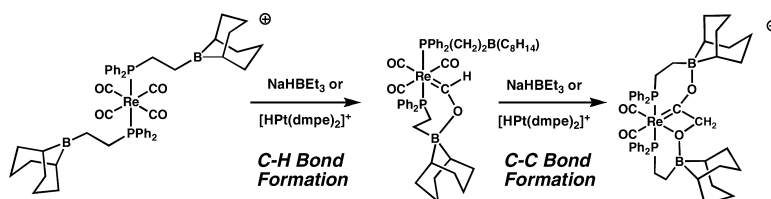


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Reductive Coupling of Carbon Monoxide in a Rhenium Carbonyl Complex with Pendant Lewis Acids

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Synthesis gas, a mix of CO and H₂, could become a key part of the global energy landscape as an intermediate in converting methane and coal to fuels or chemical feedstocks.¹ The heterogeneous Fischer–Tropsch (F–T) process, which converts syngas to a complex mixture of hydrocarbons and oxygenates and operates at 473–623 K, is becoming economically competitive as crude oil prices rise.^{2,3} During the oil crisis of the 1970s, there was much interest in developing homogeneous F–T chemistry, hoping to achieve lower temperatures and greater selectivities.⁴ Since then, however, there have been only scattered reports of homogeneous catalytic syngas-to-C₂ conversion, all under high temperature and/or high pressure conditions.^{5,6}

The difficulty of forming a C–H bond from coordinated CO appears to be a major obstacle to this approach. Stoichiometric reductions of group 6–8 metal carbonyls have been achieved with strong main group^{7,8} and early transition metal⁹ hydrides, with production of C₂ organics in the case of [CpFe(CO)₃]⁺.¹⁰ Such catalytically impractical reagents would need to be replaced with hydrides that can be formed from H₂; DuBois has shown that certain group 10 hydrides may be promising candidates.¹¹ Another challenge is the facile formation of a C–C bond from a reduced carbonyl species. Exogenous Lewis acids¹² and amphoteric additives¹³ have previously been shown to accelerate alkyl migration reactions, but reductive coupling of CO itself is unusual.¹⁴

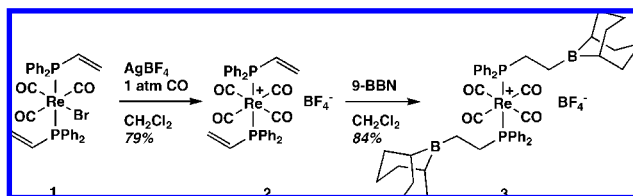
We have sought to address both of these challenges with a single design element: the incorporation of a Lewis acidic borane in the secondary coordination sphere of a rhenium carbonyl complex. We report here that this pendant Lewis acid facilitates the delivery of multiple hydride equivalents—from both main group and late transition metal hydrides—to a CO ligand, followed by spontaneous alkyl migration to form a C–C bond.

Phosphinoborane¹⁵ complex **3** was constructed as shown in Scheme 1.¹⁶ Commercially available diphenylvinylphosphine was metallated with Re(CO)₅Br at 120 °C in toluene in a sealed vessel, yielding *mer,trans*-(Ph₂PC₂H₃)₂Re(CO)₃Br (**1**) as a white powder in good yield. Treatment of **1** with AgBF₄ followed by 1 atm of CO afforded cationic *trans*-[(Ph₂PC₂H₃)₂Re(CO)₄][BF₄] (**2**). Hydroboration with 9-BBN (9-borabicyclo[3.3.1]nonane) proceeded over 48 h at 70 °C to afford the desired product *trans*-[(Ph₂P(CH₂)₂B(C₈H₁₄))₂Re(CO)₄][BF₄] (**3**).

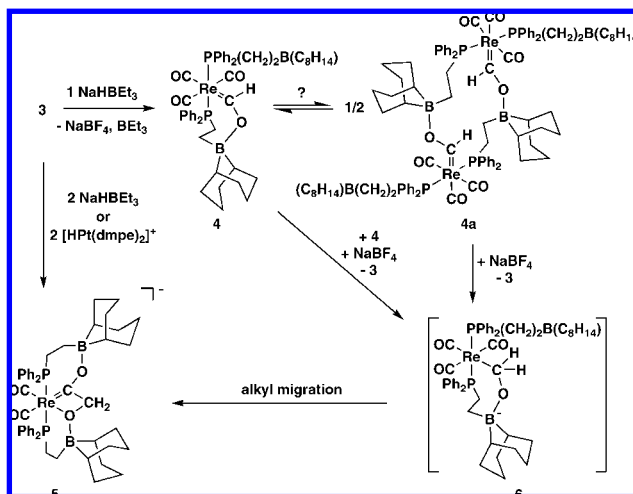
An X-ray diffraction (XRD) study confirmed the expected structure of **3** (Figure S1). As strongly donating solvents were avoided throughout the synthesis of **3**, the boron centers in the 9-BBN groups remain three-coordinate. The IR spectrum of **3** shows a single CO stretch at 1998 cm⁻¹, similar to the PPh₃ analogue [(PPh₃)₂Re(CO)₄][BF₄] (ν_{CO} = 2000 cm⁻¹).¹⁷

The pendant borane makes cation **3** a markedly better hydride acceptor despite the similar stretching frequencies.¹⁸ Addition of 1 equiv of [HPT(dmpe)₂][PF₆] (dmpe = 1,2-bis(dimethylphosphino)ethane) in either C₆D₅Cl or 1,2-C₆H₄F₂ leads to a new proton

Scheme 1



Scheme 2



resonance at δ 13.95 and precipitation of [Pt(dmpe)₂]²⁺. [(PPh₃)₂Re(CO)₄]⁺ does not react with [HPT(dmpe)₂]⁺, and even addition of BEt₃ (10 equiv) affords only ~1% conversion, highlighting the importance of the tethered borane.

We attribute the downfield NMR signal to a neutral boroxycarbene such as **4** (Scheme 2), formed in 60–70% yield. In hopes of achieving complete conversion, 1 equiv of NaHBET₃ (in toluene) was added to a C₆H₅Cl solution of **3**, affording a yellow solution which showed quantitative formation of **4**, as assessed by ³¹P{¹H} NMR, IR, and the unique ¹H NMR resonance at δ 13.95. Decomposition with formation of the starting material **3** and an unknown species took place over several days. Performing the hydride addition in CD₂Cl₂ also gave the NMR signal (along with additional products that may include Re–Cl species), and colorless crystals grew overnight. An XRD study verified that the boroxycarbene feature was present, but the structure so obtained is bimetallic **4a**, with the oxygen of the carbene on one rhenium interacting with the boron from the other, generating a 14-membered cycle (Figure 1).

Attempts to crystallize **4** by vapor diffusion of Et₂O into a C₆H₅Cl solution took days but eventually yielded colorless plates; XRD revealed transformation to complex **5** (Scheme 2), a novel boroxy-(boroxymethyl)carbene generated by formation of a new C–C bond.

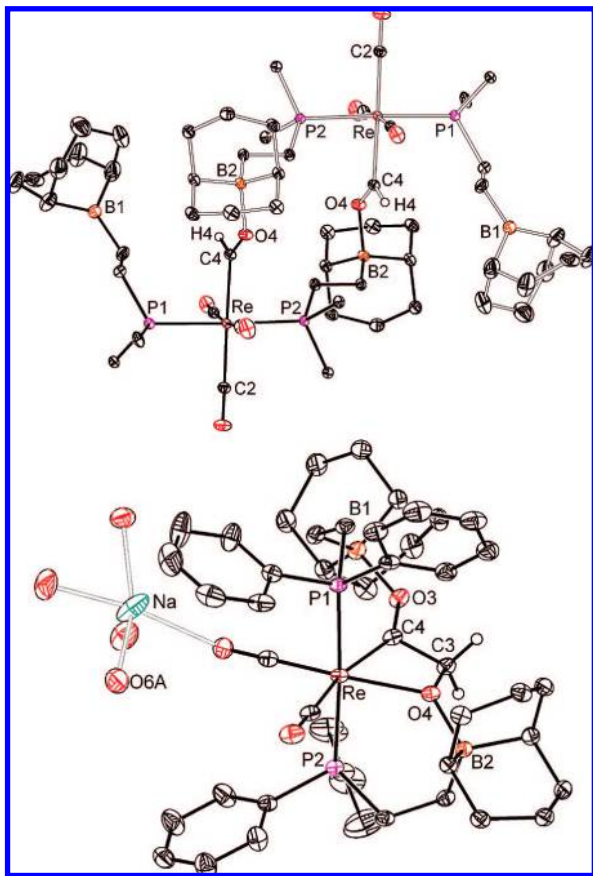


Figure 1. XRD structural representation (50% ellipsoids) of **4a**·CH₂Cl₂ (top) and **5**·3.5 THF·0.5 Et₂O (bottom). Most hydrogens omitted for clarity. In **4a**·CH₂Cl₂, solvent molecules are omitted and phenyl rings are trimmed for clarity. In **5**·3.5 THF·0.5 Et₂O, carbons from disordered Na-coordinated solvent are omitted. Selected bond lengths (Å) and angles (deg). **4a**: Re–C4 2.118(1), C4–O4 1.253(1), O4–B2 1.612(1), Re–C4–O4 126.12(8), C4–O4–B2 126.87(8). **5**: Re–C4 2.096(9), Re–O4 2.232(7), C4–O3 1.271(1), C3–C4 1.513(1), C3–O4 1.423(1), Re–C4–O3 147.27(7), C4–C3–O4 102.79(7).

The oxygen of the boroxymethyl group coordinates to rhenium, forming three rhenacycles of 7, 4, and 6 members; a sodium cation bound by ether molecules interacts with one of the two remaining CO ligands (Figure 1 and S2).¹⁹

We propose that **5** is the product of alkyl migration to CO in an unobserved Re–CH₂–O–BR₃ intermediate (**6**). Complex **6** could be formed by disproportionation of **4**, via intramolecular²⁰ hydride transfer, to yield the boroxymethyl intermediate **6** and tetracarbonyl cation **3** (Scheme 2). (The decanted supernatant after crystallization of **5** indeed contained predominantly **3**, along with some residual **5**.) It is notable that no additional CO or other ligand is needed to induce alkyl migration.

Addition of 2 equiv of NaHBET₃ to a C₆H₅Cl solution of **3** resulted in the immediate precipitation of **5** in 80–95% isolated yield. (In contrast, [(PPh₃)₂Re(CO₄)]⁺ yields a formyl with 1 equiv of NaHBET₃¹⁷ but does not react further with excess borohydride.) This preparation allowed full characterization of **5**. The asymmetry shown in the crystal structure is evident by NMR as well, with two doublets (12.0, 17.7 ppm) in the ³¹P{¹H} NMR and complex aromatic and aliphatic regions in the ¹H NMR; the [CH₂O] group resonates as two doublets at 4.55 and 4.64 ppm. The infrared spectrum of **5** exhibits two CO stretches at 1848 and 1933 cm⁻¹, consistent with a relatively electron-rich species. The carbenoid nature of **5** is apparent in the ¹³C{¹H} NMR spectrum, with a characteristic doublet of doublets at 303.4 ppm.

It is noteworthy that the conversion of **3** to **5** can also be carried out with 2 equiv of [HPt(dmpe)₂]⁺, in slightly lower yield (~70%). Since the Pt hydride can be performed externally by heterolytic cleavage of H₂ in the presence of a suitable base (KOPh or tetramethylguanidine),²¹ this transformation amounts to the net formation of a C₂ species from intermediates directly obtainable from CO and H₂.

In summary, we have found that incorporation of a borane into the secondary coordination sphere of a rhenium carbonyl complex fundamentally alters reactivity by facilitating hydride transfer, permitting a group 10 transition metal hydride generated from H₂ to serve as hydride source, and promoting C–C bond formation by alkyl migration, even in the absence of a strong donor. Ongoing work is focused on further lowering the barrier to hydride transfer as well as developing methods for liberation of the C₂ organic fragment and closing a catalytic cycle.

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Supporting Information Available: Full details on synthesis and characterization for compounds **1–5**, NMR experiments, and crystallographic information are available. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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- (18) ν_{CO} can be roughly correlated with hydride acceptor ability: e.g., [Cp*Re(CO)₂(NO)]⁺ (ν_{CO} = 2092, 2036 cm⁻¹) reacts with group 10 hydrides,¹¹ while [(PPh₃)₂Re(CO)₄]⁺ (ν_{CO} = 2000 cm⁻¹) does not.
- (19) The structure shown in Figure 1 was obtained from isolated **5**, which yielded the solvate **5**·3.5 THF·0.5 Et₂O from THF/Et₂O vapor diffusion. The structure is of higher quality than the one obtained from the solvate **5**·3 Et₂O, grown from the disproportionation reaction, Figure S2.
- (20) Or intermolecular, as **4** may not be dimeric in solution. The XRD structure of **4a** shows the two carbene carbons in the 14-membered ring separated by 5 Å, which could allow facile hydride transfer from one to the other.
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