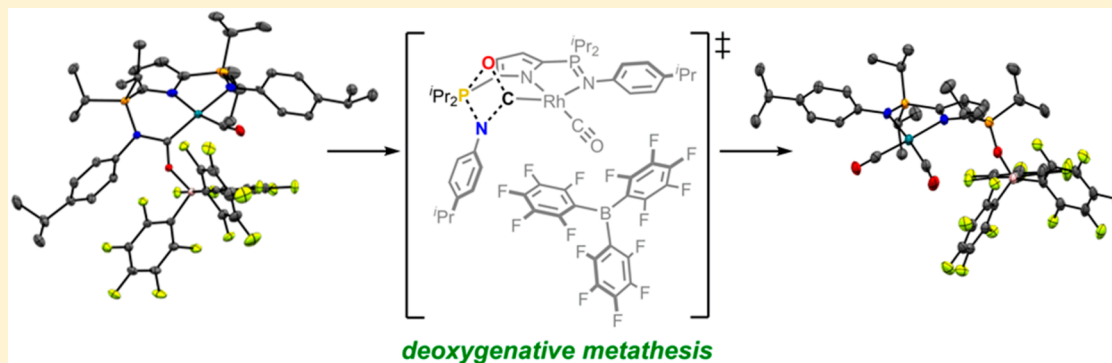# ORGANOMETALLICS

Communication

Facile Activation and Deoxygenative Metathesis of CO

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S Supporting Information

deoxygenative metathesis

ABSTRACT: The rhodium dicarbonyl complex $(^{iPr}NNN)Rh(CO)_2$ (1; ^{iPr}NNN = 2,5-$[^iPr_2P = N(4-^iPrC_6H_4)]_2N(C_4H_2)^-$) bearing a monoanionic NNN-pincer ligand was shown to promote the complete C−O bond scission of a carbonyl ligand with the addition of $B(C_6F_5)_3$ at ambient temperature. Characterization of the encounter complex $(^{iPr}NNN)Rh(CO)_2·B(C_6F_5)_3$ (3) by X-ray crystallography provided evidence to suggest a labile phosphinimine acts cooperatively with the borane to activate CO. Isotopic labeling with ^{13}CO indicated that a deoxygenative metathesis reaction between P−N and C−O atoms is operative, ultimately affording the CO-derived organic product $(C_6F_5)_3B←:C≡N(4-^iPrC_6H_4)$. To our knowledge, this work represents only the second example of a mononuclear transition-metal complex facilitating the deoxygenation of carbon monoxide.

The chemistry of C_1 oxygenates (CO, CO_2, CO_3^{2-}) defines the global carbon cycle and is intrinsically tied to energy production and consumption. Processes capable of converting CO_2 into value-added chemicals, specifically liquid hydrocarbon fuels (C_nH_{2n+2}), present an ongoing challenge in organometallic chemistry and industrial catalysis. Electro-catalytic reduction of CO_2 has been achieved,[1] providing an efficient route to CO; however, further deoxygenative transformations are rarely observed outside of cluster complexes and heterogeneous catalysts.[2] The first example of a well-defined mononuclear complex facilitating the complete activation of CO was reported in 2016 by Braunschweig and co-workers.[3] Given the considerable strength (1076 kJ mol^{-1}) of the C≡O triple bond,[4] reactions affecting deoxygenation are understandably limited under mild conditions. In studying the elementary steps of CO deoxygenation at a single-metal site, there is an opportunity to understand what variables affect reactivity which may aid in extending the knowledge of bond activation in general.

The complete scission of carbonyl ligands at molybdenum under reducing conditions has been known for decades. A representative example reported by Cummins and co-workers described the addition of electron equivalents (e.g., Na/Hg) to $(CO)Mo\{N(R)Ar\}_3$ followed by pivaloyl chloride, resulting in the formation of a carbido pivalate.[5] By leveraging the oxophilicity of carbon, and with the addition of Na metal in

THF, C−O bond scission was observed, resulting in the molybdenum methylidene $H(C)Mo\{N(R)Ar\}_3$. In a conceptually related report, KC_8 and oxophilic silyl cations (R_3Si^+) were combined to enact deoxygenative coupling of CO, leading to the release of C_2 products. In their landmark study, Agapie and Buss described the activation and cleavage of CO, leading to the formation of the terminal molybdenum carbide $L_nMo(C)(CO)$ (L_n = 1,4-bis(2-(diisopropylphosphino)-phenyl)benzene).[6] Subsequent C−C coupling generated metal-free ethynol derivatives $R_3SiOC≡CSiR_3$, (R = Me, ^iPr), providing an analogy to the synthesis of multicarbon products from CO and H_2.[7]

Isoelectronic with SiR_3^+, borane electrophiles (BR_3; R = Et, C_6F_5), introduced externally, or as the Lewis acidic component of phosphinoborane ligands ($Re−Ph_2P(CH_2)_nB(C_8H_{14})$; n = 1, 2), have also shown a propensity to activate metal−carbonyl ligands.[8] From their initial findings in this area, Bercaw and co-workers developed a working model for the reductive coupling of CO, demonstrating that a pendant borane directs the transfer of a nucleophilic hydride from $[HPt(dmpe)_2]^+$ to $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4]^+$ by activating the oxygen atom of the CO ligand.[9−11] More recently, Braunschweig reported that two Lewis acidic borylene boron atoms can

cooperatively activate and cleave a CO multiple bond.[3] Their work marked the first example of a single-site transition-metal complex facilitating complete CO bond scission. Notably, a distinguishing feature of the work is the fact that the deoxygenation reaction proceeds in the absence of explicit reducing agents (e.g., Na/Hg or KC_8). In addition, the authors claim that the zerovalent iron center exerts minimal influence on the observed chemistry.

Combinations of transition-metal fragments with reactive ligand environments capable of stabilizing CO in atypical bonding modes might lead to deoxygenation, and hence, the pursuit of such targets was of interest. Our work on the fundamental transformations of CO and other diatomics was piqued after we discovered a bifunctional ligand that enabled the heterolytic cleavage of H_2, affording a protonated phosphinimine and a bridging dirhodium hydride.[12] In a display of metal−ligand cooperation, H_2 could be liberated, affecting the hydrogenation of ethylene and other unactivated substrates.[12] In addition, work from Stephan's group has demonstrated the ability of phosphinimine−borane combinations to be effective in activating CO_2, alkynes, and H_2.[13] Recognizing this, we envisioned our phosphinimine-based ligand paired with a suitable borane that could mediate the activation of CO bound to a single electron-rich metal site, drawing inspiration from the success of FLP chemistry.[14−18]

Addition of the sodiated pincer ligand Na-^{iPr}NNN (^{iPr}NNN = 2,5-[$^iPr_2$P = N(4-^{i}PrC$_6$H$_4$)]$_2$N(C$_4$H$_2$)$^−$) to a toluene solution of 0.5 equiv of [Rh$_2$(μ-Cl)(CO)$_2$]$_2$ resulted in the formation of the rhodium dicarbonyl complex (^{iPr}NNN)Rh-(CO)$_2$ (**1**), wherein the ancillary ligand showcases κ^2-N,N bonding to the metal center through pyrrole and phosphinimine nitrogens (Figure 1). The rhodium monocarbonyl

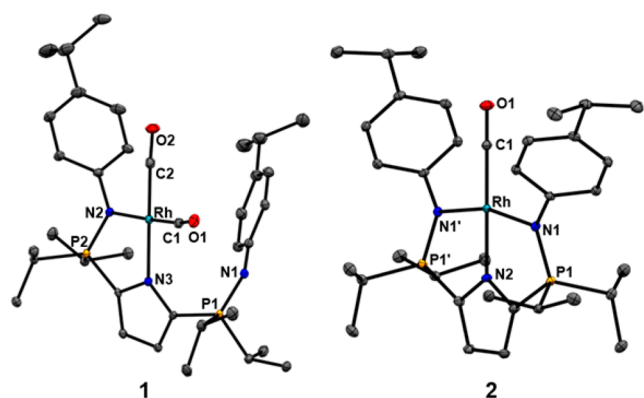**Figure 1.** X-ray crystal structures of (^{iPr}NNN)Rh(CO)$_n$ (n = 2, **1**; n = 1, **2**). Thermal ellipsoids are represented at 30% probability. Hydrogen atoms and solvent molecules of recrystallization are omitted for clarity. Selected bond distances (Å): **1**, P1−N1 = 1.562(2), P2−N2 = 1.612(2), C1−O1 = 1.149(4), C2−O2 = 1.139(4), Rh−C1 = 1.848(3), Rh−C2 = 1.847(4), Rh−N2 = 2.090(2), Rh−N3 = 2.094(2); **2**, P1−N1 = 1.629(3), C1−O1 = 1.149(6), Rh−N1 = 2.007(3), Rh−N2 = 2.111(2), Rh−C1 = 1.828(4).

complex (^{iPr}NNN)Rh(CO) (**2**), which contains the pincer ligand bound in a κ^3-N,N,N bonding motif, was identified as a minor impurity (5%). The ^{31}P NMR spectrum of complex **1** exhibits two resonances at δ 57.9 and 13.8 for the bound and free phosphinimine donors, respectively.[19] Two unique downfield ^{13}C NMR resonances for the CO ligands in **1** were observed at δ 186.3 (dd, $^1J_{CRh}$ = 68.5 Hz, $^2J_{CC}$ = 9.5 Hz)

and 184.7 (dd, $^1J_{CRh}$ = 69.3 Hz, $^2J_{CC}$ = 9.5 Hz) (Figure 2). Conversion of **1** to **2** was achieved by prolonged exposure of a
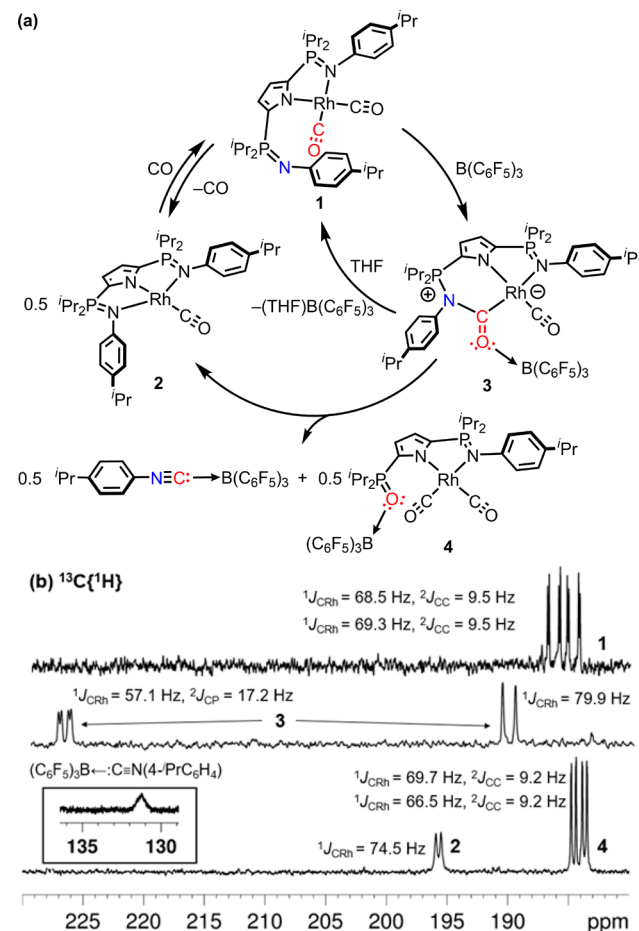

Figure 2. (a) Synthetic cycle for CO deoxygenation. (b) Downfield region of the ^{13}C{^{1}H} NMR spectra of isotopically labeled complexes **1−4**. Inset: partial ^{13}C{^{1}H} NMR spectrum of the organic product (C$_6$F$_5$)$_3$B←^{13}C≡N(4-^{i}PrC$_6$H$_4$).

stirred toluene solution of (^{iPr}NNN)Rh(CO)$_2$ to vacuum at 323 K. Complex **2** provides 7 ^{1}H and 11 ^{13}C NMR resonances, consistent with the expected C_{2v} symmetry. Dicarbonyl **1** can be regenerated by the condensation of excess CO onto a toluene solution of **2** at 77 K in aromatic solvents. The change in bonding mode from κ^2 to κ^3 is accompanied by a color change from red to bright yellow.

Reaction of the prototypical Lewis acid B(C$_6$F$_5$)$_3$ with (^{iPr}NNN)Rh(CO)$_2$ (**1**) yielded quantitative formation of a new product (**3**) in 15 min. The ^{31}P NMR spectrum of this compound exhibits two equal-intensity resonances at δ 58.8 and 54.2. Attempts to locate the ^{13}C signals associated with the CO ligands were initially unsuccessful, although a broad ^{11}B peak was found at δ −3.1. Together with $\Delta\delta_{m,p}$ = 3.8 ppm in the ^{19}F NMR spectrum, these data suggest the presence of a neutral four-coordinate borane.[20] Notably, at 243 K, the ^{19}F NMR spectrum contains 15 unique resonances, implying that B−C$_{aryl}$ bond rotation is slower than the NMR time scale.[21]

It could be reasoned that CO abstraction would give rise to the Lewis acid−base adduct (OC)B(C$_6$F$_5$)$_3$ and the monocarbonyl species (^{iPr}NNN)Rh(CO). In a contribution by Berke and Erker, the free energy change for the reaction B(C$_6$F$_5$)$_3$ + CO → (OC)B(C$_6$F$_5$)$_3$ was assigned a value of $\Delta G \approx$ +40 kJ

mol^{-1} at 298 K in the gas phase.[22] Furthermore, ^{31}P and ^{19}F NMR spectra are not consistent with the formation of (^{iPr}NNN)Rh(CO) and (OC)B(C$_6$F$_5$)$_3$. Irreversible CO abstraction from the metal was ruled out on the basis of the available evidence.

Recrystallization of complex **3** from a 1/1 pentane/toluene solution at 238 K gave bright yellow crystals suitable for X-ray diffraction. The structure revealed the identity of **3** to be the phosphinimine−borane-stabilized metalated formamide (^{iPr}NNN)Rh(CO)$_2$·B(C$_6$F$_5$)$_3$ (Figures 2a and 3), an encounter
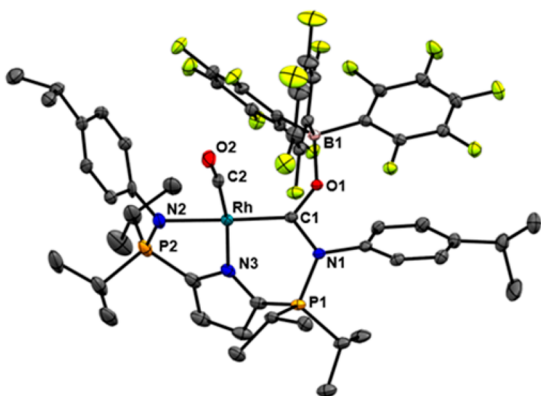

Figure 3. X-ray crystal structure of complex **3**. Thermal ellipsoids are represented at 30% probability. Hydrogen atoms and solvent molecules of recrystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): P1−N1 = 1.693(2), P2−N2 = 1.606(3), C1−O1 = 1.291(3), C2−O2 = 1.144(3), Rh−C1 = 1.958(2), Rh−C2 = 1.829(3), Rh−N2 = 2.131(2), Rh−N3 = 2.055(2), C1−N1 = 1.420(3), O1−B1 = 1.520(3), N1−C1−O1 = 106.2(2), Rh−C1−O1 = 130.9(2), N1−C1−Rh = 122.7(2).

complex between a carbonyl ligand and the Lewis acidic borane. CO activation is accompanied by formation of a new C−N bond (1.420(3) Å), completing a six-membered metallaheterocycle. This formulation in solution was verified spectroscopically, with $^2J_{PC}$ = 17.2 Hz in the ^{31}P NMR spectrum of a ^{13}CO-labeled sample of complex **3** (Figure 2b). Examination of the IR spectra of **3** and **3**-^{13}C provide ν(^{12}C≡O) and ν(^{13}C≡O) vibrations at 1993 and 1950 cm^{-1}, respectively. The isotopically labeled encounter complex thus shifts to lower frequency by 43 cm^{-1}, consistent with the predicted shift from the reduced mass calculation for a simple harmonic oscillator model (44 cm^{-1}).

Notably, **3** resembles the η^2-formyl complex Zr(η^5-C$_5$H$_5$)(BH$_4$)(HCOP^{i}Pr$_2$SiMe$_2$)N(SiMe$_2$CH$_2$P^{i}Pr$_2$BH$_3$), reported by Fryzuk, wherein a labile phosphine stabilizes a formyl ligand.[23] The unusual rhodium−carbon bond in **3** (Rh−C = 1.958(2) Å) compares well with the Fe−C^{carboxyl} σ bond (1.959(3) Å) in the Braunschweig CO bond scission product.[3]

Upon titrating in 1 equiv of THF to a benzene-d_6 solution of **3**, (^{iPr}NNN)Rh(CO)$_2$ and (THF)B(C$_6$F$_5$)$_3$ were observed, suggesting that the B−O interaction in **3** is weak. Moreover, an equilibrium mixture between **3** + THF and **1** + (THF)B(C$_6$F$_5$)$_3$ was not observed under any conditions. The C1−O1 distance of 1.291(3) Å is significantly lengthened relative to C1−O1 in (^{iPr}NNN)Rh(CO)$_2$ (1.149(4) Å) and is consistent with the bonding description of (^{iPr}NNN)Rh(CO)$_2$·B(C$_6$F$_5$)$_3$ depicted in Figure 2a. Formation of this so-called encounter complex also results in significant elongation of the P−N bond of the phosphinimine bound to CO (P1−N1 = 1.693(2) Å; cf.

P1−N1 = 1.562(2) Å in complex **1**).[24] In the solid state, boron adopts a tetrahedral geometry (average O−B−C$_{aryl}$ angle 107.3°). Further examination of the solid-state structure of **3** revealed a π-stacking interaction between one −C$_6$F$_5$ group and a proximal N-aryl ring, which is presumably responsible for the observed deviation from ideality (109.5°) in the O1−B1−C28 bond angle (101.3(2)°).

By monitoring the ^{31}P NMR spectrum in benzene-d_6 over time, it was found that complex **3** decomposes at ambient temperature ($t_{1/2} \approx$ 3 h). Prolonged heating at 323 K (18 h) led to complete consumption of **3** with concomitant formation of three new products, as confirmed by multinuclear NMR spectroscopy. The ^{31}P NMR spectrum exhibited resonances at δ 61.0 and 59.9 in a 1:1 ratio that were correlated by two-dimensional NMR experiments. In addition, a broad singlet (2P) was observed at δ 60.9. The ^{19}F NMR spectrum contained two sets of C$_6$F$_5$ resonances in a 1:1 ratio, suggesting the presence of two unique B(C$_6$F$_5$)$_3$-containing products. Notably, though, only one broad ^{11}B signal was evident (δ −21.2). These findings are consistent with a report by Stephan that describes phosphine oxide-B(C$_6$F$_5$)$_3$ adducts.[25] When this knowledge was combined with the recognition that external phosphinimines can react with metal carbonyl complexes,[26] a rhodium center ligated by a modified phosphinimine/phosphine oxide-borane adduct scaffold was the presumed fate of complex **3**.

By monitoring the products of thermal decay using labeled (^{iPr}NNN)Rh(^{13}O)$_2$·B(C$_6$F$_5$)$_3$, (**3**-^{13}C), unambiguous assignment of the relevant products in the apparent deoxygenation pathway was possible. The ^{13}C{^{31}P} NMR spectrum revealed four unique ^{13}CO resonances in a 1:1:1:1 ratio, attributed to three separate ^{13}CO-containing products, one of which possesses two chemically inequivalent Rh−^{13}CO ligands. Specifically, two multiplets were observed at δ 184.5 (dd, $^1J_{CRh}$ = 69.7 Hz, $^2J_{CC}$ = 9.2 Hz) and 183.6 (dd, $^1J_{CRh}$ = 66.5 Hz, $^2J_{CC}$ = 9.2 Hz), bearing striking resemblance to (^{iPr}NNN)Rh(^{13}CO)$_2$ (Figure 2b). In addition, a doublet was observed at δ 195.6 ($^1J_{CRh}$ = 74.5 Hz). This latter resonance can be assigned as the independently synthesized (^{iPr}NNN)Rh(CO). The final ^{13}C-labeled signal appears as a broad singlet centered at about δ 131.9 and is consistent with isocyanide-borane adducts described by Erker and Berke,[22] thus implying the formation of (C$_6$F$_5$)$_3$B←:^{13}C≡N(4-^{i}PrC$_6$H$_4$). Extraction and recrystallization from pentane confirmed the identity of this reaction byproduct (Figure 4a).

This distribution of products can be reasonably explained by a rate-determining deoxygenative metathesis between CO and the phosphinimine in complex **3** to liberate (C$_6$F$_5$)$_3$B←:CN(4-^{i}PrC$_6$H$_4$) and the putative 14-electron intermediate (Scheme 1) [^{i}Pr$_2$P═N(4-^{i}PrC$_6$H$_4$)C$_4$H$_2$N^{i}Pr$_2$P═O]Rh(CO), which would react rapidly with a second molecule of **3** to afford the phosphine oxide−borane adduct [^{i}Pr$_2$P═N-(4-^{i}PrC$_6$H$_4$)C$_4$H$_2$N^{i}Pr$_2$P═O→B(C$_6$F$_5$)$_3$]Rh(CO)$_2$ (**4**) and (^{iPr}NNN)Rh(CO) (**2**) in a 1:1 ratio (Figure 2a). The structure of **4** highlights the differences between phosphine oxide and phosphinimine donors (Figure 4b). The pronounced ylidic nature of the P−N bond facilitates C−O activation as well as deoxygenative metathesis akin to Wittig reactions between carbonyl substrates and ylidic P−C bonds.

The ^{iPr}NNN ligand reported herein serves as a platform to study the activation and deoxygenative coupling of CO at ambient temperature without the addition of reducing agents.
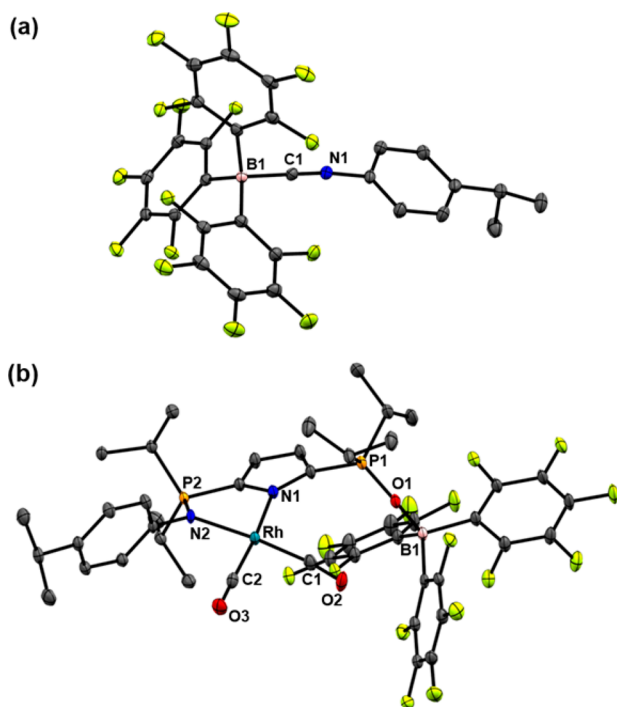
Figure 4. (a) X-ray crystal structure of the organic product of deoxygenation, $(C_6F_5)_3B\leftarrow:C\equiv N(4\text{-}^iPrC_6H_4)$. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms and solvent molecules of recrystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): B1–C1 = 1.627(3), C1–N1 = 1.143(2), B1–C1–N1 = 174.6(2). (b) X-ray crystal structure of complex **4**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms and solvent molecules of recrystallization are omitted for clarity. Selected bond distances (Å) and angles (deg): P1–O1 = 1.532(2), P2–N2 = 1.613(2), C2–O3 = 1.127(3), C1–O2 = 1.135(4), Rh–C1 = 1.850(3), Rh–C2 = 1.865(3), Rh–N1 = 2.110(2), Rh–N2 = 2.070(2), O1–B1 = 1.535(3), P1–O1–B1 = 147.3(2).

Scheme 1. Proposed Steps in CO Deoxygenation
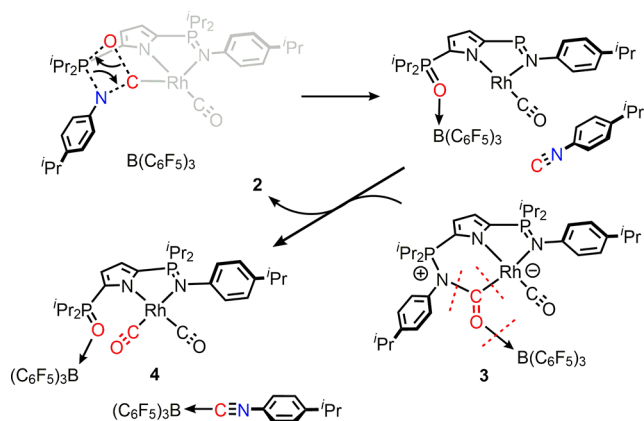
The metathetical reaction between the phosphinimine P–N ylide and the CO multiple bond was confirmed by isotopic labeling with ^{13}CO, along with characterization of the labeled isocyanide $(C_6F_5)_3B\leftarrow:^{13}C\equiv N(4\text{-}^iPrC_6H_4)$. Cooperative action of the phosphinimine and borane Lewis acid appear to promote the deoxygenation reaction with minimal influence from the metal center.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.organomet.8b00652](#).

Experimental details, characterization data, and structural data for H-^{iPr}NNN, complexes **1–4**, (^{Ph}NNN)Rh-$(CO)_2$, (^{Ph}NNN)Rh(CO), and $(C_6F_5)_3B\leftarrow:C\equiv N$-$(4\text{-}^iPrC_6H_4)$ ([PDF](#))

Accession Codes

CCDC [1822708–1822715](#) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data_request/cif](#), or by emailing [data_request@ccdc.cam.ac.uk](#), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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