

# Homogeneous CO Hydrogenation: Ligand Effects on the Lewis Acid-Assisted Reductive Coupling of Carbon Monoxide

Alexander J. M. Miller, Jay A. Labinger,\* and John E. Bercaw\*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

Received July 1, 2010

Structure-function studies on the role of pendent Lewis acids in the reductive coupling of CO are reported. Cationic rhenium carbonyl complexes containing zero, one, or two phosphinoborane ligands  $(Ph_2P(CH_2)_nB(C_8H_{14}), n = 1-3)$  react with the nucleophilic hydride  $[HPt(dmpe)_2]^+$  to reduce  $[M-CO]^+$  to M-CHO; this step is relatively insensitive to the Lewis acid, as both pendent (internal) and external boranes of appropriate acid strength can be used. In contrast, whether a second hydride transfer and C-C bond forming steps occur depends strongly on the number of carbon atoms between P and B in the phosphinoborane ligands, as well as the number of pendent acids in the complex: shorter linker chain lengths favor such reductive coupling, whereas longer chains and external boranes are ineffective. A number of different species containing partially reduced CO groups, whose exact structures vary considerably with the nature and number of phosphinoborane ligands, have been crystallographically characterized. The reaction of  $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4]^+$  with  $[HPt(dmpe)_2]^+$  takes place via a "hydride shuttle" mechanism, in which hydride is transferred from Pt to a pendent borane and thence to CO, rather than by direct hydride attack at CO. Addition of a second hydride in  $C_6D_5Cl$  at -40 °C affords an unusual anionic bis(carbene) complex, which converts to a C-C bonded product on warming. These results support a working model for Lewis acid-assisted reductive coupling of CO, in which B (pendent or external) shuttles hydride from Pt to coordinated CO, followed by formation of an intramolecular B–O bond, which facilitates reductive coupling.

#### Introduction

Many of the approaches under active investigation for obtaining fuels and commodity chemicals from coal, methane, or biomass follow an indirect route via synthesis gas (syngas, CO/H<sub>2</sub>), typified by the Fischer–Tropsch (F-T) process.<sup>1,2</sup> Selective conversion of syngas to discrete multicarbon hydrocarbons or oxygenates could offer substantial improvements over nonselective F-T.<sup>3</sup> The possibility that homogeneous catalysis might provide more promising opportunities for selective transformations has intrigued organometallic chemists for several decades.<sup>4</sup> A number of plausible reaction intermediates, such as formyl<sup>5</sup> and hydroxymethyl<sup>5d,6</sup> groups, have been synthesized by reaction of main group metal hydrides with metal carbonyls; in some cases sequential reduction and protonation of mid to late transition metal carbonyls resulted in the release of  $C_2$  and higher organics.<sup>4c,7</sup> Unfortunately, those hydrides are not readily obtainable from  $H_2$  and are incompatible with the strong acids required, precluding catalysis. Some early transition metal species (and their f-block congeners) that *can* be formed directly from  $H_2$ ,<sup>8</sup> such as  $Cp*_2ZrH_2$ ,<sup>4d</sup> can effect both CO reduction and C–C coupling, but the extremely strong M–O bonds thus generated will again preclude catalysis. A few examples of homogeneous catalytic conversion of syngas to methanol and C<sub>2</sub> products (EtOH, ethylene

<sup>\*</sup>To whom correspondence should be addressed. E-mail: jal@ caltech.edu; bercaw@caltech.edu.

<sup>(1)</sup> Khodakov, A. Y.; Chu, W.; Fongarland, P. Chem. Rev. 2007, 107, 1692.

<sup>(2)</sup> Rofer-DePoorter, C. K. Chem. Rev. 1981, 81, 447.

<sup>(3)</sup> United Nations Development Program. *World Energy Assessment Report: Energy and the Challenge of Sustainability*; United Nations, New York, 2000.

<sup>(4) (</sup>a) Gladysz, J. A. Adv. Organomet. Chem. 1982, 20, 1. (b) Herrmann,
W. A. Angew. Chem., Int. Ed. 1982, 21, 117. (c) Cutler, A. R.; Hanna, P. K.;
Vites, J. C. Chem. Rev. 1988, 88, 1363. (d) Wolczanski, P. T.; Bercaw, J. E. Acc. Chem. Res. 1980, 13, 121.

<sup>(5) (</sup>a) Collman, J. P.; Winter, S. R. J. Am. Chem. Soc. 1973, 95, 4089.
(b) Casey, C. P.; Neumann, S. M. J. Am. Chem. Soc. 1976, 98, 5395. (c) Tam,
W.; Wong, W.-K.; Gladysz, J. A. J. Am. Chem. Soc. 1979, 101, 1589.
(d) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. J. Am. Chem. Soc. 1980, 102, 1927.

<sup>(6)</sup> Sweet, J. R.; Graham, W. A. G. J. Am. Chem. Soc. 1982, 104, 2811.
(7) Brown, S. L.; Davies, S. G. J. Chem. Soc., Chem. Commun. 1986, 84.

<sup>(8) (</sup>a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. J. Am. Chem. Soc. 1978, 100, 2716. (b) Fagan, P. J.; Moloy, K. G.; Marks, T. J. J. Am. Chem. Soc. 1981, 103, 6959. (c) Gambarotta, S.; Floriani, C.; Chiesivilla, A.; Guastini, C. J. Am. Chem. Soc. 1983, 105, 1690. (d) Evans, W. J.; Grate, J. W.; Doedens, R. J. J. Am. Chem. Soc. 1985, 107, 1671. (e) Miller, R. L.; Toreki, R.; Lapointe, R. E.; Wolczanski, P. T.; Vanduyne, G. D.; Roe, D. C. J. Am. Chem. Soc. 1993, 115, 5570. (f) Werkema, E. L.; Maron, L.; Eisenstein, O.; Andersen, R. A. J. Am. Chem. Soc. 2007, 129, 2529. (g) Shima, T.; Hou, Z. J. Am. Chem. Soc. 2006, 128, 8124.



glycol) have been reported, but extremely high pressures and temperatures are required.<sup>9</sup>

Our renewed interest in this approach<sup>10</sup> was inspired by the discovery that late transition metal hydrides [HM(PP)<sub>2</sub>]<sup>+</sup> (M = Ni, Pd, Pt; PP = chelating diphosphine ligand), whichmay be formed directly from H<sub>2</sub> by heterolytic activation,<sup>1</sup> can form C-H bonds by facile nucleophilic attack on metal carbonyl complexes.<sup>12</sup> Because these metals should not form prohibitively strong M-O bonds, we proposed that a dual system, consisting of the late transition metal hydrogen activator along with a relatively electrophilic metal carbonyl complex (probably from the middle of the transition series, where C-H bond formation is well documented<sup>4a,c,5,12a</sup>), could lead to catalytic conversion, perhaps as shown in Scheme 1. We<sup>10b</sup> and others<sup>13</sup> have demonstrated stoichiometric versions of Scheme 1, but the various steps operate under conditions that are mutually incompatible; in particular, some steps require very strong acids or other electrophiles that would react with hydride sources.

In order to overcome the problems posed by strong hydride reductants, we designed metal carbonyl complexes with pendent Lewis acids. Lewis acid promotion of reductions



of organic carbonyls<sup>14</sup> and alkyl migratory insertions of coordinated CO<sup>15</sup> is well known; participation of Lewis acids in homogeneous catalytic CO reduction<sup>9b</sup> and heterogeneous F-T chemistry<sup>16</sup> has also been proposed. The additional advantage of intramolecular attachment could make conversion possible with a relatively weak acidic center, which might not be sufficiently activating as a separate promoter. A demonstration of this concept was achieved by positioning a trialkylborane center in the secondary coordination sphere of a carbonyl cation, affording the transformations shown in Scheme 2.<sup>10a</sup> Analogous chemistry is not observed in the absence of pendent Lewis acids.

While alkylborane-based systems are probably not viable catalysts because of strong B-O bonding, they do provide an excellent framework for investigating some of the key issues arising from this approach. In particular, which factors affect how the chelate effect operates? How does reactivity depend on the length of the tether connecting the borane to the metal center? Can an external borane promote the same transformations? What happens if there is only one Lewis acid center attached instead of two? We would also like to learn something about the fundamental mechanism of this transformation: how is hydride transferred from Pt to C, and how does C-C bond formation take place? We report here on our findings.

#### **Results and Discussion**

**Reduction of**  $[(PPh_3)_2Re(CO)_4]^+$  ( $[1-Ph_2]^+$ ). The chemistry of  $[(PPh_3)_2Re(CO)_4]^+$  ( $[1-Ph_2]^+$ ) with  $[HPt(dmpe)_2]^+$  ( $[HPt]^+$ ; dmpe = 1,2-bis(dimethylphosphino)ethane; see Chart 1 for the system used for abbreviations) in the absence and presence of added external Lewis acids is summarized in Scheme 3.

<sup>(9) (</sup>a) Dombek, B. D. Adv. Catal. **1983**, *32*, 325. (b) Demitras, G. C.; Muetterties, E. L. J. Am. Chem. Soc. **1977**, *99*, 2796.

<sup>(10) (</sup>a) Miller, A. J. M.; Labinger, J. Á.; Bercaw, J. E. J. Am. Chem. Soc. **2008**, 130, 11874. (b) Elowe, P. R.; West, N. M.; Labinger, J. A.; Bercaw, J. E. Organometallics **2009**, 28, 6218. (c) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc. **2010**, 132, 3301.

<sup>(11)</sup> The hydride used in this work,  $[HPt(dmpe)_2][PF_6]$ , is more easily isolated when prepared from NaBH<sub>4</sub>. This synthetic route was used rather than direct formation from H<sub>2</sub>, as detailed in the Supporting Information.

<sup>(12) (</sup>a) Miedaner, A.; DuBois, D. L.; Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1993**, *12*, 299. (b) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918. (c) DuBois, M. R.; DuBois, D. L. *Chem. Soc. Rev.* **2009**, *38*, 62.

<sup>(13)</sup> Crawford, E. J.; Bodnar, T. W.; Cutler, A. R. J. Am. Chem. Soc. 1986, 108, 6202.

<sup>(14)</sup> Yamamoto, H. Lewis Acids in Organic Synthesis; Wiley-VCH: Weinheim, 2000.

<sup>(15) (</sup>a) Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.;
Stimson, R. E.; Shriver, D. F. J. Am. Chem. Soc. 1979, 101, 5864.
(b) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.;
Shriver, D. F. J. Am. Chem. Soc. 1980, 102, 5093. (c) Labinger, J. A.; Miller,
J. S. J. Am. Chem. Soc. 1982, 104, 6856. (d) Grimmett, D. L.; Labinger,
J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. J. Am. Chem.
Soc. 1982, 104, 6858. (e) Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.;
Masuo, S. T.; Shearin, E.; Miller, J. S. Organometallics 1983, 2, 733.

<sup>(16)</sup> Maitlis, P. M.; Zanotti, V. Chem. Commun. 2009, 1619.



A solution of [1-Ph2][BPh4] and [HPt][PF6] in C6D5Cl shows no discernible reaction over 24 h, although it should be noted that  $[1-Ph_2][BPh_4]$  is only slightly soluble in C<sub>6</sub>D<sub>5</sub>Cl.<sup>10a</sup> In addition, the choice of anion can play an important role in reductions using [HPt]<sup>+</sup>: as previously reported, the equilibrium shown in Scheme 4 lies far toward the left side (unreduced  $[1-E_2]^+$ ), but can be driven to the right by precipita-tion of  $[Pt][BF_4]_x[PF_6]_{2-x}$ .<sup>10c</sup> Suspensions of  $[1-Ph_2][BF_4]$ (also fairly insoluble) and  $[HPt][PF_6]$  in C<sub>6</sub>D<sub>5</sub>Cl or THF slowly convert to a mixture of (PPh<sub>3</sub>)<sub>2</sub>Re(CO)<sub>3</sub>(CHO) (2-**Ph<sub>2</sub>**; <sup>1</sup>H NMR ReCHO,  $\delta$  15.22 in C<sub>6</sub>D<sub>5</sub>Cl), (PPh<sub>3</sub>)<sub>2</sub>Re- $(CO)_{3}(H)$  (4-Ph<sub>2</sub>), and (PPh<sub>3</sub>)Re(CO)<sub>4</sub>(H) (4-Ph<sub>1</sub>).<sup>17</sup> The halflife for consumption of  $[HPt]^+$  is 2–4 days, and the yield of **2-Ph<sub>2</sub>** never exceeds  $\sim 5\%$  (by NMR, relative to [HPt]<sup>+</sup>). Therefore, while the unassisted transfer of a hydride from  $[HPt]^+$  to  $[1-Ph_2]^+$  can be observed, it appears to be thermodynamically unfavorable, unless driven by precipitation of the  $[\mathbf{Pt}]^{2+}$  salt, and is kinetically so slow that decarbonylation

to the Re-H products dominates, preventing formation of more than a very small amount of formyl complex.

[Pt]<sup>2+</sup>

c<sub>o</sub>

2-E<sub>2</sub>

Addition of isopropyl pinacol borate, a weak Lewis acid, has no effect on the above reaction: only traces of the characteristic <sup>1</sup>H NMR formyl signal for **2-Ph**<sub>2</sub> are observed, at an essentially unchanged chemical shift (ReCHO,  $\delta$  15.21), which indicates no interaction between the formyl oxygen and the boron center. In contrast, a solution of [**1-Ph**<sub>2</sub>][BF<sub>4</sub>] with [**HPt**][PF<sub>6</sub>] and 2 equiv of 'Bu(CH<sub>2</sub>)<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>) in C<sub>6</sub>D<sub>5</sub>Cl shows clean conversion to a formyl species in a couple of hours.<sup>18</sup> The Re–CHO

<sup>(17)</sup> See Supporting Information for full details.

<sup>(18)</sup> When  $[1-Ph_2][BAr^F_4]$  was treated with  $[HPt][PF_6]$  in the presence of 2 or 10 equiv of BEt<sub>3</sub> (1.0 M in hexanes), only ~1% boroxycarbene was detected, and no further reaction was observed over ~24 h, consistent with inhibition of reduction by small amounts of  $[Pt][BAr^F_4]_2$  in solution.



Figure 1. Structural representation of  $(2-Ph_2 \cdot BEt_3) \cdot (C_6H_5CH_3)$  with thermal ellipsoids at 50% probability. Only one of the two independent molecules in the asymmetric unit is portrayed; the bond lengths and angles are similar. H atoms (except on the carbene) and two toluene solvent molecules of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re2–C4B 2.126(3), Re–CO(av) 1.985, C4B–O4B 1.252(3), O4B–B1B 1.638(3), Re2–C4B–O4B 125.2(2), C4B–O4B–B1B 129.2(2).

resonance ( $\delta$  14.60) is shifted well upfield from that observed for the Lewis acid-free reaction, and the <sup>31</sup>P NMR resonance also differs ( $\delta$  14.5, vs  $\delta$  15.8 in the absence of borane), indicating significant interaction between the borane and the formyl ligand. Treatment of [**1-Ph**<sub>2</sub>]<sup>+</sup> with NaHBEt<sub>3</sub> gave a spectroscopically similar product, which was structurally characterized by X-ray diffraction (XRD) as the boroxycarbene (PPh<sub>3</sub>)<sub>2</sub>Re(CO)<sub>3</sub>(CHOBEt<sub>3</sub>) (**2-Ph**<sub>2</sub>•**BEt**<sub>3</sub>) (Figure 1). In comparison to analogous adducts of the stronger Lewis acids BF<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>10b</sup> the boroxycarbene moiety in **2-Ph**<sub>2</sub>•**BEt**<sub>3</sub> has longer B–O and Re–C bonds and a shorter C–O bond, consistent with less carbene character<sup>19</sup> and a weaker B–O interaction. Accordingly, the BEt<sub>3</sub> can be removed under vacuum to afford **2-Ph**<sub>2</sub>.

On titration of (PPh<sub>3</sub>)<sub>2</sub>Re(CO)<sub>3</sub>(CHO) with a solution of  ${}^{'}Bu(CH_2)_2B(C_8H_{14})$  in THF- $d_8$ , the formyl  ${}^{1}H$  NMR resonance showed a steady upfield shift, with no change in line shape, consistent with fast, reversible adduct formation. The equilibrium constant for adduct formation was estimated from a Benesi–Hildebrand plot<sup>20</sup> (Figure S11) as  $K_{eq} = 100$  M<sup>-1</sup>, corresponding to a free energy of B–O bond formation of 11.4 kcal/mol.<sup>17</sup> Notably,  ${}^{'}Bu(CH_2)_2B(C_8H_{14})$  prefers to

bind to  $(PPh_3)_2Re(CO)_3(CHO)$  over THF  $(K_{eq} = 0.19 \text{ M}^{-1})^{10c}$ by roughly 3 orders of magnitude.

The BEt<sub>3</sub>-stabilized formyl **2-Ph<sub>2</sub>**·**BEt<sub>3</sub>** is somewhat longerlived than **2-Ph<sub>2</sub>**, but still decomposes over the course of a few days to Re–H species **4-Ph<sub>2</sub>** and **4-Ph<sub>1</sub>** (Scheme 3; decomposition times tend to vary widely, as has been observed for other formyls<sup>21</sup>). No further reduction was observed when **2-Ph<sub>2</sub>·BEt<sub>3</sub>** was treated with additional NaHBEt<sub>3</sub> or [**HPt**][PF<sub>6</sub>], even in the presence of excess trialkylborane.

The stronger Lewis acid  $B(C_6F_5)_3$  does not promote C–H bond formation from  $[1-Ph_2][BF_4]$  and  $[HPt][PF_6]$ . Instead, hydride is transferred from  $[HPt]^+$  to B, forming the stable salt  $[1-Ph_2][HB(C_6F_5)_3]$  along with precipitated  $[Pt]^{2+}$ .  $B(C_6F_5)_3$  forms a stable boroxycarbene when added to preformed (PPh\_3)\_2Re(CO)\_3(CHO), <sup>10b</sup> but gentle heating of  $2-Ph_2 \cdot B(C_6F_5)_3$  provides the same tetracarbonyl borohydride salt  $[1-Ph_2][HB(C_6F_5)_3]$ ,<sup>22</sup> suggesting that  $[HB-(C_6F_5)_3]^-$  is a weaker hydride donor than  $2-Ph_2$ . Similar to  $2-Ph_2 \cdot B(C_6F_5)_3$  shows no further reaction with hydride sources.<sup>22</sup>

In summary, while small amounts of an unstable formyl can be generated slowly from  $[1-Ph_2]^+$  and  $[HPt]^+$  alone, high yields of a boroxycarbene (stabilized formyl) species were generated rapidly from  $[1-Ph_2]^+$  and  $[HPt]^+$  in the presence of the *appropriate* external Lewis acid. Trialkylborate Lewis acids are too weak to have an effect; the strong Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> diverts the hydride transfer to make a stable borohydride; intermediate acid strength trialkylboranes greatly accelerate the first hydride transfer reaction and increase the lifetime of the reduced product. However, none of the external Lewis acids promote the further reduction or C–C coupling chemistry achieved by the pendent Lewis acid in  $[1-E_2]^+$ .

Synthesis of Complexes with Pendent Boranes. Given the importance of intramolecular interactions, a structurefunction study on pendent Lewis acid assistance was designed, requiring complexes in which the number of phosphinoborane ligands and the length of the hydrocarbon chain connecting P and B are varied. Complexes with one or two phosphinoborane ligands with  $(CH_2)_{1-3}$  linkers were synthesized, along with a mixed complex containing one phosphinoborane and one simple tertiary phosphine ligand. A system that identifies the phosphine ligand(s) and the class of complex will be used, as depicted in Chart 1. The ligands will be identified by the specific hydrocarbon linker (methylene, 1,2-ethanediyl, 1,3-propanediyl):  $\mathbf{M} = \mathbf{Ph}_2\mathbf{PCH}_2\mathbf{B}$ - $(C_8H_{14}), E = Ph_2P(CH_2)_2B(C_8H_{14}), P = Ph_2P(CH_2)_3B$  $(C_8H_{14})$ , and **Ph** = PPh<sub>3</sub>. The cationic rhenium carbonyl fragment is designated  $[1]^+$ , with the first reduction Re-CHO products designated 2, and the doubly reduced C-Ccoupled products designated  $[3]^-$ . The number of phosphine ligands dictates the number of carbonyl ligands on the metal complexes: for  $[1-M_1]^+$ ,  $[1]^+ = [Re(CO)_5]^+$ ; for  $[1-M_2]^+$ ,  $[1]^+ = [\text{Re}(\text{CO})_4]^+$ . Full synthetic details for all new species are provided in the Supporting Information.

Two routes are available for bis(phosphinoborane) complexes: prior generation of the entire ligand followed by

<sup>(19)</sup> Such species can be regarded either as borane-stabilized formyls or as boroxycarbenes. There is a continuum, and  $M-CHO-BR_3$  species are probably best considered intermediate between formyl and boroxycarbene. We choose to describe these as boroxycarbenes, due to the lack of observed C=O stretch in the IR and the relatively downfield <sup>13</sup>C chemical shift of Re-CHO. Solid-state structures appear to be intermediate between carbene and formyl.

<sup>(20) (</sup>a) Benesi, H. A.; Hildebrand, J. H. J. Am. Chem. Soc. 1949, 71, 2703. (b) Rose, N. J.; Drago, R. S. J. Am. Chem. Soc. 1959, 81, 6138.
(c) Baldwin, S. M.; Bercaw, J. E.; Brintzinger, H. H. J. Am. Chem. Soc. 2008, 130, 17423.

<sup>(21) (</sup>a) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. Organometallics **1984**, *3*, 802. (b) Sumner, C. E.; Nelson, G. O. J. Am. Chem. Soc. **1984**, *106*, 432. (c) Narayanan, B. A.; Amatore, C.; Kochi, J. K. Organometallics **1987**, *6*, 129.

<sup>(22)</sup> Elowe, P. R. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 2009.



coordination, or hydroboration of a precoordinated alkenylphosphine (Scheme 5). The ethylene-linked cation  $[1-E_2]$ -[BF<sub>4</sub>] was previously reported;<sup>10a</sup> the Mn analogue  $[1-E_2-$ **Mn**][BF<sub>4</sub>] was obtained in good yield by a similar procedure, as was the complex with a propylene-linked phosphinoborane ligand ([1-P<sub>2</sub>][BF<sub>4</sub>]). Hydroboration of the allylphosphine with 9-BBN (9-borabicyclo[3.3.1]nonane) proceeded significantly more readily than the vinyl analogue, possibly reflecting reduced conjugation of the double bond with the electrondeficient metal center.

The ligand with a methylene spacer is inaccessible by hydroboration; the reaction of Ph<sub>2</sub>PCH<sub>2</sub>Li and ClB(C<sub>8</sub>H<sub>14</sub>) in cold pentane affords an insoluble white powder from which Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>) is obtained.<sup>23</sup> Treatment of Re-(CO)<sub>5</sub>Br with 2 equiv of Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>) produced *trans, mer*-(Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>))<sub>2</sub>Re(CO)<sub>3</sub>Br, from which halide abstraction could not be achieved with Ag<sup>+</sup> (which reacts with trialkylboranes<sup>24</sup>) or Tl<sup>+</sup> salts; but addition of [Et<sub>3</sub>Si][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>25</sup> to a C<sub>6</sub>H<sub>5</sub>Cl solution under 1 atm of CO gave the desired cation, *trans*-[(Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>))<sub>2</sub>Re-(CO)<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([**1**-M<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), whose structure was confirmed by XRD (Figure 2). As in [**1**-E<sub>2</sub>][BF<sub>4</sub>], no intramolecular CO···B interaction is observed (although there are close contacts between the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] anion and nearby CO's: O3-F19 2.867 Å, O4-F19 3.042 Å).



**Figure 2.** Structural representation of  $[1-M_2][B(C_6F_5)_4]$ , with ellipsoids shown at 50% probability. One of the  $B(C_8H_{14})$  groups was disordered by a rotation around the B–C bond; only the major component (66%) is shown (represented as light blue isotropic atoms).<sup>17</sup> All H atoms and a disordered dichloroethane solvent molecule of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re–P1 2.4521(5), Re–P2 2.4509(5), Re–C(av) = 1.99, P1–Re–P2 172.34(2).

Reaction of  $[(PPh_3)Re(CO)_5]OTf$  with  $Ph_2P(CH_2)_2B-(C_8H_{14})$  seemed an obvious route to an asymmetric cation with only one Lewis acid, but under both thermal and photolytic conditions only intractable mixtures were obtained. Instead, the reaction of *trans*-Re(PPh\_3)(I)(CO)\_4<sup>26</sup> with AgOTf followed by Ph\_2P(CH\_2)\_2B(C\_8H\_{14}) under gentle heating gives *trans*-[(Ph\_2P(CH\_2)\_2B(C\_8H\_{14})(PPh\_3)Re(CO)\_4]-[OTf] (1-E\_1Ph\_1) in good yield (Scheme 6).

<sup>(23)</sup> This insoluble material is likely an oligomer of the desired phosphinoborane. The crude material was treated with pyridine, which led to dissolution of monomeric adduct Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>)·pyridine, which was fully characterized. Treatment with BF<sub>3</sub>·Et<sub>2</sub>O prompted reprecipitation of Ph<sub>2</sub>PCH<sub>2</sub>B(C<sub>8</sub>H<sub>14</sub>) as an analytically pure white powder. See Supporting Information for full details.

<sup>(24) (</sup>a) Brown, H. C.; Hébert, N. C.; Snyder, C. H. J. Am. Chem. Soc.
1961, 83, 1001. (b) Brown, H. C.; Snyder, C. H. J. Am. Chem. Soc. 1961, 83, 1002. (c) Brown, H. C.; Verbrugge, C.; Snyder, C. H. J. Am. Chem. Soc.
1961, 83, 1001.

<sup>(25)</sup> Lambert, J. B.; Zhang, S.; Ciro, S. M. Organometallics 1994, 13, 2430.

<sup>(26)</sup> Ingham, W. L.; Coville, N. J. Organometallics 1992, 11, 2551.









Complexes with a single phosphinoborane ligand were synthesized starting with  $Re(CO)_5OTf$  (Scheme 7). Both  $Ph_2PCH_2B(C_8H_{14})$  and  $Ph_2P(CH_2)_2B(C_8H_{14})^{27}$  displace triflate from  $Re(CO)_5OTf$  at 60 °C to give [( $Ph_2PCH_2B-(C_8H_{14})$ ) $Re(CO)_5$ ][OTf] ([**1-M**\_1][OTf]), which was characterized crystallographically (Figure 3), and [( $Ph_2P(CH_2)_2B-(C_8H_{14})$ ) $Re(CO)_5$ ][OTf] ([**1-E**\_1][OTf]), respectively. The propylene-linked analogue was obtained by reaction of  $Ph_2PCH_2CHCH_2$  with  $Re(CO)_5$ OTf at 60 °C, affording [( $Ph_2PCH_2CHCH_2$ ) $Re(CO)_5$ ][OTf]; hydroboration with 9-BBN gave [( $Ph_2P(CH_2)_3B(C_8H_{14})$ ) $Re(CO)_5$ ][OTf] ([**1-P**\_1][OTf]).

[1-P1][OTf]

**Reduction of**  $[(Ph_2PCH_2B(C_8H_{14}))_2Re(CO)_4]^+$   $([1-M_2]^+)$ . [1-M<sub>2</sub>]<sup>+</sup> was readily synthesized only as the  $[B(C_6F_5)_4]^-$  salt, which complicated reductions with  $[HPt]^+$ : reduction with  $[HPt][PF_6]$  proceeded very slowly to ~90% conversion (by NMR) over 6 days. Partially soluble  $[Pt][B(C_6F_5)_4]_2$ , visible by NMR in small amounts throughout the reaction, may inhibit reduction according to the equilibrium in Scheme 4 (precipitation of  $[Pt]^{2+}$  cannot drive the reaction). To circumvent this problem,  $[1-M_2][B(C_6F_5)_4]$  was treated with both  $[N(heptyl)_4][BF_4]$  (or NaBF<sub>4</sub>) and  $[HPt][PF_6]$  in C<sub>6</sub>D<sub>5</sub>Cl, which led to complete consumption of  $[1-M_2]^+$  and formation of a new Re species over ~3 h in >95% yield





Figure 3. Structural representation of  $[1-M_1]$ [OTf], with ellipsoids at 50% probability. A highly disordered solvent molecule was omitted for clarity. The two phenyl groups were disordered by rotation about the P–C bond, and only the major contributor is included for clarity.<sup>17</sup> Selected bond lengths (Å) and angles (deg): Re–C1 2.027(2), Re–C2 2.000(2), Re–C3 2.016(2), Re–C4 2.021(2), Re–C5 1.973(2), Re–P 2.4846(5), P–Re–C5 176.54(6), C1–Re–C3 176.96(8).

(by NMR), with concomitant precipitation of  $[Pt][BF_4]_{x}$ -[PF<sub>6</sub>]<sub>2-x</sub>. At room temperature the <sup>1</sup>H NMR spectrum of the product exhibits a diagnostic triplet at  $\delta$  13.89 ( $J_{PH} = 5.9$ Hz) but is otherwise broad and nondescript, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows two very broad resonances. (Similar reactivity and spectroscopy was observed in THF- $d_8$ .) Variable-temperature NMR studies show fluxional behavior; at low temperatures both the <sup>1</sup>H and <sup>31</sup>P NMR spectra display sharp doublets indicating nonequivalent P and CH<sub>2</sub> groups. These results strongly indicate the boroxycarbene structure **2-M<sub>2</sub>** (Scheme 8), although we were unable to obtain an analytically pure sample. (See SI for details of the NMR and assignment; a related intramolecular boroxycarbene has been obtained for a CpFe system.<sup>28</sup>)

The fluxional process in  $2-M_2$  interconverts the two phosphinoborane ligands ( $\Delta G^{\ddagger} = 13.6 \pm 0.2$  kcal/mol, estimated from the coalescence temperature of 323 K). A sequence of B-O bond breaking, rotation, and B-O bond formation with the other ligand seems a plausible mechanism. <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy is not entirely consistent with this, however, as the CO carbon signals are very broad at room temperature, suggesting their involvement in the exchange process. Transfer of a hydride from a formyl to an adjacent carbonyl ligand (Scheme 8, bottom) has been observed previously ( $\Delta G^{\ddagger} = 11.7 \text{ kcal mol}^{-1}$ );<sup>29</sup> that may be more consistent with our observations. Furthermore, treatment of 2-M<sub>2</sub> with up to 100 equiv of pyridine leads to no B-O cleavage; only coordination of pyridine to the free B center is observed (Scheme 8, top), resulting in sharp NMR resonances expected for a nonfluxional product.<sup>17</sup> If reversible B–O cleavage were occurring rapidly on the NMR time scale, pyridine binding might be expected to intervene. This observation stands in stark contrast to B-O bonds involving intermolecular Lewis acids as well as phosphinoboranes with

<sup>(28)</sup> Kubo, K.; Nakazawa, H.; Nakahara, S.; Yoshino, K.; Mizuta, T.; Miyoshi, K. Organometallics 2000, 19, 4932.

<sup>(29)</sup> Luan, L.; Brookhart, M.; Templeton, J. L. Organometallics 1992, 11, 1433.



longer linkers, which are readily broken in the presence of pyridine (*vide infra*). Similarly, carbene **2-M**<sub>2</sub> is remarkably stable in comparison to **2-Ph**<sub>2</sub> and **2-Ph**<sub>2</sub>**·BEt**<sub>3</sub>: no decomposition is observed over short periods at 95 °C or weeks at room temperature.

Treatment of  $[1-M_2][B(C_6F_5)_4]$  with 2 equiv each of  $[N(heptyl)_4][BF_4]$  and  $[HPt][PF_6]$  in THF-d<sub>8</sub> led to formation of a single new Re-containing product ( $\sim 70\%$  yield by NMR, relative to  $[N(heptyl)_4]^+$ ), again with precipitation of  $[\mathbf{Pt}]^{2+}$ . Because the presence of soluble salts such as  $[N(heptyl)_4][B(C_6F_5)_4]$  prevented isolation and structural determination by XRD, the product was characterized spectroscopically. Two sharp doublets are found in the  ${}^{31}P{}^{1}H$ NMR spectrum at  $\delta$  22.2 and 37.3 ( $J_{PP} = 127$  Hz), and two slightly broadened doublets are also found in the <sup>1</sup>H NMR spectrum,  $\delta$  3.12 and 4.63 ( $J_{\rm HH}$  = 13.0 Hz). The downfield <sup>31</sup>P NMR shift is consistent with a five-membered ring,<sup>30</sup> as expected for a structure analogous to the C-C coupled product  $[3-E_2]^-$  (Scheme 2),<sup>10a</sup> but a number of other spectroscopic features rule out this assignment, including the absence of a downfield <sup>13</sup>C NMR signal for a carbon carbon and the mer-tricarbonyl geometry assigned by <sup>13</sup>C NMR and IR. A simple alkyl is also ruled out by the five-membered-ring structure, no observed P coupling to the CH2 group, and no three-coordinate <sup>11</sup>B NMR signals. All the spectroscopic data are consistent with the doubly reduced "confused" alkyl species  $[5]^{-}$  (Scheme 9), in which the CH<sub>2</sub> is bound to one B, and O is bound to Re and the other B, forming a bicyclic ring system. The very broad C signal and slightly broad H signals of the CH<sub>2</sub> group point to coordination to quadrupolar B, the B-O-Re fragment would provide the expected downfield <sup>31</sup>P NMR shift due to a five-membered ring, and two <sup>11</sup>B NMR signals consistent with four-coordinate BR<sub>4</sub><sup>-</sup> and  $BR_3(OR')^-$  are observed. In addition, high-resolution mass spectrometry (HRMS) gives the expected mass for [5]<sup>-</sup>. Thus although a second reduction was facilitated by the pendent Lewis acid, an entirely different product was obtained than in the complex supported by ethylene-linked ligands: no C-C bond formation occurred, and an unusual isomerization was instead observed, presumably driven by formation of four-coordinate B in favorable ring sizes. The pendent



Scheme 9



acid is clearly required for this transformation: whereas  $2-M_2$  (preformed *in situ*) reacted with [HPt][PF<sub>6</sub>] and [N(heptyl)<sub>4</sub>]-[BF<sub>4</sub>] to give [5]<sup>-</sup>, similar treatment of  $2-M_2-py$  produced no observable reaction.

Reduction of  $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4]^+$  ([1-E<sub>2</sub>]<sup>+</sup>). As previously reported, <sup>10a</sup> treatment of  $[1-E_2][BF_4]$  in C<sub>6</sub>D<sub>5</sub>Cl with 1 equiv of NaHBEt<sub>3</sub> or [HPt][BF<sub>4</sub>] affords boroxycarbene  $2-E_2$  (Scheme 2). The carbene is identified by a characteristic downfield signal in the <sup>1</sup>H NMR spectrum ( $\delta$  13.96) and a closely separated pair of doublets in the  ${}^{31}P{}^{1}H$  NMR spectrum ( $\delta$  9.9). Boroxycarbene 2-E<sub>2</sub> spontaneously crystallizes from CD<sub>2</sub>Cl<sub>2</sub>, and XRD revealed a binuclear structure in which the pendent borane from one Re center acts as an intermolecular Lewis acid for the other; the two carbene carbons are separated by  $\sim 5$  Å.<sup>10a</sup> Pulsed gradient spinecho (PGSE) diffusion NMR experiments<sup>31</sup> on 2-E<sub>2</sub>, using (PPh<sub>3</sub>)<sub>2</sub>Re(CO)<sub>3</sub>Br (6) as an internal standard of similar size and shape to the proposed monomer, suggest that significant intermolecular interactions are maintained in solution. Initial measurements provided a ratio of hydrodynamic volumes of 2-E<sub>2</sub>:6; then excess pyridine was added to the NMR tube, and the experiment was repeated. If  $2-E_2$  were strictly monomeric in solution, the ratio would be expected to increase, since pyridine binding would increase the hydrodynamic volume; if  $2-E_2$  were strictly dimeric, the second ratio should be close to 0.5 times the first, as the monomer should have roughly half the hydrodynamic volume of the dimer. The values of the ratio were 2.34(7) before pyridine addition and 1.6(1) after; the decrease by a factor of 0.69(5)could reflect a monomer-dimer equilibrium, giving a

<sup>(31)</sup> Li, D. Y.; Keresztes, I.; Hopson, R.; Williard, P. G. Acc. Chem. Res. 2009, 42, 270.





time-averaged PGSE value.<sup>32</sup> The broad <sup>1</sup>H and <sup>31</sup>P NMR resonances of **2-E**<sub>2</sub> at 298 K support such a conclusion, although full variable-temperature NMR experiments could not be carried out due to the thermal instability (*vide infra*).<sup>17</sup> Perhaps owing to its fluxional solution behavior, **2-E**<sub>2</sub> is quite reactive: C<sub>6</sub>D<sub>5</sub>Cl solutions of **2-E**<sub>2</sub> disproportionate (at a rate dependent on the concentration of **2-E**<sub>2</sub>) to a 1:1 mixture of  $[1-E_2]^+$  and  $[3-E_2]^-$  (Scheme 10).

The same reduction chemistry is operative in THF, although the carbene is quite short-lived in this solvent: disproportionation is complete after a few minutes at room temperature, in stark contrast to the extremely stable methylenelinked analogue  $2-M_2$ . This rate enhancement might be due to the more polar solvent facilitating transformation to the ionic products  $[1-E_2]^+$  and  $[3-E_2]^-$ , the enhanced solubility of NaBF<sub>4</sub> in THF (with Na<sup>+</sup> being incorporated into the product), or the ability of THF to break intermolecular B-O bonds in 2-E<sub>2</sub>. The  ${}^{31}P{}^{1}H{}$  NMR signal for 2-E<sub>2</sub> in THF appears as a singlet ( $\delta$  10.3), probably a result of competitive borane binding by THF and formyl, implying relatively weak B-O bonds in 2-E<sub>2</sub> when compared to 2-M<sub>2</sub>. The aforementioned PGSE experiment is consistent with this description, as reaction of pyridine with carbene 2- $E_2$  (in C<sub>6</sub>D<sub>5</sub>Cl) displaces the formyl group from the borane, forming an unstabilized formyl  $({}^{31}P{}^{1}H{}$  singlet at  $\delta$  11.7, <sup>1</sup>H Re–CHO signal at  $\delta$  15.21) that decomposes without disproportionation to give Re-H by decarbonylation (the normal pathway for formyl decomposition).<sup>4a</sup>

While **2-E**<sub>2</sub> is stable for a number of hours at room temperature in C<sub>6</sub>D<sub>5</sub>Cl, it decomposes as the temperature is raised: up to 40 °C, disproportionation is the main path followed, but heating at 90 °C for a few minutes converts **2-E**<sub>2</sub> to a single new product whose <sup>31</sup>P{<sup>1</sup>H} NMR spectrum





**Figure 4.** Structural representation of  $8 \cdot (C_6H_6)_{2.5}(C_5H_{12})_{0.5}$ , with ellipsoids at 50% probability. H atoms and solvents of crystallization are omitted, and Ph groups are truncated for clarity. One site of solvent cocrystallization was a disordered mixture of benzene and pentane.<sup>17</sup> Selected bond distances (Å) and angles (deg): Re1-CO(av) 1.988, Re1-P1 2.4437(6), Re1-P2 2.4490(6), B1-O10 1.609(4), B2-O9 1.597(3), B1-O10-B4 143.0(2). B2-O9-B3 141.7(2).

shows two doublets,  $\delta$  12.6 and 39.9 ( $J_{PP} = 124.8$  Hz); the uncommonly downfield-shifted doublet is consistent with a five-membered phosphorus-containing ring.<sup>30</sup> In the <sup>1</sup>H NMR spectrum, the downfield carbene resonance has been replaced by a new broad resonance at  $\delta$  5.85. These observations along with 2-D NMR experiments support structure 7 (Scheme 10), in which a B–C bond has been cleaved and the ethylene linker has added to the carbene carbon, giving a (boroxyalkyl)metal complex.<sup>17</sup>

Boroxycarbene 2-E<sub>2</sub> acts as a strong hydride donor, liberating H<sub>2</sub> with reagents such as H<sub>2</sub>O and [HNMe<sub>3</sub>]-[BPh<sub>4</sub>] (Scheme 10). In the latter case, the parent cationic tetracarbonyl  $[1-E_2]^+$  re-forms; with water the binuclear B-O(H)-B-bridged complex 8, which contains a 20-membered ring, was formed and characterized by XRD (Figure 4).  $[^{T}Bu_{3}PH][HB(C_{6}F_{5})_{3}]$ , which is a potential hydride source as well as a protic reagent (and which can be formed directly, without any metal complex required, from  $H_2^{33}$ ), was tested to see if further reduction and C-C coupling could be obtained with such a weak hydride. Instead, H<sub>2</sub> release was observed again, and the ion pair [1-E2][HB(C6F5)3] was obtained, in addition to free P'Bu<sub>3</sub>. Thus  $[HB(C_6F_5)_3]^-$  is too weak a hydride to reduce the rhenium carbonyl cation, 10b consistent with the stability of  $[1-Ph_2][HB(C_6F_5)_4]$  (Scheme 3) and despite the presence of a pendent acid group.

Carbene **2-E<sub>2</sub>** can be directly reduced (before disproportionation occurs) to  $[3-E_2]^-$  with a second equivalent of NaHBEt<sub>3</sub> or [HPt][BF<sub>4</sub>].<sup>10a</sup> In contrast to **2-E<sub>2</sub>**,  $[3-E_2]^-$  is thermally stable up to 70 °C in THF solution, as well as

<sup>(33) (</sup>a) Welch, G. C.; Stephan, D. W. J. Am. Chem. Soc. 2007, 129, 1880. (b) Stephan, D. W.; Erker, G. Angew. Chem., Int. Ed. 2010, 49, 46.



toward further reduction with excess NaHBEt<sub>3</sub>, presumably because a dianionic product would be disfavored. The B–O bonds of  $[3-E_2]^-$  appear to be much stronger than those of 2-E<sub>2</sub>; they are not cleaved by addition of pyridine. Unlike 2-E<sub>2</sub>, treatment of  $[3-E_2]^-$  with  $[Pt][BAr^F_4]_2$  did not lead to any reaction, implying that its formation is essentially irreversible.  $[3-E_2]^-$  reacts with strong acids (HBF<sub>4</sub>, HOTf) to give a single product before going on to multiple species, and addition of MeOTf cleanly yields a stable neutral product, but none of these have been reliably characterized.

Mechanism of C–H Bond Formation: Evidence for Hydride Shuttling. Plausible pathways for the transfer of hydride from  $[HPt]^+$  to Re–CO in  $[1-E_2]^+$  include (Scheme 11) the following: (path A) hydride transfer to the pendent borane, followed by intramolecular hydride transfer from boron to carbon; (path B) hydride transfer from  $[HPt]^+$  directly to the Re–CO fragment, yielding a formyl, which is trapped by the pendent borane; (path C) transient borane coordination to a Re–CO oxygen, activating the carbon for nucleophilic attack.

When the reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy at -40 °C, a new broad resonance was observed at  $\delta$  -6, near the sharper signal for [**HPt**]<sup>+</sup> at  $\delta$  -7. Both signals disappear as the reaction goes on, although the broad resonance is consumed first. The appearance of a broad Pt-H signal suggests the possibility of a Pt-H-B-bridged intermediate, which would be most consistent with pathway A. In further support, reaction of [**HPt**][PF<sub>6</sub>] with BEt<sub>3</sub> led to precipitation of [**Pt**][PF<sub>6</sub>]<sub>2</sub> and the appearance of a broad <sup>31</sup>P resonance at  $\delta$  -2.4, along with a broadened resonance for [**HPt**]<sup>+</sup> at  $\delta$  -7.1. Fluxionality was also apparent in a broad <sup>1</sup>H NMR signal in the hydride region at  $\delta$  -11.7 and a <sup>11</sup>B NMR signal at 14.8 (compare Li[Et<sub>3</sub>BHBEt<sub>3</sub>],  $\delta$  8.7<sup>34</sup>). At -40 °C the signals sharpened and separated into two sets. The <sup>31</sup>P NMR spectrum showed two singlets, one corresponding to [**HPt**]<sup>+</sup> ( $\delta$  -7.4, <sup>1</sup>J<sub>PtP</sub> = 2240 Hz) and one





conspicuously lacking Pt satellites ( $\delta$  –1.6). The <sup>1</sup>H NMR spectrum showed the hydride signal expected for [**HPt**]<sup>+</sup> ( $\delta$  –12.02, pent, <sup>2</sup>*J*<sub>PH</sub> = 29.3 Hz, <sup>1</sup>*J*<sub>PtH</sub> = 694 Hz) along with another broad doublet with Pt satellites at  $\delta$  –3.25 (*J*<sub>PH</sub> = 166 Hz, *J*<sub>PtH</sub> = 958 Hz), downfield of most Pt hydrides, but closer to the chemical shift expected for [HBEt<sub>3</sub>]<sup>-</sup> ( $\delta \approx$  –0.5) or [Et<sub>3</sub>BHBEt<sub>3</sub>]<sup>-</sup> ( $\delta \approx$  –2.7).<sup>34 11</sup>B NMR at this temperature showed signals for free BEt<sub>3</sub> and another close to that of [HBEt<sub>3</sub>]<sup>-</sup>.

These observations strongly indicate that H has been transferred (partly or entirely) to B; we tentatively assign the broad Pt–H signal to  $[(dmpe)_2Pt–H–BEt_3]^+$  or the borane adduct  $[(dmpe)_2Pt(HBEt_3)(BEt_3)]^+$  (Scheme 12), since the large  $J_{PH}$  would be consistent with a phosphine *trans* to the hydride<sup>35</sup> and the broadening with quadrupolar interaction with boron. The added bulk of the coordinated BEt<sub>3</sub> group could favor a trigonal-bipyramidal geometry; phosphines in such systems have been observed to undergo rapid interchange, leading to loss of Pt satellites in the <sup>31</sup>P NMR.<sup>36</sup>

<sup>(34)</sup> DuBois, D. L.; Blake, D. M.; Miedaner, A.; Curtis, C. J.; DuBois, M. R.; Franz, J. A.; Linehan, J. C. *Organometallics* **2006**, *25*, 4414.

<sup>(35)</sup> Miedaner, A.; Raebiger, J. W.; Curtis, C. J.; Miller, S. M.; DuBois, D. L. *Organometallics* **2004**, *23*, 2670.

<sup>(36)</sup> Lin, W. B.; Wilson, S. R.; Girolami, G. S. Inorg. Chem. 1997, 36, 2662.

Precipitation of  $[Pt]^{2+}$  is consistent with the stoichiometry required to form  $[Et_3BHBEt_3]^-$ . The reaction of preformed  $[Li][Et_3BHBEt_3]$  with  $[Pt]^{2+}$  afforded multiple products; the major product was Pt(dmpe)<sub>2</sub>, but some of the *trans* hydride was also observed. Similar chemistry has been previously reported for HRh(dmpe)<sub>2</sub>.<sup>34</sup>

While hydride transfer between B and Pt appears facile when the  $[PF_6]$  anion is employed, no reaction is observed when  $[HPt][BAr^{F}_{4}]$  is treated with BEt<sub>3</sub>. This difference is consistent with our previous observation that  $[1-E_2][BAr_4^F]$ is not reduced by [HPt][BAr<sup>F</sup><sub>4</sub>] in  $C_6D_5Cl^{10c}$  and suggests that an equilibrium involving hydride transfer from Pt to B could be driving the chemistry of Scheme 4. Furthermore, we recently reported that the combination of a suitably strong and bulky base and H<sub>2</sub> is sufficient to directly reduce  $[1-E_2]^+$ ;<sup>10c</sup> that reduction must go through a pendent borohydride intermediate. All of this evidence supports the "hydride shuttle" mechanism of path A (Scheme 11), wherein formation of a small amount of trialkylborohydride is followed by rapid intramolecular carbonyl reduction. Note also that  $[1-Ph_2]^+$  does react with  $[HPt]^+$  to give an (unstable) formyl (vide supra), but that reaction is very slow and is strongly accelerated by the addition of BEt<sub>3</sub>, suggesting that direct transfer of hydride to carbonyl carbon as in path B is possible but much slower than the shuttle route.

Mechanism of C-C Bond Formation: Evidence for a Bis-(carbene) Intermediate. Reaction of [1-E2][BF4] with 2 equiv of NaHBEt<sub>3</sub> or [HPt][PF<sub>6</sub>], or of preformed 2-E<sub>2</sub> with 1 equiv of either reductant, affords  $[3-E_2]^-$  rapidly at room temperature. The reaction is irreversible and, in contrast to the first hydride transfer, is not driven by precipitation  $([3-E_2]^-$  does precipitate from C<sub>6</sub>D<sub>5</sub>Cl, but remains in solution in THF- $d_8$ ), as evidenced by the lack of observed reaction when  $[3-E_2]^-$  is treated with  $[Pt][BAr^F_4]_2$ . The second reduction and subsequent C-C coupling necessarily involves a number of elementary steps. The mononuclear form of 2-E<sub>2</sub> (accessible according to the PGSE NMR data, vide supra), containing intramolecular borane coordination, is proposed to be an intermediate in the transformation to mononuclear product  $[3-E_2]^-$ . Two reasonable pathways for the formation of  $[3-E_2]^-$  are shown in Scheme 13: path A, reduction at the carbene center to give an anionic boroxyalkyl species, which undergoes Lewis acid-assisted migratory insertion; or path B, reduction at a second CO to give an anionic bis(carbene) (or doubly stabilized bis(formyl): [CpRe(NO)(CHO)<sub>2</sub>]<sup>-</sup> has been previously reported<sup>5c,d</sup>) species, followed by carbene coupling and hydrogen shift to give the observed product. Related hydrogen shifts have been previously observed in Fe<sup>37</sup> and Mn<sup>10b</sup> systems.

Evidence for pathway B is provided by low-temperature NMR studies. When 1 equiv of NaHBEt<sub>3</sub> is added to an NMR tube containing a frozen solution of  $2-E_2$  in C<sub>6</sub>D<sub>5</sub>Cl and the solution is warmed to -40 °C, clean conversion to a new symmetric species is observed. This species features a sharp singlet at  $\delta$  10.0 in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, a new downfield singlet at  $\delta$  16.43 in the <sup>1</sup>H NMR, which integrates as two protons, and only one CO resonance and one boroxy-carbene resonance in the <sup>13</sup>C{<sup>1</sup>H} NMR, all consistent with the bis(carbene) structure [9]<sup>-</sup>. Upon slowly warming the sample, no new species were observed by NMR spectroscopy; instead, the signal-to-noise decreased until essentially





no signals attributable to Re species were visible, and a large amount of white precipitate was found upon removal of the tube from the probe. The precipitate was isolated and dissolved in THF- $d_8$ , and NMR showed it to be [3-E<sub>2</sub>]<sup>-</sup>.

It should be noted that the observation of  $[9]^-$  in C<sub>6</sub>D<sub>5</sub>Cl does not necessarily rule out a migratory insertion mechanism, since bis(carbene) formation could be reversible. Migratory insertion of a carbonyl into a Re–C bond has been reported to proceed with assistance from a (much stronger) Lewis acid.<sup>38</sup> The reduction of  $[1-M_1]^+$  (*vide infra*) appears unambiguously to proceed via migratory insertion as well, but that reaction is quite slow.

Reduction of  $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Mn(CO)_4]^+$  ([1-E<sub>2</sub>-Mn]<sup>+</sup>). Treatment of  $[1-E_2-Mn][BF_4]$  with 1 equiv of NaH-BEt<sub>3</sub> in C<sub>6</sub>D<sub>5</sub>Cl showed significant conversion to a Mn-CHO species, with broad singlets at  $\delta$  13.81 (<sup>1</sup>H NMR) and  $\delta$  61.0 (<sup>31</sup>P NMR). When  $[1-E_2-Mn][BF_4]$  was similarly treated with 1 equiv of NaHBEt<sub>3</sub> in THF-d<sub>8</sub>, a mixture of products formed, showing no downfield <sup>1</sup>H NMR signal;<sup>39</sup> however, addition of 2 equiv of NaHBEt<sub>3</sub> in THF-d<sub>8</sub> led to rapid and clean conversion to a single species that exhibits NMR signals—in particular, two doublets each in the <sup>1</sup>H and <sup>31</sup>P-{<sup>1</sup>H} NMR spectra and correlation between the two proton doublets ( $\delta$  4.32 and 4.82) and a carbene carbon signal ( $\delta$  332) by <sup>1</sup>H-<sup>13</sup>C gHMBC spectroscopy—very similar to those of

<sup>(37)</sup> Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. J. Am. Chem. Soc. 1985, 107, 3130.

<sup>(38)</sup> Lindner, E.; von Au, G. *Angew. Chem., Int. Ed.* **1980**, *19*, 824. (39) The reactivity in THF is consistent with the initially formed carbene undergoing fast disproportionation chemistry, just as the Re analogue.



the Re C–C coupling product  $[3-E_2]^-$ . Accordingly we assign the two products as  $2-E_2-Mn$  and  $[3-E_2-Mn]^-$  (Scheme 14).  $2-E_2-Mn$  is presumed to be dimeric like the Re analogue, although we have no direct evidence for that.<sup>17</sup> The  $J_{PP}$  value of 27 Hz in  $[3-E_2-Mn]^-$  is much smaller than that in  $[3-E_2]^-$ , suggesting the former has *cis* phosphines (one possible isomer is drawn in Scheme 14). Both  $2-E_2-Mn$  and  $[3-E_2-Mn]^-$  appear to be considerably less stable than their Re analogues; attempts to isolate  $[3-E_2-Mn]^-$  by concentration led only to decomposition.

Treatment of  $[1-E_2-Mn][BF_4]$  with 2 equiv of  $[HPt][PF_6]$  in THF- $d_8$  also led to formation of  $[3-E_2-Mn]^-$ , although the reaction did not go to completion. Manganese, an inexpensive first-row alternative to rhenium, is thus capable of effecting the same reductive coupling chemistry, albeit with decreased product stability.

**Reduction of** [(**Ph**<sub>2</sub>**P**(**CH**<sub>2</sub>)<sub>3</sub>**B**(**C**<sub>8</sub>**H**<sub>14</sub>))<sub>2</sub>**Re**(**CO**)<sub>4</sub>]<sup>+</sup> ([1-**P**<sub>2</sub>]<sup>+</sup>). Treatment of [1-**P**<sub>2</sub>][BF<sub>4</sub>] with 1 equiv of NaHBEt<sub>3</sub> in C<sub>6</sub>D<sub>5</sub>Cl appears to afford a single product in good yield by NMR spectroscopy. The <sup>1</sup>H NMR spectrum includes a singlet at  $\delta$  14.10, characteristic of a formyl or boroxycarbene proton. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a broad singlet ( $\delta$  6.6), in contrast to the AB pattern of 2-E<sub>2</sub> and the widely spaced broad resonances in 2-M<sub>2</sub>. The same species is obtained using [**HPt**]<sup>+</sup>, with essentially identical NMR signals, indicating that free BEt<sub>3</sub> does not play a role in the broadening of the <sup>31</sup>P signal.

A white solid precipitates from this solution over a few hours; it is insoluble in common organic solvents and water, but can be redissolved by addition of excess pyridine. The resulting solution exhibits a [Re–CHO] resonance, shifted downfield by ~1 ppm ( $\delta$  14.99) from the original position, while the <sup>31</sup>P{<sup>1</sup>H} NMR resonance is slightly shifted ( $\delta$  6.2) and significantly sharpened; the <sup>11</sup>B{<sup>1</sup>H} NMR shows a single resonance at  $\delta$  2.2, consistent with nonfluxional fourcoordinate boron.

On the basis of these results structure  $[2-P_2]_n$  is assigned to the initially formed soluble species (Scheme 15). This species presumably contains only weak B–O interactions, consistent with the shift of the formyl proton<sup>40</sup> and the broadness of the <sup>31</sup>P resonance (attributed to moderately fast B–O bond breaking/forming). Complex  $[2-P_2]_n$  precipitates as an oligomer; addition of pyridine redissolves it by coordinating to boron and breaking the B–O bonds, generating complex  $2-P_2 \cdot 2py$ . Because the "bare" formyl  $2-P_2 \cdot 2py$  is not stabilized by any Lewis acid interaction, it decomposes over a period of hours, resulting in two new Re–H <sup>1</sup>H NMR signals, one a triplet and the other a doublet, which can be assigned to  $4-P_2 \cdot 2py$  and  $4-P_1 \cdot py$ (Scheme 15), respectively. These products were not isolated; the pyridine adduct of the free ligand (Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>B-(C<sub>8</sub>H<sub>14</sub>)·pyridine) was also observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

Treatment of  $[1-P_2][BF_4]$  with 2 equiv of NaHBEt<sub>3</sub> led to NMR spectra that indicated the formation of multiple asymmetric species, possibly including one or more with new C–C bonds, but they could not be separated or fully characterized. Treatment of  $[1-P_2][BF_4]$  with 2 equiv of  $[HPt][PF_6]$  gave only boroxycarbene  $[2-P_2]_n$  and unreacted  $[HPt][PF_6]$ . This failure to undergo a second hydride addition may support our hypothesis that intramolecular facilitation is required for multiple reductions by  $[HPt]^+$ : an intramolecular B–O interaction in 2-P<sub>2</sub> would require an eight-membered ring, which is probably too large for effective stabilization.

Overview of (Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>B(C<sub>8</sub>H<sub>14</sub>))<sub>2</sub>Re Complexes: Ring Size Effects. Only methylene-linked boroxycarbene 2-M2 clearly exhibits intramolecular interaction of the pendent borane with the [Re-CHO] moiety, forming a favorable six-membered ring. The corresponding seven- and eightmembered rings that would result from intramolecular coordination in the ethylene- and propylene-linked analogues are not observed;<sup>41</sup> instead intermolecular coordination leads to a dimer or an insoluble oligomer, respectively. In the absence of significant intramolecular interactions in the ethylene- and propylene-linked systems, the two boroxycarbenes are expected to exhibit similar stability and hydride strength. Indeed, mixing preformed  $2-E_2$  with  $[1-P_2]^+$  (or **2-P<sub>2</sub>** with  $[1-E_2]^+$ ) gives an equilibrium mixture (Scheme 16), with  $K_{eq} \approx 1$ . Similarly, addition of carbene 2-E<sub>2</sub> to simple phosphine complex  $[1-Ph_2]^+$ , or of simple formyl complex **2-Ph<sub>2</sub>** to B-linked carbonyl complex  $[1-E_2]^+$ , establishes an equilibrium, also with  $K_{eq} \approx 1.^{17}$ 

In contrast, mixing preformed  $2-E_2$  with the methylenelinked  $[1-M_2]^+$  results in *complete* hydride transfer, giving only the intramolecularly stabilized carbene  $2-M_2$ , which does not react with  $[1-E_2][BF_4]$ . Furthermore,  $2-M_2$  is able to accept a second hydride from  $2-E_2$ , affording the "confused" alkyl  $[5]^-$  (Scheme 9) as the major product. Clearly the favorability of intramolecular coordination with the methylene linker effects a substantial difference in stability and reactivity. The fact that ethylene-linked boroxycarbene  $2-E_2$ *can* undergo a second hydride addition and C-C coupling, which in general does not appear to be well facilitated by external Lewis acids, is further evidence that  $2-E_2$  exists in solution as an equilibrium between the dimer and an intramolecularly coordinated monomer.

<sup>(40)</sup> As the linker length is increased, the chemical shift of the formyl in  $C_6D_5Cl$  moves downfield, which may indicate less B–O interaction. A similar trend is observed upon titration of (PPh<sub>3</sub>)<sub>2</sub>Re(CO)<sub>3</sub>(CHO) with trialkylboranes, as the formyl shifts upfield with added borane.

<sup>(41)</sup> The large size of Re and P in these rings is expected to favor smaller ring sizes than organic counterparts, which suggests that sevenand eight-membered rings are more destablized than organic systems.



Scheme 16

2-E<sub>2</sub> + [1-P<sub>2</sub>]<sup>+</sup> 
$$\xrightarrow{K_{eq} \sim 1}$$
 2-P<sub>2</sub> + [1-E<sub>2</sub>]<sup>+</sup>  
2-E<sub>2</sub> + [1-Ph<sub>2</sub>]<sup>+</sup>  $\xrightarrow{K_{eq} \sim 1}$  2-Ph<sub>2</sub> + [1-E<sub>2</sub>]<sup>+</sup>

2-M<sub>2</sub> + [1-E<sub>2</sub>]<sup>+</sup>

2-E<sub>2</sub> + [1-M<sub>2</sub>]<sup>+</sup>

Reduction of  $[(PPh_3)Re(CO)_5]^+$  ([1-Ph\_1]<sup>+</sup>). In general we would expect monophosphine rhenium pentacarbonyl cations to be more electrophilic than their bis(phosphine) counterparts, rendering them better hydride acceptors, and indeed, in contrast to  $[1-Ph_2]^+$ ,  $[(PPh_3)Re(CO)_5]^+$  ( $[1-Ph_1]^+$ ) is readily reduced by [HPt]<sup>+</sup> in the absence of any Lewis acid assistance.<sup>10b</sup> Furthermore, precipitation of a  $[Pt]^{2+}$  salt is not required to drive the reaction, although reduction of [1-Ph<sub>1</sub>]-[OTf] with [HPt][PF<sub>6</sub>] (which results in precipitation of  $[Pt][OTf]_x[PF_6]_{2-x}$  is more rapid than that of  $[1-Ph_1][BAr^F_4]$ with  $[HPt][BAr^{F}_{4}]$  (in which case  $[Pt][BAr^{F}_{4}]_{2}$  remains in solution).<sup>42</sup> The resultant monophosphine formyl species  $(PPh_3)Re(CO)_4(CHO)$  (2-Ph<sub>1</sub>) is much less stable than **2-Ph<sub>2</sub>**<sup>43</sup> it quickly ( $t_{1/2} \approx 30$  min) deinserts to give Re–H<sup>21</sup> and cannot easily be further reduced (unless a strong electrophile such as MeOTf is added, to afford an electrophilic methoxycarbene<sup>10b</sup>)

**Reduction of**  $[(Ph_2PCH_2B(C_8H_{14}))Re(CO)_5]^+$   $([1-M_1]^+)$ . Reaction of  $[1-M_1][OTf]$  with 1 equiv of  $[HPt][PF_6]$  in C<sub>6</sub>D<sub>5</sub>Cl gives boroxycarbene **2-M**<sub>1</sub> as the major (~90% isolated yield) product in ~10 min at room temperature (Scheme 17).<sup>44</sup> The minor (~10%) side product was tentatively assigned as an alkyl species bridging two Re centers, a hypothesis later solidified by spectroscopic analogy to related reduced monophosphine-ligated species (*vide infra*). Similar results were obtained in CD<sub>2</sub>Cl<sub>2</sub>, although a slow background reaction of  $[\mathbf{HPt}]^+$  with the solvent gives some  $CD_2HCl.^{17}$  In both solvents  $[\mathbf{Pt}][OTf]_x[PF_6]_{2-x}$  precipitates, but that is not a requisite driving force: treatment of  $[\mathbf{1}-\mathbf{M}_1][BAr^F_4]$  with  $[\mathbf{HPt}][BAr^F_4]$  (which forms soluble  $[\mathbf{Pt}][BAr^F_4]_2$ ) led to complete reduction as well (albeit more slowly, as with the  $[\mathbf{1}-\mathbf{Ph}_1]^+$  salts above; also see below).  $\mathbf{2}-\mathbf{M}_1$  exhibits the characteristic downfield <sup>1</sup>H NMR signal ( $\delta$  14.07, d, <sup>3</sup> $J_{PH} = 2.5$  Hz in C<sub>6</sub>D<sub>5</sub>Cl); a broad <sup>13</sup>C{<sup>1</sup>H} resonance at  $\delta$  283 is attributed to the carbene carbon. In contrast to most of the other boroxycarbenes studied, which show either broad or no <sup>11</sup>B resonances,  $\mathbf{2}-\mathbf{M}_1$  displays a relatively sharp <sup>11</sup>B{<sup>1</sup>H} signal at  $\delta$  11.2, consistent with four-coordinate boron.<sup>45</sup>

Reaction of 2-M<sub>1</sub> with pyridine led after ~30 min to complete disappearance of the carbene resonance and growth of a new doublet at  $\delta$  4.91 ( $J_{PH} = 5.8$  Hz, 2H) in the <sup>1</sup>H NMR spectrum; two equal-intensity singlets were observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. These spectroscopic characteristics are quite similar to those of the product of [HPt]<sup>+</sup> reduction of the ethylene-linked analogue 1-E<sub>1</sub> (*vide infra*), as well as of the minor side product that accompanied formation of 2-M<sub>1</sub>; accordingly we assign it as the bridging alkyl-carbene dirhenium species 10-M<sub>1</sub>·py (Scheme 18), formed via disproportionation. It is noteworthy that the B–O bond of 2-M<sub>1</sub> can be cleaved by pyridine, in contrast to that in 2-M<sub>2</sub> (Scheme 8); perhaps the more electrophilic nature of the monophosphine complexes places more of the negative charge at C instead of O.

By itself,  $2-M_1$  is quite stable in solution: there is no observable decarbonylation over a month, indicating a particularly strong B-O interaction that inhibits the normal formyl deinsertion path. This stability is far greater than 2-Ph<sub>2</sub>, 2-E<sub>2</sub>, and 2-Ph<sub>1</sub>, in line with that of 2-M<sub>2</sub>. There is eventually some decomposition after two months to a new species (Scheme 19), identified by XRD as the alkoxy-boroxycarbene complex 11 (Figure 5), whose formation likely involves B-C cleavage to extrude 9-BBN, coupling of the methylene fragment to the formyl carbon, and addition of the resulting alkoxy oxygen to a carbonyl carbon on another Re center, although the exact mechanistic sequence is not known. 11 exhibits an unusually upfield  ${}^{31}P{}^{1}H$  NMR signal,  $\delta$  – 54.0, typical of P in a four-membered ring;<sup>30</sup> the alkoxyboroxycarbene  ${}^{13}C{}^{1}H$  resonance is observed at  $\delta$  210.2  $(d, J_{PC} = 9.4 \text{ Hz}).$ 

<sup>(42)</sup> One possibility for this kinetic discrepancy could be tighter ion pairing for the smaller anions, which may aid in the transfer of hydride between two cationic species.

<sup>(43) (</sup>a) Tam, W.; Lin, G.-Y.; Gladysz, J. A. Organometallics **1982**, *1*, 525. (b) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. Organometallics **1989**, *8*, 498.

<sup>(44)</sup> Stronger hydrides such as NaHBEt<sub>3</sub> generally resulted in much more hydride formation and were thus avoided. These reactions were sometimes accompanied by intense color changes consistent with reduction processes, which would labilize the CO ligands and lead to reactivity at Re itself.

<sup>(45)</sup> Eaton, G. R. J. Chem. Educ. 1969, 46, 547.

Ph<sub>2</sub>

Ph Or

00

00 0

RE



(+ other products)

Figure 5. Structural representation of 11 with ellipsoids at 50% probability. Most H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Re1-C92.20(1)C9-O91.33(1), C9-O10 1.25(1), O10-B1 1.59(2), O9-C32 1.49(1), Re2-C32 2.28(1), P2-Re2-C8 159.0(5), P1-Re1-C2 172.2(4).



[Na][3-M<sub>1</sub>]

(46) (a) Mckinney, R. J.; Kaesz, H. D. J. Am. Chem. Soc. 1975, 97, 3066. (b) Casey, C. P.; Scheck, D. M. J. Am. Chem. Soc. 1980, 102, 2723. (c) Casey, C. P.; Jones, J. J. Am. Chem. Soc. 1980, 102, 6154. (d) Warner, K. E.; Norton, J. R. Organometallics 1985, 4, 2150. (e) Martin, B. D.; Warner, K. E.; Norton, J. R. J. Am. Chem. Soc. 1986, 108, 33.

Addition of a second equivalent of  $[HPt][PF_6]$  to 2-M<sub>1</sub> produces two new species over a period of hours. At early

stages the major species exhibits a <sup>1</sup>H doublet at  $\delta$  4.54 (<sup>3</sup>J<sub>PH</sub> = 2.6 Hz), which in <sup>1</sup>H-<sup>13</sup>C and <sup>1</sup>H-<sup>31</sup>P gHMBC

NMR experiments showed three-bond coupling (through

Re) to CO and P ligands; these and other multinuclear and multidimensional NMR experiments support assignment

as the mononuclear Re alkyl complex 12.17 Over 48 h 12

is converted quantitatively (by NMR) to the second species, assigned as Re-acyl  $[3-M_1]^-$  (Scheme 20), based on (*inter alia*) the following NMR evidence: (1) an AB pattern ( $J_{HH} =$ 16 Hz) corresponding to geminal CH<sub>2</sub> protons, further coupled to an acyl carbon at 275 ppm (by  $^{1}H^{-13}C$ -gHMBC,

which also shows that there is no longer any two- or threebond coupling between the CH<sub>2</sub> group and CO ligands); (2)

a single <sup>31</sup>P{<sup>1</sup>H} NMR resonance with a downfield shift,  $\delta$ 38.1, consistent with a five-membered ring structure,<sup>30</sup> which

It is unclear whether the migratory insertion leading from 12 to  $[3-M_1]^-$  is Lewis acid-assisted (which would require

is weakly coupled to one of the CH<sub>2</sub> protons.

B-O cleavage). Migratory insertion on Re in the absence of a Lewis acid is very rare and usually slow,<sup>38,46</sup> but the



**Figure 6.** Structural representation of  $[Na(THF)_3][3-M_1]$  with ellipsoids at 50% probability. Most H atoms, and C atoms of THF molecules, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re-C1 1.935(5), Re-C2 1.849(5), Re-C3 1.951(5), Re-C5 2.130(4), Re-O4 2.206(3), O4-C4 1.440(4), O4-B 1.575(5), C4-C5 1.532(6), C5-O5 1.218(5), O5-Na 2.238(3), O2#1-Na 2.411(3), Re-C5-O5 143.2(3).

reaction here *is* quite slow compared to the insertions observed following reduction of  $2-E_2$  and  $2-E_2-Mn$ . (The analogous reaction in the  $2-E_1Ph_1$  system is also faster; *vide infra*.) Reaction of  $2-M_1$  with the stronger hydride NaHBEt<sub>3</sub> led to  $[3-M_1]^-$  much more rapidly. Acceleration could be due to BEt<sub>3</sub>- or Na<sup>+</sup>-assisted migratory insertion or product stabilization, but separate experiments probing any additive effect of BEt<sub>3</sub> or NaBF<sub>4</sub> (on [HPt]<sup>+</sup>-mediated reductions) were inconclusive.

Reduction of  $[1-M_1][BAr^F_4]$  using  $[HPt][BAr^F_4]$  resulted in a change in the rate-limiting step, as reduction of the carbene was slower than migratory insertion. Therefore, no alkyl intermediate was observed, and the reaction took about 1 week to reach completion.

The presence of the Na<sup>+</sup> counterion in the synthesis of  $[3-M_1]^-$  allowed for crystallization of single crystals of  $[Na(THF)_3][3-M_1]$  from a cold THF/pentane mixture, with an XRD study confirming the structure assigned by NMR (Figure 6). A B–O bond is formed between the cyclic alkoxide and the borane in the secondary coordination sphere; the bond distances are consistent with an acyl functionality, as illustrated, with a relatively short C=O distance of 1.218(5) Å. The Na<sup>+</sup> counterion bridges an acyl O of one molecule and a carbonyl O of another molecule, forming a zig-zagging network in the crystal lattice.

**Reduction of**  $[(Ph_2P(CH_2)_2B(C_8H_{14}))Re(CO)_5]^+$  ([1-E<sub>1</sub>]<sup>+</sup>). The reaction of  $[1-E_1][OTf]$ , with 1 equiv of  $[HPt][PF_6]$  in  $C_6D_5Cl$  proceeds readily at ambient temperature, but the expected boroxycarbene product is not observed; instead a single species is formed in good yield, whose NMR properties (in particular, a <sup>1</sup>H doublet at  $\delta$  5.06 ( ${}^3J_{PH} = 6.9$  Hz, 2H); two  ${}^{31}P$  peaks in a 1:1 ratio, one of which correlates to <sup>1</sup>H  $\delta$  5.06 in  ${}^{1}H-{}^{31}P$  gHMBC; a  ${}^{13}C$  resonance at  $\delta$  209.6) are reminiscent of the dioxycarbene linkage in **11** and suggest the related structure **10-E**<sub>1</sub> (Scheme 21). The expected carbene species **2-E**<sub>1</sub> can be observed as an intermediate at low temperature: NMR spectroscopic monitoring of the reaction in a thawing  $C_6D_5Cl$  solution at -40 °C showed nearly complete conversion to a carbene species, which at 25 °C is cleanly and quickly converted to **10-E**<sub>1</sub> (Figure S157).



Two pathways can be envisioned for disproportionation of 2-E<sub>1</sub> to 10-E<sub>1</sub>: (1) hydride donation from one Re-CHO group (exposed by B-O cleavage) to a second Re=CHOBR<sub>3</sub> to give a Re-CH<sub>2</sub>O<sup>-</sup> fragment capable of nucleophilic attack on the M–CO of re-formed  $[1-E_1]^+$  or (2) nucleophilic attack by the O of the Re-CHO group (again exposed by B–O cleavage) on another carbene, followed by a hydride shift. The first would require breaking a bond between  $Re-CH_2O^-$  and B, which is expected to be quite strong (recall the inability of pyridine to break the B-O bond in  $[3-E_2]^-$ ), perhaps favoring the second. The two alternatives can be distinguished by reaction of  $2-M_1$  with  $2-P_1$ , in which the routes beginning with hydride transfer (left, Scheme 22) and O attack (right, Scheme 22) would produce different products. Only one mixed-ligand dinuclear complex, 10-M<sub>1</sub>P<sub>1</sub>, in which the alkyl group is bound to the Re ligated by the propylene-linked ligand, is observed by NMR (>90%),<sup>1</sup> supporting the preferred nucleophilic O attack mechanism. The same mechanism is likely operating in the reaction of methylene-linked  $2-M_1$  with pyridine (vide supra), with the Lewis base inducing B-O bond cleavage, exposing a formyl O that attacks unperturbed  $2-M_1$  to afford the related  $10-M_1$ . Very similar mechanisms have been proposed for the formation of related metalloesters (lacking borane stabilization).<sup>5d,47,48</sup>

Reduction of  $[(Ph_2P(CH_2)_2B(C_8H_{14}))(Ph_3P)Re(CO)_4]^+$  $([1-E_1Ph_1]^+)$ . When  $[1-E_1Ph_1][OTf]$  was treated with NaHBEt<sub>3</sub> in C<sub>6</sub>D<sub>5</sub>Cl, a single species formed immediately, which exhibited a downfield <sup>1</sup>H NMR singlet,  $\delta$  13.74, and two <sup>31</sup>P{<sup>1</sup>H} NMR doublets,  $\delta$  9.3 and 15.4 ( $J_{PP} = 97$  Hz), but after a few minutes solids precipitated, which could be redissolved by adding pyridine, suggesting that the initial product is **2-E<sub>1</sub>Ph<sub>1</sub>** (Scheme 23), which rearranges to an insoluble oligomer (similar to propylene-linked **2-P<sub>2</sub>**). No evidence of disproportionation or any other transformation of  $[1-E_1Ph_1]^+$  was observed before precipitation.

Treatment of  $[1-E_1Ph_1][OTf]$  with 2 equiv of NaHBEt<sub>3</sub> in THF cleanly afforded a new reduced species whose NMR

<sup>(47)</sup> Casey, C. P.; Andrews, M. A.; McAlister, D. R. J. Am. Chem. Soc. **1979**, 101, 3371.

<sup>(48)</sup> Berke, H.; Weiler, G. Angew. Chem., Int. Ed. Engl. 1982, 21, 150.



and IR data are consistent with C–C bond formation analogous to that found in  $[3-E_2]^-$ , except for an IR band at 1572 cm<sup>-1</sup>, suggesting structure  $[3-E_1Ph_1]^-$  (Scheme 23), with a free acyl group (in contrast to the boroxycarbene functionality in  $[3-E_2]^-$ , Scheme 2). [Na(THF)<sub>3</sub>][ $3-E_1Ph_1$ ] was crystallized and the structure confirmed by XRD (Figure 7); the single borane is bound to the alkoxide oxygen, leaving a free

[Na][3-E1Ph1]

13

acyl whose O interacts with the sodium counterion, which also interacts with a CO of a neighboring molecule, forming long chains of repeating units in the crystal lattice. These chains are more linear than the zigzag network of [Na-(THF)<sub>3</sub>][**3-M**<sub>1</sub>], due to Na<sup>+</sup> bridging *trans*-disposed ligands rather than *cis*-disposed ones. The metrical parameters are also quite similar to [Na(THF)<sub>3</sub>][**3-M**<sub>1</sub>].

Reaction of  $[3-E_1Ph_1]^-$  with MeOTf gives the neutral methoxycarbene complex 13 (Figure 7). A smooth trend in the Re-C and C-O bond distances, reflecting decreased acyl and increased carbene character, can be seen on comparing the "free" acyl group in the sodium salt of  $[3-E_1Ph_1]^-$ , 2.133(1) and 1.251(2) Å, the boroxycarbene in the sodium salt of  $[3-E_2]^-$ , 2.0960(9) and 1.271(1) Å, <sup>10a</sup> and the methoxycarbene in 13, 2.0250(6) and 1.3079(7) Å, respectively. (The Re-C and C-O bonds in  $[3-E_1Ph_1]^-$  are only ~0.02 Å shorter and longer, respectively, than that of structurally similar anionic Re-acyl species,49 indicating that the O-Na interaction does not much perturb the acyl bonding.) Notably, the B-O distances in these three species, which presumably are related to B–O bond strength, are quite similar–1.593-(1) Å (boroxycarbene) and 1.580(1) Å in  $[3-E_2]^-$ , 1.574(2) Å in  $[3-E_1Ph_1]^-$ , and 1.5897(8) Å in 13—and shorter than the (easily broken) boroxycarbene B–O bond in  $2-E_2$ , 1.612(1) Å.

In contrast to the result when 2 equiv of NaHBEt<sub>3</sub> is employed, treatment of [1-E1Ph1][OTf] with 2 equiv [HPt]- $[PF_6]$  in THF-d<sub>8</sub> does not afford C-C bond formation: after initial rapid formation of the carbene species 2-E<sub>1</sub>Ph<sub>1</sub>, no further reaction was observed before precipitation of the carbene (which occurs over a few hours under these conditions). This may be compared to the reaction of  $[1-E_2][BF_4]$ with  $[HPt][PF_6]$ , which proceeds to  $[3-E_2]^-$  within a few minutes, suggesting that a major role of the second pendent Lewis acid in the latter system is to promote hydride transfer from the weaker hydride source  $[HPt]^+$ , besides aiding the CO insertion step. Further comparison can be made to 2-M2-py, which also effectively has only one Lewis acid and also is not reduced by [HPt]<sup>+</sup>. It is somewhat surprising that CO coupling proceeds so readily in the formation of  $[3-E_1Ph_1]^-$  from [1-E<sub>1</sub>Ph<sub>1</sub>][OTf] and 2 equiv of NaHBEt<sub>3</sub>, as unassisted migratory insertion is not generally observed in simple alkyl species of rhenium under such mild conditions (especially without added ligand);<sup>38,46</sup> perhaps BEt<sub>3</sub> (the byproduct of reduction by [HBEt<sub>3</sub>]<sup>-</sup>) provides the needed assistance as an external Lewis acid.

Reduction of  $[(Ph_2P(CH_2)_3B(C_8H_{14}))Re(CO)_5]^+$  ([1-P<sub>1</sub>]<sup>+</sup>). Treatment of 1,3-propanediyl-linked phosphinoborane cation [1-P<sub>1</sub>][OTf] with 1 equiv of [HPt][PF<sub>6</sub>] in C<sub>6</sub>D<sub>5</sub>Cl gives a new species with a <sup>1</sup>H NMR resonance at  $\delta$  13.74 (s), a <sup>31</sup>P{<sup>1</sup>H} resonance at  $\delta$  1.7, and a broad <sup>11</sup>B resonance at  $\delta$  85. The <sup>11</sup>B chemical shift indicates three-coordinate boron,<sup>45</sup> suggesting the unstabilized formyl structure 2-P<sub>1</sub> (Scheme 24). Consistent with this formulation, and unlike all of the other [Re–CHO] species with pendent boranes reported here, 2-P<sub>1</sub> undergoes CO loss and Re–H formation over a period of several hours, similar to the behavior of (PPh<sub>3</sub>)Re(CO)<sub>4</sub>(CHO) (2-Ph<sub>1</sub>). A small amount (<5% by NMR) of an additional species, possibly an alkyl, formed

<sup>(49) (</sup>a) Lenhert, P. G.; Lukehart, C. M.; Sotiropoulos, P. D.; Srinivasan,
K. *Inorg. Chem.* 1984, 23, 1807. (b) Djukic, J. P.; Dotz, K. H.; Pfeffer, M.;
De Cian, A.; Fischer, J. *Inorg. Chem.* 1998, 37, 3649. (c) Padolik, L. L.; Gallucci,
J. C.; Wojcicki, A. J. Am. Chem. Soc. 1993, 115, 9986.



**Figure 7.** Structural representation of  $[Na(THF)_3]$ [**3-E**<sub>1</sub>**Ph**<sub>1</sub>] (left) and **13** · (C<sub>6</sub>H<sub>5</sub>Cl)<sub>0.5</sub> (right), with thermal ellipsoids at 50% probability. Most H atoms, C atoms of THF molecules, and solvent molecules of crystallization are omitted for clarity. The chlorobenzene molecule cocrystallized with **13** was disordered and sat near a center of symmetry. Selected bond distances (Å) and angles (deg):  $[Na(THF)_3]$ [**3-E**<sub>1</sub>**Ph**<sub>1</sub>]: Re-C1 1.9428(6), Re-C2 1.8799(6), Re-C3 2.1361(6), Re-O4 2.2470(5), O4-C4 1.4379(8), O4-B1 1.5731(9), C4-C3 1.5181(9), C3-O3 1.2416(8), O3-Na 2.2935(6), Re-O3-C3 143.20(5). **13** · (C<sub>6</sub>H<sub>5</sub>Cl)<sub>0.5</sub>: Re-C1 1.9902(6), Re-C2 1.8772(7), Re-C4 2.0250(6), Re-O3 2.2263(5), O3-C3 1.4359(8), O3-B1 1.5897(8), C3-C4 1.496(1), C4-O4 1.3079(7), O4-C5 1.457(1), Re-C4-O4 145.15(6).



initially and remained through the reaction, but no C–C coupling was observed before complete decomposition, even with excess [HPt][PF<sub>6</sub>]. Apparently an eight-membered ring is too large for intramolecular stabilization of the formyl; the absence of any effective intermolecular stabilization may reflect lower basicity of the formyl O for this monophosphine complex, compared to the bis-(phosphine) complexes where dimeric and oligomeric species are observed.

**Overview of**  $(Ph_2P(CH_2)_nB(C_8H_{14}))Re$  **Complexes: Ring Size Effects.** The effect of changing chelate ring size is summarized in Scheme 25; remarkably, each system exhibits different reduction chemistry. With a methylene spacer, boroxycarbene 2-M<sub>1</sub> is stable and can be further reduced by  $[HPt]^+$ to undergo C–C coupling; with an ethylene spacer, the less stabilized 2-E<sub>1</sub> rapidly disproportionates to dinuclear alkyl 10-E<sub>1</sub> (which *does not* undergo spontaneous C–C coupling); with a propylene spacer, neither stabilization *nor* novel reactivity of the Re–CHO species is observed, and the formyl rapidly decarbonylates, similar to borane-free systems.<sup>43b</sup> Addition of pyridine to 2-M<sub>1</sub> disrupts the B–O bond and leads to 10-M<sub>1</sub>·py, a product very similar to that obtained in the ethylene-linked case, showing that under appropriate conditions the selectivity can be tailored.

The chain-length effect may be attributed to the relative stability of the intramolecular B–O interaction; the sixmembered ring in  $2-M_1$  is quite favorable, and the resulting stable boroxycarbene readily undergoes further reduction. For  $2-E_1$  there is an apparently rapid equilibrium between free formyl and boroxycarbene (an intramolecular seven-membered ring), leading to disproportionation; the potential eight-membered ring in  $2-P_1$  is not at all favorable, and the species behaves as a simple, unstabilized formyl.

### Conclusions

The precise nature of Lewis acid additives has a large impact on the reductive coupling of CO. External trialkylborane additives can facilitate reduction of [(PPh<sub>3</sub>)<sub>2</sub>Re- $(CO)_4$ <sup>+</sup> by [**HPt**]<sup>+</sup> and stabilization of the resultant formyl, but no further reduction or C-C bond formation is observed. To achieve the latter transformation, intramolecular interaction between boron and oxygen appears to be required, which is possible when the phosphine ligand contains a pendent alkylborane. We hypothesize that the size of the ring formed by intramolecular B-O interaction determines speciation, as shown in Scheme 26: shorter chain lengths give smaller, more stable rings, giving monomeric boroxycarbenes, while longer chain lengths give larger rings, which are destabilized, leading to either more formyl character (little interaction) or intermolecular interactions being dominant (with the pendent borane from one molecule binding oxygen on another). The monomeric species that contain intramolecular borane coordination appear to be readily reduced by [HPt]<sup>+</sup> (although bis(phosphine) complexes require a second pendent acid to shuttle the Pt-H), while oligomeric or externally borane-coordinated species do not show reductive coupling chemistry. This could be due to a geometric change of the boroxycarbene, imposed by the rigid ring structure (Figure 8). When the geometry is constrained



Scheme 26



in the P–Re plane, the back-bonding is competing with three CO ligands, whereas the more favored geometry, essentially  $90^{\circ}$  out of plane, competes with only two CO ligands. This subtle change would render the chelated boroxycarbene more electrophilic and perhaps more prone to nucleophilic attack.

The number of Lewis acids is also important. Reductive coupling in systems with only one Lewis acid was observed in only two cases ( $[1-M_1]^+$  and  $[1-E_1Ph_1]^+$ ), although in the case of the less electrophilic bis(phosphine) complex, strong hydride sources were required. This implies that the C–C bond forming step does not require Lewis acid assistance



## Figure 8

and may be driven more by ring-strain arguments. A second acid is required to shuttle a hydride from Pt to B in the case of bis(phosphine) complexes, if  $[HPt]^+$  is used as the reductant.

We have identified key requirements for successful integration of pendent boranes and have a preliminary understanding of the key steps of Lewis acid-facilitated CO hydrogenation. The number of Lewis acids and their strength are both important factors, and having a favorable ring size for intramolecular B-O coordination is essential. Work still remains in understanding the mechanistic subtleties of this system and in closing the cycle on rhenium by liberating the organic fragment.

Acknowledgment. Larry Henling and Mike Day assisted with crystallography. The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU award to the California Institute of Technology (CHE-0639094). David VanderVelde assisted with 2D and PGSE NMR spectroscopy. Dr. Daniel L. DuBois and Dr. Nathan M. West contributed enlightening discussions. This work was funded by BP (MC<sup>2</sup> Program) and the Moore Foundation.

**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.