperfine interactions with both the nitrogen and boron atoms (Figure 3). The observed hyperfine coupling constants of $A(^{14}\text{N}) = 18.3$ MHz and $A(^{11}\text{B}) = 10.7$ MHz suggest that the unpaired electron is primarily delocalized over the B–C_{CAAC}–N_{CAAC} linkage. This assignment is reminiscent of previously reported CAAC-stabilized boryl radicals.^{8,37}

In brief, we have succeeded in preparing **2-CO**, a carbonyl adduct of the relatively unhindered and highly reactive [(CAAC)DurB:] borylene fragment, through a novel synthetic method from a metal borylene precursor. Photolytic CO extrusion of **2-CO** proved a selective and productive way to generate a reactive dicoordinate boron(I) species under mild conditions and in the absence of additional reagent, which could be trapped quantitatively by Lewis bases. The reactivity of the in situ generated **2** with small molecules, organic

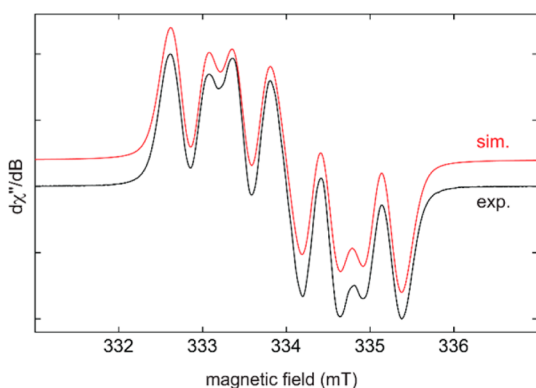


Figure 3. Experimental (bottom) and simulated (top) solution X-band (9.38 GHz) EPR spectra of $[2\text{-CN}]^{\bullet}$ in benzene solution.

substrates and main-group compounds is currently being investigated in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13047.

Complete synthetic and characterization information (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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