

# CO<sub>2</sub> Activation by Frustrated Lewis Pair Transition Metal Systems

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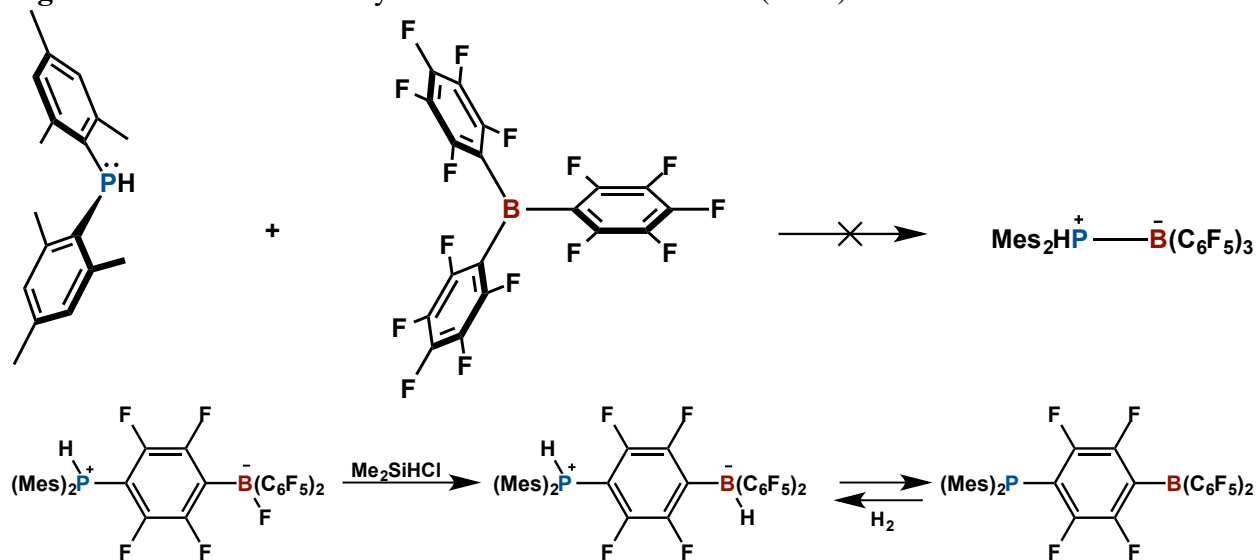
Literature Seminar

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The significant rise in the production of CO<sub>2</sub> as a byproduct of natural and anthropogenic processes has dominated recent scientific discourse. The “methanol economy” proposed by scientists such as Olah<sup>1</sup> has piqued considerable interest in the reduction of CO<sub>2</sub> and other substrates whose thermodynamic stability has thus far frustrated chemists’ attempts to utilize them as chemical feedstocks.<sup>2</sup> Although in some cases the reduction of molecules such as CO<sub>2</sub> is thermodynamically favorable, such transformations commonly require high energy (and thus expensive) co-reactants, or produce unwanted side-products.

Recent developments in the area of “frustrated Lewis pairs”, commonly referred to as FLPs, have generated considerable attention owing to the ability of such systems to activate traditionally challenging substrates.<sup>3,4,5</sup> Unlike classical Lewis base and Lewis acid pair, which form a dative bond between the lone pair of the Lewis base and the acceptor orbital of the Lewis acid, FLPs are combinations of bases and acids whose steric congestion prevents the formation of an adduct. The unquenched nature of such pairs results in the observation of unusual, alternate reactivity.<sup>6</sup> The work of Stephan and coworkers has been particularly seminal in exploring this reactivity.<sup>6</sup> By employing a pair of sterically bulky phosphine and boranes, Stephan and coworkers demonstrated one of the few examples of reversible H<sub>2</sub> cleavage by a non-metal system (Figure 1).<sup>6</sup> Since then, catalytic hydrogenation of bulky imines and enamines,<sup>7</sup> CO<sub>2</sub> reduction,<sup>8</sup> the ring opening of cyclic ethers,<sup>9</sup> and other reactions have been accomplished using main group FLPs.

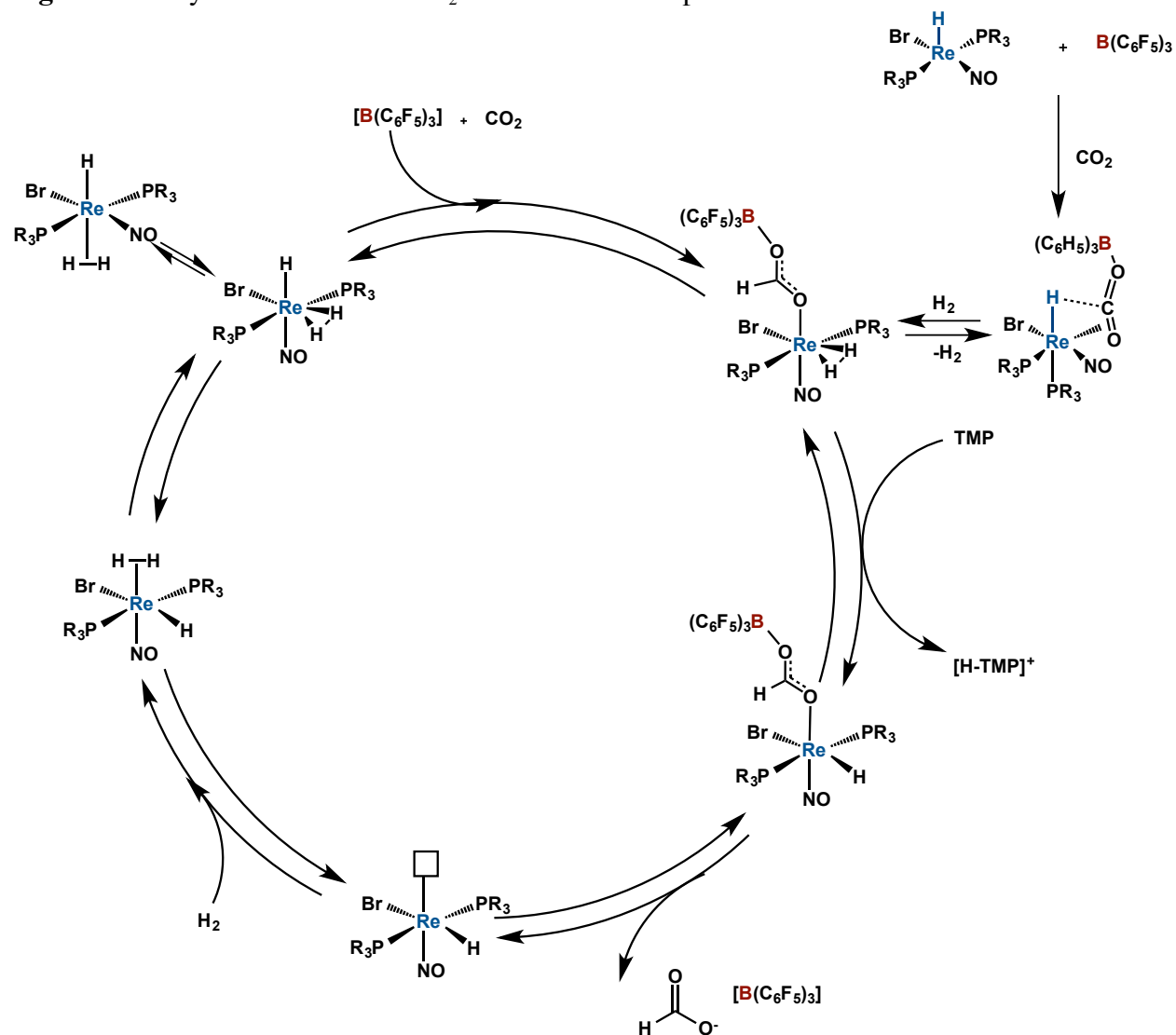
**Figure 1** Alternate Reactivity with Frustrated Lewis Pairs (FLPs)



Although the reactivity exhibited by these main group systems is promising, few catalytic reactions have been described. This limitation has inspired an extension of the FLP concept to transition metal systems, which exhibit a greater structural diversity and repertoire of reactions. The use of Lewis acidic metal centers and basic pendant donor atoms in the ligand features prominently in the work of DuBois and others.<sup>10</sup> Also noteworthy are recent examples of catalytic CO<sub>2</sub> reduction reported by Stephan<sup>11</sup> and Berke.<sup>12</sup> Recognizing that a transition metal-hydride bond is essentially “isolobal” to the free electron pair of a Lewis base, Berke and

coworkers designed a rhenium-hydride complex which, when used with an external base and Lewis acid, catalytically hydrogenates  $\text{CO}_2$  in the presence of  $\text{H}_2$  (Figure 2). Similarly, using a Lewis acidic ruthenium center, a pendant phosphine in the ligand, and a borane as a reducing agent, Stephan reports the isolation of a methoxy-borane which yields methanol and regenerates the borane upon hydrolysis.

**Figure 2** Catalytic Activation of  $\text{CO}_2$  with a Re–H Complex



Despite these early successes, transition metal FLP systems remain a nascent area of chemistry and, with a few exceptions, remain unexplored. The unusual, sometimes non-classical reactivity<sup>13</sup> of these systems, however, will ensure their study for years to come.

## References

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