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Homogeneous CO Hydrogenation: Dihydrogen Activation Involves a Frustrated Lewis Pair Instead of a Platinum Complex

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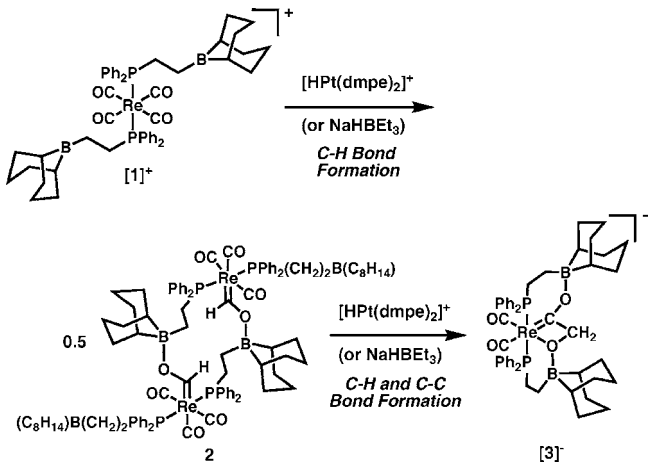
Since the oil crisis of the 1970s there has been interest in developing selective, homogeneously catalyzed conversion of synthesis gas (syngas; CO/H_2) to valuable hydrocarbons and oxygenates, as an alternative to the nonselective Fischer−Tropsch (FT) process.[1,2] Our approach to homogeneous CO hydrogenation involves a multicomponent catalyst system consisting of a metal carbonyl complex where CO is coordinated and activated, a late-transition-metal complex that heterolytically cleaves H_2 to form a nucleophilic metal hydride,[3] and a (Lewis or Brønsted) acid site to promote hydride transfer to CO and/or C−C bond formation steps.[4,5] A stoichiometric example was achieved using $[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4][BF_4]$ ([**1**][BF_4]), which contains a carbonyl cation with pendant Lewis acidic borane moieties that facilitate hydride transfer from $[HPt(dmpe)_2][PF_6]$ ([**HPt**][PF_6]; dmpe = 1,2-bis(dimethylphosphino)ethane) as well as further reduction and C−C bond formation (Scheme 1).[4]

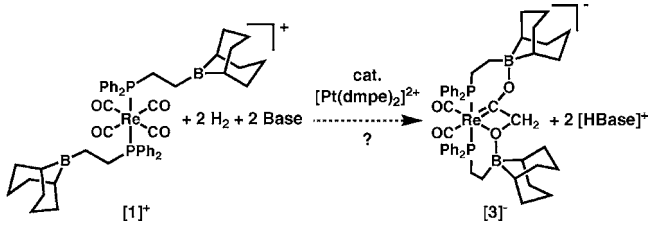
The transformation in Scheme 1 used preformed [**HPt**]$^+$. In principle, it could be carried out with H_2 and catalytic amounts of $[Pt(dmpe)_2]^{2+}$ ([**Pt**]$^{2+}$) (Scheme 2), but the strong bases (conjugate acid pK_a > 23 in MeCN[6]) that are required in order to produce [**HPt**]$^+$ from H_2 are very likely to attack the carbonyls and/or interact strongly with the Lewis acid sites, disrupting the intended pathway.[7] Instability of the resultant formyl species has also confounded related efforts.[8] While a weak Lewis base such as THF coordinates to [**1**][BF_4] at boron only weakly and reversibly[9] and does not interfere with the chemistry of Scheme 1, addition of 2 equiv of pyridine resulted in strong Lewis pair adduct formation, evidenced by a substantial upfield shift of the ^{11}B resonance of [**1**][BF_4] and complete inhibition of the reaction of [**1**][BF_4] with [**HPt**][PF_6] (see Scheme 3). Interestingly, however, addition of 2 equiv of the stronger Lewis base NEt_3 to [**1**][BF_4] shifted the ^{11}B NMR resonance only slightly, indicating minimal interaction, and [**HPt**][PF_6] did reduce [**1**][BF_4] to [**3**]$^-$ in the presence of added NEt_3. This observation suggested to us that [**Pt**]$^{2+}$, in combination with a strong but sterically bulky Lewis base, might catalyze H_2 activation and hydride transfer to a carbonyl of [**1**]$^+$ (Scheme 2).

The bulky, strong phosphazene base ^{t}BuNP(pyrrolidinyl)$_3$[10,11] (**P$_1$**) seemed to be a promising candidate. Addition of 2 equiv of **P$_1$** to a solution of [**1**][BF_4] caused only slight changes in chemical shifts and line shapes of ^{1}H, ^{31}P, and ^{11}B NMR resonances, indicating a weak, reversible interaction. Consequently, [**1**][BF_4] was smoothly reduced by [**HPt**][PF_6] in THF in the presence of **P$_1$**, albeit with concomitant precipitation of [**Pt**][PF_6]$_2$. The insolubility of [**Pt**][PF_6]$_2$ in THF necessitated a change from [BF_4] and [PF_6] salts to the more solubilizing [BAr^F_4] anion [BAr^F_4 = tetrakis(3,5-trifluoromethylphenyl)borate] before attempting catalysis. Gratifyingly, [**1**][BAr^F_4] underwent reductive coupling to form [**3**]$^-$ in the presence of substoichiometric amounts of [**Pt**][BAr^F_4]$_2$ along with excess **P$_1$** and H_2. Presumably, steric repulsion prevents **P$_1$** from tightly binding the borane or attacking the carbonyl, even

Scheme 1



Scheme 2

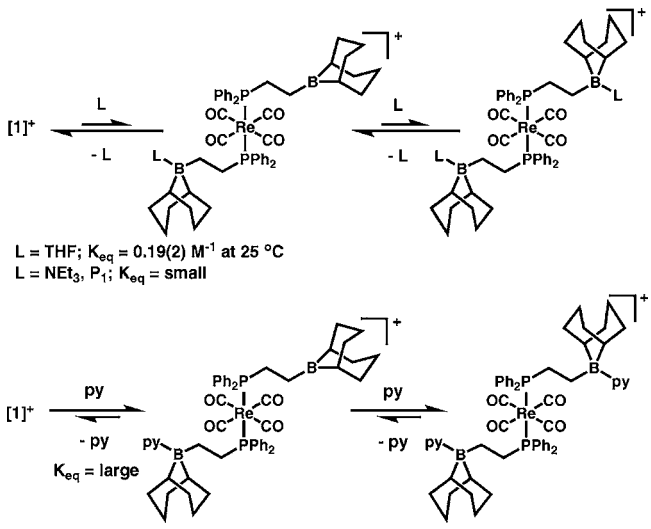


though [**HP$_1$**]$^+$ has a pK_a of 28.4 in MeCN,[12] making **P$_1$** a far stronger base than pyridine (which deactivates the system by binding the borane) and similar to KOPh (pK_a = 26.6[13]), which reacts irreversibly with [**1**][BF_4]. Furthermore, as expected for such a strong base,[6] THF solutions of **P$_1$** and [**Pt**][BAr^F_4]$_2$ readily reacted with H_2 to afford [**HP$_1$**][BAr^F_4] and [**HPt**][BAr^F_4], with $t_{1/2} \approx 10.2$ h (at an H_2 pressure of ∼3 atm; the dependence of the rate on H_2 pressure was not investigated).

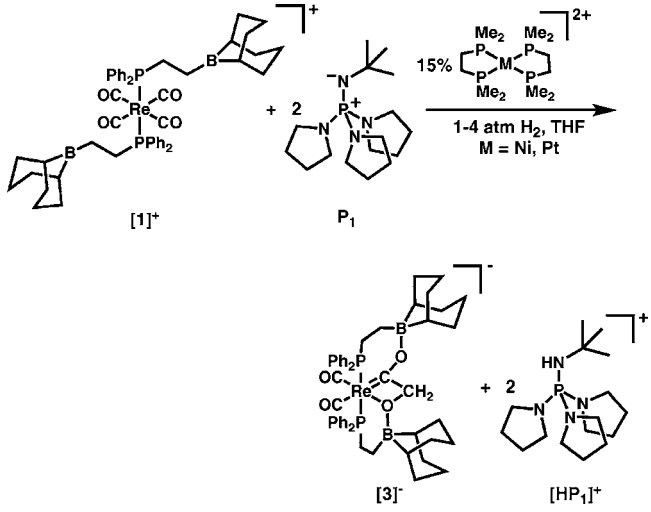
When an NMR tube was charged with [**1**][BAr^F_4], 4 equiv of **P$_1$**, and 15 mol % [**Pt**][BAr^F_4]$_2$ in THF-d_8, no significant reaction was observed; subsequent introduction of 1−4 atm H_2 led to the formation of [**HP$_1$**][BAr^F_4] and [**HPt**][BAr^F_4] over a few hours. Notably, no reduction of [**1**]$^+$ was seen as the hydride built up; however, after this induction period, the doubly reduced C−C-coupled anion [**3**]$^-$ formed in high yield over a few days at 23 °C (Scheme 4).

The observed induction period was unexpected, since [**HPt**][PF_6] reacts with [**1**][BF_4] quickly and in high yield;[4] this turns out to be a consequence of the choice of counterion. The seemingly innocuous substitution of [BAr^F_4] for [BF_4]/[PF_6] to keep [**Pt**]$^{2+}$ soluble in THF has the unintended effect of *completely inhibiting* the stoichiometric reaction of [**1**][BAr^F_4] with [**HPt**][BAr^F_4]. Hydride

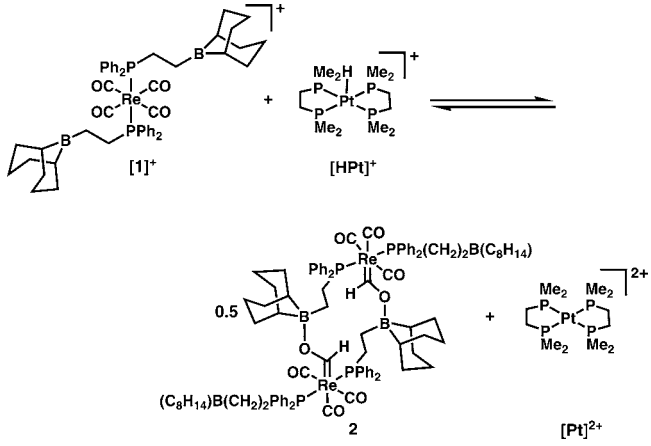
Scheme 3



Scheme 4



Scheme 5



transfer therefore appears to be an equilibrium that lies far toward unreacted $[\mathbf{1}]^+$ (Scheme 5) but can be pushed toward carbene **2** by precipitation of $[\mathbf{Pt}][BF_4]_x[PF_6]_{2-x}$, as in our original report.[4] Indeed, when carbene **2** was independently prepared in C_6D_5Cl and $[\mathbf{Pt}][BAr^F{}_4]_2$ was added, $[\mathbf{1}]^+$ and $[\mathbf{HPt}]^+$ formed rapidly.[14] The presence of $[\mathbf{Pt}][BAr^F{}_4]_2$ thus inhibits reduction of $[\mathbf{1}]^+$ to $[\mathbf{3}]^-$ according to the equilibrium in Scheme 5, accounting for the induction period. Hydride transfer cannot proceed until all of the $[\mathbf{Pt}]^{2+}$ is converted to $[\mathbf{HPt}]^+$.

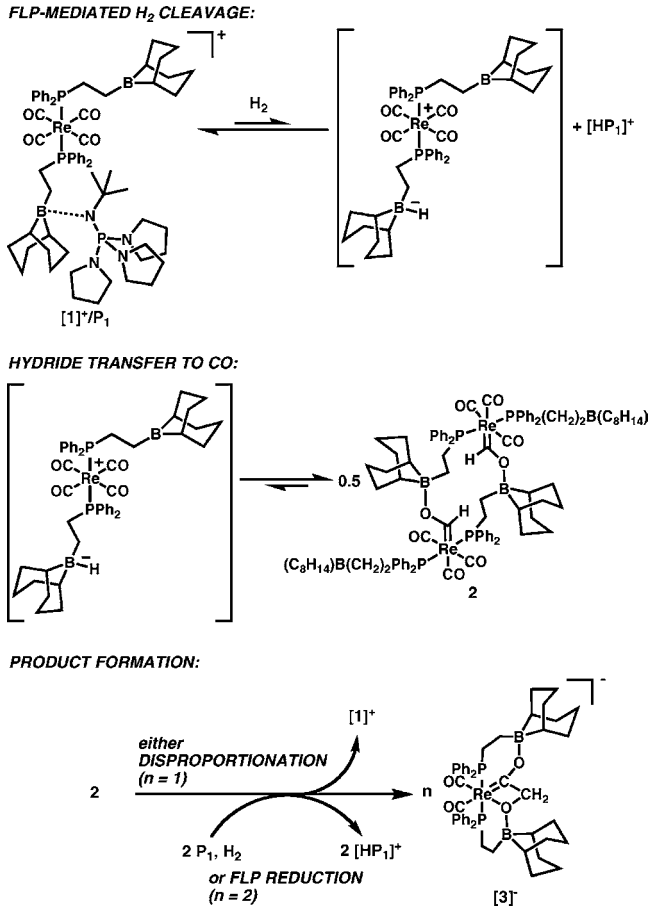
The above observations appear to be consistent with catalytic H_2 activation by $[\mathbf{Pt}][BAr^F{}_4]_2$ and subsequent reduction of $[\mathbf{1}]^+$ to $[\mathbf{3}]^-$ by $[\mathbf{HPt}][BAr^F{}_4]$, which proceeds only after all of the $[\mathbf{Pt}][BAr^F{}_4]_2$ has been converted to hydride. However, additional observations did not seem to support our hypothesis. While changing the catalyst loading altered the length of the induction period as expected, it did not significantly change the *rate* of reduction of $[\mathbf{1}]^+$ to $[\mathbf{3}]^-$ (Figure S17 in the Supporting Information). Furthermore, $[Ni(dmpe)_2][BAr^F{}_4]_2$ appeared to catalyze the reduction of $[\mathbf{1}]^+$ by H_2 with rates similar to the Pt analogue, despite the observation that $[HNi(dmpe)_2][PF_6]$ *does not react* with $[\mathbf{1}][BF_4]$. Finally, $[\mathbf{HPt}]^+$ formed markedly *faster* under the catalytic conditions ($t_{1/2} \approx 2.8$ h) than in the absence of $[\mathbf{1}]^+$ ($t_{1/2} \approx 10.2$ h) (Figure S18).

These observations suggest the possibility of activation of H_2 and reduction of $[\mathbf{1}]^+$ by some species that does not involve the group-10 metal "catalyst" at all. When a mixture of $[\mathbf{1}][BAr^F{}_4]$ and $\mathbf{P_1}$ *without Pt complex* was exposed to H_2, reduction to $[\mathbf{3}]^-$ began immediately, with no induction period, and proceeded to give a high yield of $[\mathbf{3}]^-$ (~92% after 8 days) with concomitant formation of $[\mathbf{HP_1}]^+$. We propose that in our "catalytic" reaction, H_2 cleavage and hydride delivery is actually mediated by a "frustrated" Lewis pair (FLP). FLPs consist of sterically demanding Lewis acids and bases that cannot form stable Lewis pairs; they have been found to carry out a number of interesting transformations,[15−17] most notably the cleavage of H_2[18−20] and metal-free hydrogenation of bulky imines[21,22] by a number of $B(C_6F_5)_3$/base pairs. Here the FLP would consist of $\mathbf{P_1}$ and the trialkylborane group appended to the ligands of $[\mathbf{1}]^+$.

According to this proposal, the (stoichiometric) reaction proceeds as shown in Scheme 6. First, FLP-mediated H_2 cleavage (formation of a weakly interacting acid−base pair, as shown in Scheme 6, is generally invoked as preceding H_2 activation[15]) generates small equilibrium amounts of the conjugate acid of $\mathbf{P_1}$ and a pendant borohydride (not observed), which can rapidly transfer H^- to CO to afford **2**. (Small amounts of **2** are usually observed at early reaction times.[23]) The subsequent transformation involves disproportionation of **2** to give $[\mathbf{3}]^-$ and $[\mathbf{1}]^+$ (rapid in THF relative to the reduction by H_2) and/or reduction of **2** to $[\mathbf{3}]^-$ by another FLP-mediated H_2 cleavage and hydride transfer involving the second appended borane.

A number of observations support our revised proposal of FLP mediation. The Lewis acid is essential: when 2 equiv of pyridine (which coordinates tightly to the boron centers of $[\mathbf{1}]^+$) was added to $[\mathbf{1}]^+$ prior to treatment with $\mathbf{P_1}$ and H_2, no discernible conversion to $[\mathbf{3}]^-$ was observed. The Lewis base is also required: $[\mathbf{1}]^+$ did not react with H_2 in the absence of $\mathbf{P_1}$. Removal of $[\mathbf{Pt}]^{2+}$ from the system lifts the requirement for the solubilizing $[BAr^F{}_4]$ anion, and indeed, $[\mathbf{1}][BF_4]$ was readily reduced by H_2 in the presence of $\mathbf{P_1}$ in a similar fashion. Addition of D_2 instead of H_2 resulted in >95% deuterium incorporation at the expected site in $[\mathbf{3}]^-$ [=C(O−)C*D*$_2$O−], confirming that dihydrogen is the source of hydride. The rate of reduction of $[\mathbf{1}]^+$ increases with the amount of $\mathbf{P_1}$, as 20 equiv of $\mathbf{P_1}$ afforded ~70% yield of $[\mathbf{3}]^-$ after 22 h.[24] The accelerated formation of $[\mathbf{HPt}][BAr^F{}_4]$ in the "catalytic" reaction is also understandable if H_2 activation is faster by the FLP than by $[\mathbf{Pt}]^{2+}$ and $\mathbf{P_1}$. The FLP would cleave H_2 to give first the borohydride and then **2**, as in Scheme 6, but before irreversible formation of $[\mathbf{3}]^-$ could occur, the fast equilibrium in Scheme 5 would take over, with $[\mathbf{Pt}]^{2+}$ abstracting a hydride to produce

Scheme 6



$[\mathbf{HPt}]^+$.[25] This alternate pathway for formation of $[\mathbf{HPt}]^+$ (as opposed to direct heterolytic cleavage of H_2 in conjunction with $\mathbf{P_1}$) explains the rate enhancement in the presence of $[\mathbf{1}]^+$.

The mechanism proposed in Scheme 6 suggests that an external borane could mediate a similar hydride transfer from H_2 to CO. A metal-free FLP was generated by mixing ^{t}BuCH$_2$CH$_2$B(C$_8$H$_{14}$) (**4**, a trialkylborane closely related to that in $[\mathbf{1}]^+$) and $\mathbf{P_1}$. No reaction of $\mathbf{4}/\mathbf{P_1}$ with H_2 was observed by NMR spectroscopy, but the pair does catalyze isotopic comproportionation of H_2 and D_2 to HD, implicating reversible H_2 activation with an equilibrium that lies far toward the FLP.[26] Estimates extrapolated from previous calculations[27] suggest that H_2 cleavage by such a FLP should be close to thermoneutral. A solution of cation $[(PPh_3)_2Re(CO)_4][BAr^F{}_4]$ (the unadorned analogue of $[\mathbf{1}]^+$), 10 equiv of $\mathbf{P_1}$, and **4** in THF-d_8 under an H_2 atmosphere showed conversion (~70% after 24 h at 23 °C) to $(PPh_3)_2Re(CO)_3(CHO)$ along with $(PPh_3)_2Re(CO)_3H$ and $(PPh_3)Re(CO)_4H$, the products of decarbonylation of the relatively unstable formyl complex[28] (1.0:0.7 formyl/hydride). No further reduction or C−C coupling steps were observed; those transformations apparently require the assistance of the pendant Lewis acid in $[\mathbf{1}]^+$.

The simple metal-free pair $\mathbf{4}/\mathbf{P_1}$ thus constitutes, to our knowledge, the first example of a trialkylborane-derived FLP that activates H_2. Such FLPs appear to be quite different from those previously reported: their equilibrium constants for formation lie much further toward free H_2 rather than the $[\mathbf{HP_1}]^+$/borohydride salts, but they provide a borohydride (generated directly from H_2) that is significantly more potent than the commonly used $[HB(C_6F_5)_3]^-$ (which does not react with $[\mathbf{1}]^+$). The implementation of an external FLP demonstrates that this novel type of FLP may be generally applicable in hydride transfers to CO ligands and, perhaps, a wider variety of substrates that require strong hydride donors, directly utilizing H_2 as the hydride source.

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Supporting Information Available: Full details of the synthesis and characterization of new compounds, experimental details, reaction time course plots, and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The K_{eq} for THF adduct formation with one of the pendant boranes was determined to be 0.19(2) M^{-1} by NMR titration experiments (presumably, the K_{eq} for binding to the second borane is similar, but the bis-THF adduct would be only a minor contributor), and $[1\cdot(THF)_2][BF_4]$, which was characterized crystallographically, readily loses THF on exposure to vacuum. See the Supporting Information for details.
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(23) Small amounts of other unknown species were also observed, especially as the amount of $\mathbf{P_1}$ was increased.
(24) Minor degradation was observed as the excess of $\mathbf{P_1}$ was increased, leading to slightly reduced yields at these shorter reaction times.
(25) The stoichiometric formation of **2** by trialkylborohydrides and production of $[\mathbf{HPt}]^+$ by hydride abstraction from **2** are both much faster processes than the heterolytic cleavage of H_2 by $[\mathbf{Pt}]^{2+}$ and $\mathbf{P_1}$.
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