Single-Electron Transfer in Frustrated Lewis Pair Chemistry

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Abstract: Frustrated Lewis pairs (FLPs) are well known for their ability to activate small molecules. Recent reports of radical formation within such systems indicate single-electron transfer (SET) could play an important role in their chemistry. Herein, we investigate radical formation upon reacting FLP systems with dihydrogen, triphenyltin hydride, or tetrachloro-1,4-benzoquinone (TCQ) both experimentally and computationally to determine the nature of the single-electron transfer (SET) events; that is, being direct SET to B(C$_6$F$_5$)$_3$ or not. The reactions of H$_2$ and Ph$_3$SnH with archetypal P/B FLP systems do not proceed via a radical mechanism. In contrast, reaction with TCQ proceeds via SET, which is only feasible by Lewis acid coordination to the substrate. Furthermore, SET from the Lewis base to the Lewis acid–substrate adduct may be prevalent in other reported examples of radical FLP chemistry, which provides important design principles for radical main-group chemistry.

Introduction

Frustrated Lewis pairs (FLPs) combine a Lewis acidic electron-pair acceptor and a Lewis basic electron-pair donor to activate small molecules, most notably H$_2$ and CO, granting access to fascinating main group chemistry and catalysis.$^{[1]}$ It is generally accepted that the FLP components cooperatively interact with the substrate to facilitate heterolytic bond cleavage;$^{[2]}$ however, recent reports suggest that radicals may play an important role too and, in some cases, provide alternative homolytic pathways.$^{[2b,c,3]}$ Stephan et al. reported the detection of a weak radical signal by electron paramagnetic resonance (EPR) spectroscopy for the archetypal FLP PMes$_3$/B(C$_6$F$_5$)$_3$, (Mes = 2,4,6-triphenylmethyl), and after switching the Lewis acid to Al(C$_6$F$_5$)$_3$, found a similar, yet much clearer, EPR signal that could be unambiguously attributed to the phosphine radical cation (PMes$_3^+$).$^{[2c]}$ Furthermore, reaction of PMes$_3$/B(C$_6$F$_5$)$_3$ with Ph$_3$SnH resulted in formation of [Mes·Ph][HB(C$_6$F$_5$)$_3$] and Ph$_3$SnSnPh$_3$, instead of the [Mes·P·Sn·Ph][HB(C$_6$F$_5$)$_3$] product that would be expected for heterolytic cleavage of the Sn–H bond.$^{[2d]}$ In the case of PhBu$_3$/B(C$_6$F$_5$)$_3$, for which no radicals were detected in the reaction mixture, indeed [tBu–P·Sn·Ph][HB(C$_6$F$_5$)$_3$] was obtained, corresponding to nuclophilic substitution at tin (Scheme 1a). As the difference in products was proposed to be caused by a change in mechanism (homolytic vs. heterolytic), this led to the use of Ph$_3$SnH as a probe for determining the mechanistic nature of FLP reactions.$^{[2c-4]}$ Furthermore, Stephan et al. determined that reacting PMes$_3$/B(C$_6$F$_5$)$_3$ with tetrachloro-1,4-benzoquinone (TCQ) leads to radical forma-

Scheme 1. a) Different pathways proposed by Stephan et al. for reactions of FLPs with Ph$_3$SnH. b) Reactivity observed by Stephan et al. for Mes$_3$/P/B(C$_6$F$_5$)$_3$, with tetrachloro-1,4-quinone (TCQ). c) Reactivity observed by Melen et al. (Ar$^F$ = Ph, p-F-Ph or fluorene; Ar = variety of aryl groups, see Ref. [6]). d) Reactivity observed by Ooi et al. utilizing catalytic B(C$_6$F$_5$)$_3$ (10 mol%) (R = Me or Br); e) Light dependence for radical ion pair generation from archetypal FLP systems observed by Slootweg et al. (For P: R = Mes or tBu, for N: R = Ph or p-Me-Ph).

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Results and Discussion

First, we assessed the influence of light on the reaction of PMes$_3$ and B(C$_6$F$_5$)$_3$ with H$_2$ (1 atm), which is known to generate the corresponding phosphonium borate [Mes$_3$PH]--[HB(C$_6$F$_5$)$_3$].\[^{12}\] We previously showed that this combination of donor (PMes$_3$) and acceptor (B(C$_6$F$_5$)$_3$) forms a yellow charge-transfer complex in solution from which the corresponding radical ion pair [PMes$_3$°°', B(C$_6$F$_5$)$_3$°°'] is generated by irradiating this electron donor--acceptor (EDA) complex with visible light (534 nm).\[^{10}\] Thus, if formation of this radical ion pair is a significantly contributing factor in hydrogen splitting, the reaction should exhibit a change in reaction rate depending on the absence or presence of light. Comparison of reaction samples kept in the dark or irradiated (534 nm, 2.2 W LEDs; Scheme 2) whilst stirring for 2.5 hours showed near-identical conversions to the phosphonium borate [Mes$_3$PH]--[HB(C$_6$F$_5$)$_3$] and showed that for common donor (PMes$_3$) and acceptor (B(C$_6$F$_5$)$_3$) pairs, the reaction proceeds rapidly in the absence of light and, in both cases, within minutes full conversion to [Mes$_3$PH][HB(C$_6$F$_5$)$_3$] and Ph$_3$Sn--SnPh$_3$ was observed by multi-nuclear NMR spectroscopy ($\delta^{31}$P = -28.6, $\delta^{19}$B = -26.1, $\delta^{119}$Sn = -131.7; Supporting Information, Figure S5–S9; Scheme 1a). This suggests that also in this case radicals are not responsible for the reaction outcome.

But how is [Mes$_3$PH][HB(C$_6$F$_5$)$_3$] formed when using Ph$_3$SnH instead of H$_2$? For this, changing the phosphine to PrBu$_3$ provided insight. Addition of 1 equiv of Ph$_3$SnH to PrBu$_3$/B(C$_6$F$_5$)$_3$ in C$_6$H$_6$/Cl at room temperature instantly led to heterolytic cleavage of the Sn–H bond and the formation of [PrBu$_3$P–SnPh$_3$][HB(C$_6$F$_5$)$_3$] ($\delta^{31}$P = 65.8, $\delta^{19}$B = 58.1, $\delta^{119}$Sn = -410 Hz; Supporting Information, Figure S12) as well as Ph$_3$Sn–SnPh$_3$ (Scheme 3; Supporting Information, Figure S14) was observed.\[^{13}\] We also noted that this reaction proceeds equally in the absence of light, in ambient light, or under direct irradiation of the charge-transfer band of [PrBu$_3$P–SnPh$_3$] (400 nm, 2.2 W LED). These findings show that for both phosphines R,P (R = Mes and iBu) a polar, heterolytic mechanism is operative and that the initial product [R,P-
To elucidate the heterolytic splitting of Ph$_2$SnH in more detail, we first combined it with B(C$_6$F$_5$)$_3$, in calculations and found the formation of an adduct with a bridging hydride [Ph$_2$Sn–H–B(C$_6$F$_5$)$_3$] (Δ$E = -21.3$, Δ$G^\text{298K}$ = -1.9 kcal mol$^{-1}$; Figure 1, left), which is analogous to the key, transient intermediate in the B(C$_6$F$_5$)$_3$-catalyzed hydrosilylation.\textsuperscript{14} We also observed the [Ph$_2$Sn–H–B(C$_6$F$_5$)$_3$] adduct in CH$_2$Cl$_2$ solution by $^3$F-NMR spectroscopy that shows a decrease in resonance difference between the meta- and para-fluorines (Δ$\delta$ 18.2 to 13.7 ppm), which is indicative of a transition from a trigonal planar borane to a more tetrahedral geometry.\textsuperscript{15} Furthermore, $^{19}$Sn-NMR spectroscopy supports this notion, the clear downfield shift indicates a more electron deficient Sn nucleus (δ = 165 to 130 ppm; Supporting Information, Figure S15, S16).\textsuperscript{16} These observations evidence activation of the tin hydride by B(C$_6$F$_5$)$_3$, making it more susceptible to nucleophilic attack by a phosphine in an Sn$_3$ fashion to produce the initial [R$_3$P–SnPh$_3$][HB(C$_6$F$_5$)$_3$] species.

To investigate the subsequent reaction steps and determine the influence of the P-substituent (Mes vs. tBu), we again employed computational chemistry (ωB97X-D/def2-TZVP; [HB(C$_6$F$_5$)$_3$]$^-$ anion omitted),\textsuperscript{17} which highlighted a formal metathesis reaction of the [R$_3$P–SnPh$_3$]$^+$ cation with Ph$_3$Sn–H, reminiscent of reactions between tin hydrides and neutral stannyl phosphines.\textsuperscript{17} When using PMes$_3$, (Figure 2, in green), [Mes,P–SnPh$_3$]$^+$ undergoes a facile reaction with Ph$_3$SnH to afford the bridging hydride [Ph$_3$Sn–H–SnPh$_3$]$^+$ (Δ$E_{TS1}$ ≈ 9, Δ$E$ = -4.9 kcal mol$^{-1}$),\textsuperscript{18} akin to the tin hydride-B(C$_6$F$_5$)$_3$ adduct (Figure 1). Subsequent deprotonation by the liberated phosphine, which induces Sn–Sn bond formation (Δ$E_{TS2}$ = 19.9, Δ$E$ = -13.1 kcal mol$^{-1}$), affords [Mes,P]$_+$ and Ph$_3$Sn–SnPh$_3$. This reaction profile supports the notion that [Mes,P–SnPh$_3$][HB(C$_6$F$_5$)$_3$] is a transient, unobserved intermediate in the formation of [Mes,P][HB(C$_6$F$_5$)$_3$].\textsuperscript{18}

Changing the phosphine to PbBu$_3$ has a significant impact. First, the formation the bridging hydride [Ph$_3$Sn–H–SnPh$_3$]$^+$ is now endothermic (Δ$E^*_{TS1}$ = 14.1, Δ$E$ = 9.5 kcal mol$^{-1}$; Figure 2, in blue) and the subsequent deprotonation faces a sizeable barrier (Δ$E^*_{TS2}$ = 30.9, Δ$E$ = -0.2 kcal mol$^{-1}$). The near thermoneutral reaction profile and high barrier accounts for the slow and modest formation of [Bu$_3$P,PH][HB(C$_6$F$_5$)$_3$] and explains why the [Bu$_3$P–SnPh$_3$][HB(C$_6$F$_5$)$_3$] intermediate can be isolated after short reaction times and immediate work-up.\textsuperscript{19}

To support the intermediacy of the bridging [Ph$_3$Sn–H–SnPh$_3$]$^+$ cation, we combined [Ph$_3$C][B(C$_6$F$_5$)$_3$] with 2 equiv of Ph$_3$SnH in C$_6$H$_6$Cl at -35 °C in order to access this species by hydride abstraction (Scheme 4). Indeed, after 1 hour, the characteristic yellow color of the trityl cation disappeared, and an expected downshift of the aromatic $^1$H nuclei of the Ph$_3$Sn species in combination with a broadening of the hydride peak at 6.91 ppm was observed by $^1$H NMR spectroscopy (Supporting Information, Figures S20, S21).\textsuperscript{18} In addition, the spectrum evidenced formation of triphenylmethane (δ$^1$H = 5.55).\textsuperscript{18} As predicted by DFT, subsequent addition of PMes$_3$, led to formation of [Mes,P][B(C$_6$F$_5$)$_3$] by deprotonation, as observed by $^1$H- and $^{19}$P-NMR spectroscopy (Supporting Information, Figure S23, S24), and the formation of Ph$_3$Sn$^+$ was confirmed by ESI-MS.

\textbf{Scheme 4.} Hydride abstraction from Ph$_3$SnH using [Ph$_3$C][B(C$_6$F$_5$)$_3$] and subsequent reaction with PMes$_3$. 

\begin{align*}
2 \text{equiv.} \quad & \text{Ph}_3\text{SnH} \quad \text{[Ph}_3\text{C]} \quad \text{[B(C}_6\text{F}_5)_3] \quad \text{Mes}_3\text{P} \quad \text{[Mes}_3\text{P][B(C}_6\text{F}_5)_3] \quad + \text{Ph}_3\text{Sn-SnPh}_3 \\
& \text{[Ph}_3\text{Sn}] \quad \text{[B(C}_6\text{F}_5)_3] \quad \text{[B(C}_6\text{F}_5)_3] \\

\end{align*}
of Ph3Sn–SnPh3, evidenced by 119Sn NMR spectroscopy (Supporting Information, Figure S25). Addition of PbBu3 instead of PMes2 afforded both [Bu3PH][B(C6F5)3] and [Bu3P–SnPh3][B(C6F5)3] according to 31P-NMR spectroscopy (approx. 4:5 ratio; Supporting Information, Figure S26), since both the forward and reverse pathways (in blue, Figure 2) have accessible barriers (21.4 and 4.6 kcal mol⁻¹, respectively); this yields the thermodynamically controlled product distribution. These findings demonstrate that after heterolytic Sn–H bond cleavage to form [R3P-SnPh3][HB(C6F5)3], subsequent bond metathesis leads to formation of [R3PH][HB(C6F5)3] via a bridging hydride intermediate and highlights that the complete reaction of PMes2/B(C6F5)3 and PbBu3/B(C6F5)3 with Ph3SnH is accessible via heterolytic polar pathways.

Next, we set out to analyze the reaction of PMes3/B(C6F5)3 with tetrachloro-1,4-benzoquinone (TCQ) for which Stephan et al. detected radical formation (PMes3•+) by EPR spectroscopy.24 They postulated that this proceeds via SET from PMes3 to B(C6F5)3 to form the corresponding radical ion pair [PMes3•+, B(C6F5)3•−], after which 2 equiv of B(C6F5)3•− react with the quinone to form dianion 7, while 1 equiv of B(C6F5)3•− affords the neutral adduct Mes2P-TCQ-B(C6F5)3 4 (Scheme 5).25 We performed this reaction in the absence of light and found that the reaction still proceeds, forming a deep purple solution for which EPR spectroscopy confirmed the formation of PMes3•+ (two-line signal simulated with giso = 2.0050, Aiso = 670.00 MHz), but also showed for the first time a featureless signal (giso = 2.0058) that we attribute to a TCQ centered radical anion, most likely TCO-B(C6F5)3•− (Figure 3). Furthermore, we noted an unknown smaller third signal, which was also reported by Müller and Klare et al. when combining PMes3 and the strongly accepting silyl and trityl cations.26

So, how is it possible that radicals are formed in the dark? Clearly, a strong electron acceptor is required to oxidise PMes3 (IE = 5.25 eV; SCRF[15]/ωB97X-D/6–311 + G(d,p), solvent = chlorobenzene) and neither B(C6F5)3 nor TCQ are suitable (EA = 3.31 and 4.45 eV, respectively) to accommodate the needed thermal SET. Yet, B(C6F5)3 can coordinate to one of the carbonyl moieties of TCQ, affording the corresponding Lewis adduct TCQ-B(C6F5)3, which has an increased electron affinity (EA = 5.57 eV) and therefore should be capable of oxidizing PMes3.31 Note that such interactions between a Lewis acid and a carbonyl moiety are typically exploited in photo-redox catalysis to facilitate SET events.22 As the carbonyl moieties of TCQ are electron poor, the interaction with B(C6F5)3 is weak (ΔE = −4.6, ΔG° = 10.7 kcal mol⁻¹) leading to an equilibrium featuring low concentrations of the TCQ-B(C6F5)3 adduct, which supports the

![Scheme 5](image)

**Scheme 5.** a) Orbitals involved in the SET between PMes3 and the TCQ-B(C6F5)3 adduct. b) Reactivity, featuring all possible pathways for the reaction of TCQ, B(C6F5)3, and PMes3.
However, in presence of PMes, the transient TCO-B(CF₃)₃ adduct will undergo SET from the PMes, HOMO to the TCO-B(CF₃)₃ LUMO (Scheme 5, left) generating the radical ion pair [PMes⁺, TCO-B(CF₃)₃⁻] 3, which drives the equilibrium towards the TCO-B(CF₃)₃ adduct (Scheme 5b, blue). Subsequent radical coupling of PMes⁺ and TCO-B(CF₃)₃⁻ via a computed 8 kcal mol⁻¹ (ΔG²[298K]) barrier leads to the formation of Mes⁺P-TCO-B(CF₃)₃ 4 as observed experimentally by Stephan et al. (Scheme 5b, black). This mechanism highlights that, rather than directly participating in SET, B(CF₃)₃ acts as Lewis acid coordination to the carbonyl moiety facilitating the process by increasing the electron affinity of the quinone acceptor.

As TCO features two carbonyl moieties, coordination of two B(CF₃)₃ molecules can also occur prior to SET (2→5 ΔE = -16.0, ΔG²[298K] = -2.9 kcal mol⁻¹; coordination after SET is unlikely: 3→6 ΔE = 2.7, ΔG²[298K] = 18.8 kcal mol⁻¹), yielding radical ion pair [PMes⁺, (CF₃)₂B-TCO-B(CF₃)₃⁻] 6 (Scheme 5b, green). The radical anion of 6 has a high electron affinity (Eₐ = 6.11 eV), which allows another SET from a second equiv of PMes to generate diion 7.[6] To complete the picture, diion 7 is in equilibrium with TCO-B(CF₃)₃ radical anion 3 (ΔE = 5.2, ΔG²[298K] = 2.3 kcal mol⁻¹, Scheme 5b, purple) that can, as noted earlier, undergo radical coupling with PMes⁺ to form 4 (ΔE = -48.9, ΔG²[298K] = -20.4 kcal mol⁻¹; Scheme 5b, black).

Changing the phosphine to PrBu₃ was shown by Stephan et al. to only yield the Bu₃P-TCQ-B(CF₃)₃ adduct, akin to 4, without detectable radicals or diion 7, which could indicate a different mechanism. The ionization energy of Bu₃P (IEₐ = 5.42 eV), however, suggests that SET from the phosphine to the TCO-B(CF₃)₃ adduct (Eₐ = 5.57 eV) is still feasible. In this case, though, the subsequent radical coupling is barrierless[23] which leads to the immediate formation of Bu₃P-TCQ-B(CF₃)₃ (ΔE = -5.6, ΔG²[298K] = -20.4 kcal mol⁻¹) and prevents detection of radical species or subsequent reactivity to form diion 7. This shows that, similar to our findings for Ph₂SnH, changing from PMes to PrBu₃ does not alter the mechanism, but merely the energy levels along the reaction path leading to observation of radical intermediates for PMes, but not in case of PrBu₃.

Since the groups of Melen and Ooi recently reported FLP type reactions featuring radical formation when using B(CF₃)₃ and carbonyl containing substrates,[6,7] we postulated that also in these cases Lewis acid coordination to the substrate could increase its electron acceptor capacity and promote SET (Scheme 6). Indeed, for methylvinylketone (MVK), the substrate utilized by Ooi et al. (Scheme 1d),[3] we found that B(CF₃)₃ forms an adduct (ΔE = -16.3, ΔG²[298K] = 0.9 kcal mol⁻¹; SCRF/ particulate d/p, solvent = dichloroethane) and increases its electron affinity from 1.43 to 2.73 eV (Scheme 7, left). This decreases the energy gap between the ground state amine donor (IEₐ = 5.11 eV, R = Me; Scheme 1d) and methylvinylketone acceptor pair to the corresponding radical ion pair [amine•⁺, MVK-SCH₂(CF₃)₃•] from 3.68 to 2.38 eV, which results in visible light induced (1.5–3.1 eV, 400–800 nm) SET becoming feasible. Indeed, Ooi et al. used 400 nm light to promote this reaction. In case of substrate 9, used by Melen et al. (Scheme 1c),[6] we found a similar result. Binding of B(CF₃)₃ (ΔE = -19.1, ΔG²[298K] = -0.2 kcal mol⁻¹; SCRF/ particulate d/p, solvent = THF) increases the electron affinity from 2.31 to 3.56 eV (Scheme 7, right) bringing the energy required for SET (with PMes, as donor) down from 2.89 to 1.74 eV. This reduced energy gap (40.0 kcal mol⁻¹) is still sizeable and suggests that, also in this case, the SET is photo-induced and thus performing this reaction in broad daylight (or using a high-power LED) will be beneficial. These results, in combination with the transient nature of the highly reactive B(CF₃)₃• species, complete the picture, diion 6 from a second equiv of PMes completing the picture, diion 6 from a second equiv of PMes.
in solution,[16,24] make it highly plausible that also for these systems, B(C5F5)3 is facilitating SET through binding to the substrate and increasing its electron affinity, instead of participating directly in SET.

Conclusion

Although the archetypical PMes2/B(C5F5)3 and PrBu3/B(C5F5)3 FLP systems can form high energy radical ion pairs via photo-induced single-electron transfer, we found that this pathway is not a major contributor in the reaction with H2 or Ph3SnH, and that in both cases the reactions occur via polar, heterolytic mechanisms. Furthermore, we discovered that the SET reactivity observed for FLP systems with substrates featuring carbonyl moieties is not the result of SET from the Lewis base directly to the borane Lewis acid. Instead, adduct formation between the Lewis acid and substrate activates the substrate for SET, after which electron donor-acceptor complex formation with the Lewis base provides the corresponding radical ion pair, via either thermal or photoinduced SET, depending on the energy required. To promote radical reactivity in cases based on photoinduced SET, it is thus important to locate the CT-band arising after Lewis acid coordination to determine the optimal wavelength for irradiation of reaction mixtures. These important mechanistic insights are of fundamental importance for both efficient usage of current radical FLP systems as well as the design of novel radical FLP systems and new examples of main-group redox catalysis,[25] which we are currently exploring in our laboratories.

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Conflict of interest

The authors declare no conflict of interest.

Stichwörter: frustrated Lewis pairs · radicals · reactivity · single-electron transfer · substrate coordination

[13] Note that the conversion values are based on the relative integrals of the βBuP and [βBu'PH+] resonances in each case. These values do not accurately correspond to conversion because the spectra were not obtained in a quantitative manner;
however, the key result is that the values are the same regardless of whether the samples were irradiated or not.


[16] See the Supporting Information.


[21] The third signal corresponds to either a radical species which shows hyperfine coupling with two $^{31}$P nuclei, or a species featuring two uncoupled (that is, non-interacting) unpaired electrons, for which one shows hyperfine coupling to a $^{31}$P nucleus. One possible assignment would be $\text{MesP=PMe}_3^\cdot$, although this species has no stable minimum on the potential energy surface; see also: S. Tojo, S. Yasui, M. Fujitsuka, T. Majima, *J. Org. Chem.* 2006, 71, 8227–8232.


[23] The computed barrier ($\Delta G_{298K}^\ominus = -0.4 \text{ kcal mol}^{-1}$) is less than the error margin and can thus be considered approximately equal to zero.
