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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 H_2, 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-C_2 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 metal[9] hydrides, with production of C_2 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 H_2; 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 acids[12] and amphoteric additives[13] have previously been shown to accelerate alkyl migration reactions, but reductive coupling of CO itself is unusual.[14]

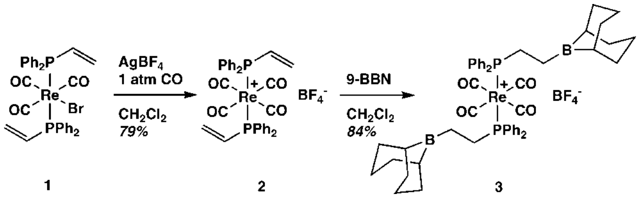
We have sought to address both of these challenges with a single design element: the incorporation of a Lewis acidic borane in the secondary coordination sphere of a rhenium carbonyl complex. We report here that this pendant Lewis acid facilitates the delivery of multiple hydride equivalents—from both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

Phosphinoborane[15] 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*-$(Ph_2PC_2H_3)_2Re(CO)_3Br$ (**1**) as a white powder in good yield. Treatment of **1** with $AgBF_4$ followed by 1 atm of CO afforded cationic *trans*-$[(Ph_2PC_2H_3)_2Re(CO)_4][BF_4]$ (**2**). Hydroboration with 9-BBN (9-borabicyclo[3.3.1]nonane) proceeded over 48 h at 70 °C to afford the desired product *trans*-$[(Ph_2P(CH_2)_2B(C_8H_{14}))_2$-$Re(CO)_4][BF_4]$ (**3**).

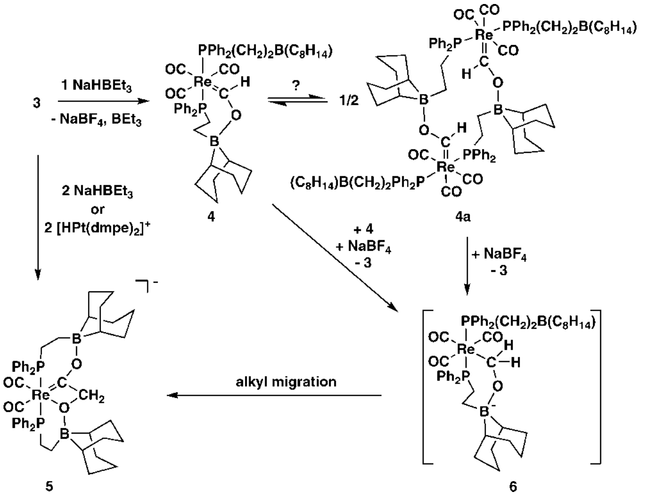
An X-ray diffraction (XRD) study confirmed the expected structure of **3** (Figure S1). As strongly donating solvents were avoided throughout the synthesis of **3**, the boron centers in the 9-BBN groups remain three-coordinate. The IR spectrum of **3** shows a single CO stretch at 1998 cm^{-1}, similar to the PPh_3 analogue $[(PPh_3)_2Re(CO)_4][BF_4]$ ($\nu_{CO} = 2000\ cm^{-1}$).[17]

The pendant borane makes cation **3** a markedly better hydride acceptor despite the similar stretching frequencies.[18] Addition of 1 equiv of $[HPt(dmpe)_2][PF_6]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) in either C_6D_5Cl or 1,2-$C_6H_4F_2$ leads to a new proton resonance at δ 13.95 and precipitation of $[Pt(dmpe)_2]^{2+}$. $[(PPh_3)_2Re(CO)_4]^+$ does not react with $[HPt(dmpe)_2]^+$, and even addition of BEt_3 (10 equiv) affords only ~1% conversion, highlighting the importance of the tethered borane.

Scheme 1



Scheme 2



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 $NaHBEt_3$ (in toluene) was added to a C_6H_5Cl solution of **3**, affording a yellow solution which showed quantitative formation of **4**, as assessed by $^{31}P\{^1H\}$ 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 CD_2Cl_2 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 Et_2O into a C_6H_5Cl 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.

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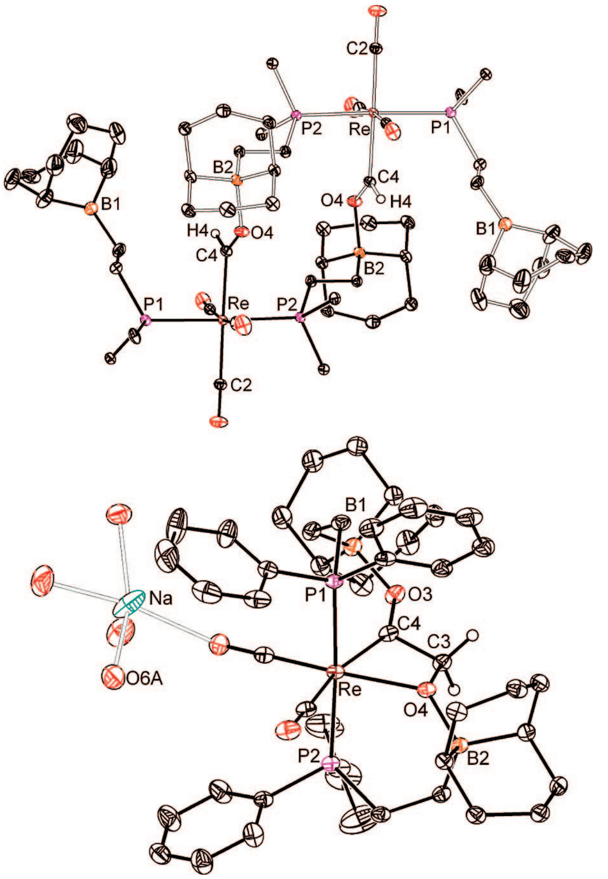

Figure 1. XRD structural representation (50% ellipsoids) of **4a**·CH_2Cl_2 (top) and **5**·3.5 THF·0.5 Et_2O (bottom). Most hydrogens omitted for clarity. In **4a**·CH_2Cl_2, solvent molecules are omitted and phenyl rings are trimmed for clarity. In **5**·3.5 THF·0.5 Et_2O, carbons from disordered Na-coordinated solvent are omitted. Selected bond legnths (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 2.0960(9), Re−O4 2.2322(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−CH_2−O−BR_3 intermediate (**6**). Complex **6** could be formed by disproportionation of **4**, via intramolecular[20] 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 $NaHBEt_3$ to a C_6H_5Cl solution of **3** resulted in the immediate precipitation of **5** in 80−95% isolated yield. (In contrast, $[(PPh_3)_2Re(CO_4)]^+$ yields a formyl with 1 equiv of $NaHBEt_3$[17] 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 $^{31}P\{^1H\}$ NMR and complex aromatic and aliphatic regions in the ^1H NMR; the [CH_2O] 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 $^{13}C\{^1H\}$ 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 preformed externally by heterolytic cleavage of H_2 in the presence of a suitable base (KOPh or tetramethylguanidine),[21] this transformation amounts to the net formation of a C_2 species from intermediates directly obtainable from CO and H_2.

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 H_2 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 C_2 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 $[(PPh_3)_2Re(CO)_4]^+$ (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 Et_2O from THF/Et_2O vapor diffusion. The structure is of higher quality than the one obtained from the solvate **5**·3 Et_2O, 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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