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Preview

How Important Are Radical Mechanisms in Frustrated Lewis Pair Chemistry?

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Reaction mechanism is the foundation of understanding chemical reactivity. In this issue of *Chem*, Stephan and co-workers overturn long-held assumptions regarding the reactivity of frustrated Lewis pairs by providing compelling evidence that radical mechanisms might operate in some cases.

Frustrated Lewis pair (FLP) chemistry has been perhaps the most significant development in molecular main-group chemistry over the past decade. The realization that certain sterically encumbered combinations of Lewis acids and Lewis bases can act cooperatively to activate small molecules such as hydrogen has led to a wealth of new chemistry, not least in the use of such systems in catalysis.[1] One of the features that has caught the imagination of the community is that this area builds on one of the very first concepts we are taught in studying chemistry, namely Lewis's description of acids and bases as electron-pair acceptors or donors. It is inherently exciting to have something original to say about a nearly 100-year-old concept, particularly when it leads to such rich, varied, and useful chemistry.[2] The received wisdom in FLP chemistry is that, on the basis of Lewis's original insight for acids and bases, it involves the transfer of electron pairs. Previous work in this area has always corroborated, or assumed, that the activation of small molecules with FLPs is a two-electron process.

The work published in this issue of *Chem* by Stephan and co-workers[3] suggests that we need to revisit this assumption; a purely heterolytic, two-electron model of FLP-mediated small-molecule activa-tion might not always be applicable. This work provides compelling evidence that, in some circumstances, a single-electron transfer (SET) mechanism is operating. This challenge to the previous assumption is all the more remarkable in that the systems studied are some of the most well-known FLPs based on boron or aluminum Lewis acids and triarylphosphine Lewis bases. The subtleties of FLP chemistry clearly require more so-phisticated rationales than has hitherto been the case, and this will enable a deeper understanding of the mecha-nistic processes involved.

Starting with the well-established FLP combinations of ${}^t\text{Bu}_3\text{P}$ and $\text{E}(\text{C}_6\text{F}_5)_3$ (E = B, Al), Stephan and co-workers first demonstrate the inherent "frustration" of these FLPs before presenting their reactivity with tetrachloro-1,4-benzo-quinone ($p\text{-}\text{O}_2\text{C}_6\text{Cl}_4$). Equimolar reac-tions afford the expected products ${}^t\text{Bu}_3\text{POC}_6\text{Cl}_4\text{OE}(\text{C}_6\text{F}_5)_3$.

$\text{E}(\text{C}_6\text{F}_5)_3$ shows only weak interactions when combined with Ph_3SnH, but each ${}^t\text{Bu}_3\text{P}/\text{E}(\text{C}_6\text{F}_5)_3$ FLP results in the formation of the (stannyl)phosphonium salt $[{}^t\text{Bu}_3\text{PSnPh}_3][\text{HB}(\text{C}_6\text{F}_5)_3]$ or $[{}^t\text{Bu}_3\text{PSnPh}_3][(\mu\text{-H})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$. The structures of these were elucidated through nu-clear magnetic resonance (NMR) spec-troscopic and crystallographic analysis. These heterolytic-cleavage and FLP-addition reactions portrayed "classic" FLP behavior—the acceptance and dona-tion of an electron pair between the sub-strate and the two components of the FLP. However, when the phosphine was changed from ${}^t\text{Bu}_3\text{P}$ to Mes_3P, still a well-known FLP combination, the results were surprising. Instant color changes were seen when Mes_3P was mixed with the two Lewis acids, even though there was little NMR evidence to suggest any change from the starting reactants. Ex-periments with electron paramagnetic resonance (EPR) spectroscopy were the key to unlocking the nature of this sys-tem—the results clearly pertain to the ex-istence of the $[\text{Mes}_3\text{P}\cdot]^+$ radical cation for the $\text{Mes}_3\text{P}/\text{Al}(\text{C}_6\text{F}_5)_3$ FLP. This insinuates the presence of the $[\cdot\text{Al}(\text{C}_6\text{F}_5)_3]^-$ coun-terion, the short lifetime of which explains its absence in the EPR spectrum. Weaker signals were seen in the EPR spectrum for the $\text{Mes}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ FLP, making any con-clusions less definitive; however, the presence of a single-electron transfer (SET) equilibrium between $\text{Mes}_3\text{P}/$ $\text{Al}(\text{C}_6\text{F}_5)_3$ and the respective charged radical species is certainly an intriguing suggestion.

Reactions with 0.5 equiv of $p\text{-}\text{O}_2\text{C}_6\text{Cl}_4$ provide further evidence for the pres-ence of radical species, such that UV-visible spectroscopy supports the existence of the $[\text{Mes}_3\text{P}\cdot]^+$ cation after the $\text{Mes}_3\text{P}/\text{E}(\text{C}_6\text{F}_5)_3$ (E = B, Al) FLP was combined with the quinone. It should be noted that this was not the case when the phosphine and quinone were analyzed together in the absence of $\text{E}(\text{C}_6\text{F}_5)_3$. $[\text{Mes}_3\text{P}\cdot]_2[(\text{C}_6\text{F}_5)_3\text{EOC}_6\text{Cl}_4\text{OE}(\text{C}_6\text{F}_5)_3]$ is the expected product of these FLP reactions with quinone. Crystallo-graphic data were obtainable only upon the addition of Ph_3SnH, which afforded $[\text{Mes}_3\text{PH}]_2[(\text{C}_6\text{F}_5)_3\text{BOC}_6\text{Cl}_4\text{OB}(\text{C}_6\text{F}_5)_3]$.

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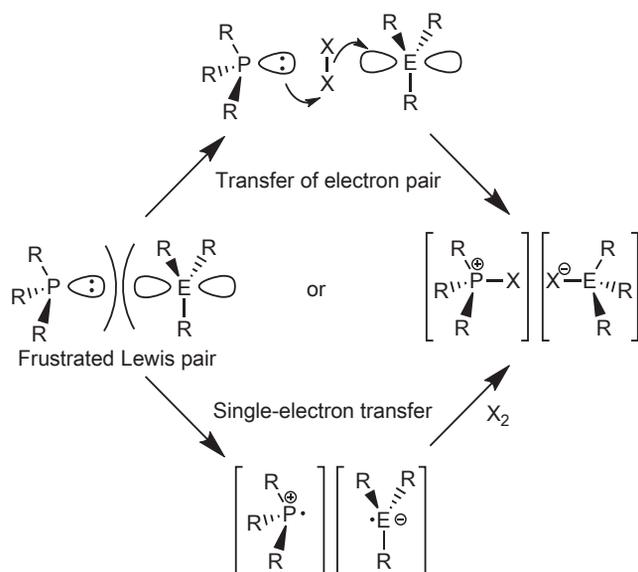
Figure 1. Electron-Pair Transfer or SET Mechanisms in FLP Chemistry

The addition of 1 equiv of p-$O_2C_6Cl_4$ to the FLPs produced a purple solution, which changed to pale yellow after a short amount of time. This suggests a two-step process whereby $[Mes_3P·]_2[(C_6F_5)_3EOC_6Cl_4OE(C_6F_5)_3]$ (E = B, Al) is initially formed and then converted to $[(Mes_3POC_6Cl_4OE(C_6F_5)_3]$. NMR spectroscopic and crystallographic data support this chain of events. This argument is further supported by the absence of any reaction between $[Mes_3P·][(\mu\text{-HO})(Al(C_6F_5)_3)_2]$ and p-$O_2C_6Cl_4$, showing that $[·OC_6Cl_4OE(C_6F_5)_3]^-$ is not formed in this way.[4]

Additional evidence for this mechanism was obtained through the addition of Ph_3SnH to the $Mes_3P/E(C_6F_5)_3$ (E = B, Al) FLPs; NMR spectra indicated the formation of $[Mes_3PH][HB(C_6F_5)_3]$ and $[Mes_3PH][(\mu\text{-H})(Al(C_6F_5)_3)_2]$ and the release of $Ph_3SnSnPh_3$ as a side product. This is indicative of H· abstraction from Ph_3SnH, demonstrating homolytic cleavage of the Sn–H bond, which was cleaved heterolytically by the $^tBu_3P/E(C_6F_5)_3$ (E = B, Al) FLPs.

The crucial point here is that although both $Mes_3P/E(C_6F_5)_3$ and $^tBu_3P/E(C_6F_5)_3$ give analogous products upon activation of H_2,[1,5] the route by which this is achieved is likely to be different: either a standard, two-electron transfer process in the case of $^tBu_3P/E(C_6F_5)_3$ or SET in the case of $Mes_3P/E(C_6F_5)_3$ (Figure 1). This

has important implications for the scope and selectivity of these systems.

These results should inspire many future studies, and two aspects immediately come to mind. First, it is intriguing that the FLPs described here are well known but that some of the key observations (for example, the color change in mixing Mes_3P and $E(C_6F_5)_3$) have previously been either ignored or not deemed worthy of further investigation. How many previous FLP systems actually operated via a SET mechanism? A systematic study would be valuable and would greatly aid a more sophisticated description of FLP processes. Analysis of these systems via computational methods should also aid understanding. Second, using this more detailed understanding of the factors that lead to electron-pair or single-electron pathways should enable the design of FLPs that specifically operate via one or the other mechanism. This should allow further expansion of an already compelling area of chemistry.

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