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DOI
10.1002/anie.202009717
10.1002/ange.202009717

Publication date
2020

Document Version
Final published version

Published in
Angewandte Chemie, International Edition

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Citation for published version (APA):
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,F) or not. The reactions of H and PhSnH 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 H2 and CO2, 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/B(C,F), (Mes = 2,4,6-triphenylmethyl), and after switching the Lewis acid to Al(C,F), found a similar, yet much clearer, EPR signal that could be unambiguously attributed to the phosphine radical cation (PMes).3 Furthermore, reaction of PMes/B(C,F) with PhSnH resulted in formation of [Mes,Ph][HB(C,F)] and PhSnSnPhH, instead of the [Mes,P-SnPh][HB(C,F)] product that would be expected for heterolytic cleavage of the Sn–H bond.4 In the case of PrBu/B(C,F), for which no radicals were detected in the reaction mixture, indeed [Bu,P-SnPh]-[HB(C,F)] was obtained, corresponding to nucleophilic 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 PhSnH as a probe for determining the mechanistic nature of FLP reactions.2b,c,4 Furthermore, Stephan et al. determined that reacting PMes/B(C,F), with tetrachloro-1,4-benzoquinone

Scheme 1. a) Different pathways proposed by Stephan et al. for reactions of FLPs with PhSnH. b) Reactivity observed by Stephan et al. for Mes,P/B(C,F), with tetrachloro-1,4-quinone (TCQ). c) Reactivity observed by Melen et al. (Ar = Ph, p-F-Ph or fluorocene; Ar = variety of aryl groups, see Ref. [6]). d) Reactivity observed by Ooi et al. utilizing catalytic B(C,F), (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 1Bu; for N: R = Ph or p-Me-Ph).
Furthermore, Melen et al. recently showed that the PMes₂/B(C₆F₅)₃ pair can be utilized to facilitate C–C bond formation by coupling diarylmethyl groups to styrenes via a mechanism involving single-electron transfer (SET; Scheme 1c). Ooi et al. also achieved C–C bond formation using an amine/B(C₆F₅)₃ system to couple methylvinylketone to the amine employing catalytic amounts of borane (Scheme 1d). They also showed that the reaction requires light and proceeds via radical species which they postulated to be the result of photo-induced SET from the amine directly to B(C₆F₅)₃ yielding the corresponding radical ion pair [amine⁺, B(C₆F₅)₃⁻]. Subsequent addition of this species to the substrate was proposed, which then led to product formation.

Recently, we demonstrated the generality of SET for FLP type donor–acceptor systems[8,9] and showed that for common P/B FLPs (PMes₂/B(C₆F₅)₃ and Ph₃Bu/B(C₆F₅)₃) and analogous N/B systems visible light is required to induce SET to generate the corresponding transient radical ion pairs (Scheme 1e).[10] This light dependence provides an excellent probe for determining whether an FLP reaction proceeds via a radical mechanism or via concerted, polar pathways, as carrying out the reaction in the absence of light precludes the formation of the radical ion pair. The work presented herein focuses on applying this notion to investigate the reaction of archetypal FLPs with the substrates H₂, Ph₃SnH and TCO. In addition, we analyzed the nature of the initial single-electron transfer event that is responsible for the radical chemistry observed by Melen et al. and Ooi et al. For all cases, we determine whether the boron Lewis acid is directly involved in SET, or plays a facilitating role by enhancing the oxidizing power of the substrate.[11]

Results and Discussion

First, we assessed the influence of light on the reaction of PMes₂ and B(C₆F₅)₃ with H₂ (1 atm), which is known to generate the corresponding phosphonium borate [Mes₃P][HB(C₆F₅)₃]. We previously showed that this combination of donor (PMes₂) and acceptor (B(C₆F₅)₃) forms a violet charge-transfer complex in solution from which the corresponding radical ion pair [PMes₂⁺, B(C₆F₅)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 nearly identical conversions to the phosphonium borate [Mes₃P][HB(C₆F₅)₃], and again after 4 hours, as determined by 3¹P NMR spectroscopy (Supporting Information, Figures S1, S2).[13] These data show that the reaction is not light dependent and therefore the formation of the radical ion pair does not significantly influence the reaction kinetics. This finding suggests that the photo-stationary concentration of the radical ion pair [PMes₂⁺, B(C₆F₅)₃⁻] is too low and/or its lifetime is too short to significantly affect the reaction rate. Indeed, this charge-separated state lies much higher in energy (54.4 kcal mol⁻¹) than the neutral donor-acceptor pair [PMes₂, B(C₆F₅)₃] and undergoes rapid back-electron transfer (lifetime = 237 ps) as determined by transient absorption spectroscopy to regenerate the FLP[10] thus preventing build-up of a concentration of radicals large enough to influence the reaction kinetics. This leads to the conclusion that the splitting of dihydrogen by PMes₂ and B(C₆F₅)₃ proceeds via a two-electron, heterolytic pathway, even when the reaction is performed in ambient light.[22–4]

Next, we probed the reaction between PMes₂/B(C₆F₅)₃ and Ph₃SnH (2 equiv) to analyse whether light affects the formation of phosphonium borate [Mes₂PH][HB(C₆F₅)₃] and Ph₃Sn–SnPh₃. We found that the reaction proceeds rapidly in both darkness and ambient light and, in both cases, within minutes full conversion to [Mes₂PH][HB(C₆F₅)₃] and Ph₃Sn–SnPh₃ was observed by multi-nuclear NMR spectroscopy (δ³¹P = –28.6, δ¹B = –26.1, δ₁³Sn = –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 [Mes₂PH][HB(C₆F₅)₃] formed when using Ph₃SnH instead of H₂? For this, changing the phosphine to Ph₃Bu provided insight. Addition of 1 equiv of Ph₃SnH to Ph₃Bu/B(C₆F₅)₃ in C₆HCl at room temperature instantly led to heterolytic cleavage of the Sn–H bond and the formation of [Bu₃P-SnPh₃][HB(C₆F₅)₃] (δ³¹P = 65.8, ¹Fₙm = 90 Hz; Scheme 3; Supporting Information, Figure S10), supporting the observations by Stephan et al.[23] We noted, however, that when more Ph₃SnH (up to 2.5 equiv) was used, the reaction continued and after 20 hours [Bu₃P][HB(C₆F₅)₃] (δ³¹P = 58.1, ¹Fₙm = 410 Hz; Supporting Information, Figure S12) as well as Ph₃Sn-SnPh₃ (Scheme 3; Supporting Information, Figure S14) was observed.[11] 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 [Ph₃Bu, B(C₆F₅)₃] (400 nm, 2.2 W LED). These findings show that for both phosphines R₂P (R = Mes and Ph₃Bu) a polar, heterolytic
mechanism is operative and that the initial product [{R,P-SnPh₃}[HB(CF₃)₃]] can convert into [{R,PH][HB(CF₃)₃]] in the presence of Ph₃SnH.

To elucidate the heterolytic splitting of Ph₃SnH in more detail, we first combined it with B(CF₃)₃ in calculations and found the formation of an adduct with a bridging hydride [Ph₃SnH–B(CF₃)₃] (ΔE = −21.3, ΔG°₂₉₈K = −1.9 kcal mol⁻¹; Figure 1, left), which is analogous to the key, transient intermediate in the B(CF₃)₃-catalyzed hydroisilylation.¹⁴ We also observed the [Ph₃SnH–B(CF₃)₃] adduct in C₄H₉Cl solution by ¹³C-NMR spectroscopy that shows a decrease in resonance difference between the meta- and para-fluorines (Δδ 18.2 to 13.7 ppm), which is indicative of a transition from a trigonal planar borane to a more tetrahedral geometry.¹⁵ Furthermore, ¹⁹F-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).¹⁶ These observations evidence activation of the tin hydride by B(CF₃)₃, making it more susceptible to nucleophilic attack by a phosphate in an Sn₂2 fashion to produce the initial [{R,P-SnPh₃}[HB(CF₃)₃]] species.

To investigate the subsequent reaction steps and determine the influence of the P-substituent (Mes vs. iPr), we again employed computational chemistry (ωB97X-D/def2-TZVP; [HB(CF₃)₃]⁻ anion omitted),¹⁷ which highlighted a formal metathesis reaction of the [{R,P–SnPh₃}]⁺ cation with Ph₃Sn⁻H, reminiscent of reactions between tin hydrides and neutral stannyl phosphines.¹⁸ When using PMes₂ (Figure 2, in green), [{Mes,P-SnPh₃}]⁺ undergoes a facile reaction with Ph₃SnH to afford the bridging hydride [Ph₃SnH–SnPh₃]⁺ (ΔE°¹TS = 9.5 kcal mol⁻¹), akin to the tin hydride-B(CF₃)₃ adduct (Figure 1). Subsequent deprotonation by the liberated phosphate, which induces Sn–Sn bond formation (ΔE°¹TS = 19.9, ΔE = −13.1 kcal mol⁻¹), affords [{Mes,PH}]⁺ and Ph₃Sn–SnPh₃. This reaction profile supports the notion that [{Mes,P–SnPh₃}[HB(CF₃)₃]] is a transient, unobserved intermediate in the formation of [{Mes,PH}[HB(CF₃)₃]].¹⁹

Changing the phosphate to PrBu₃ has a significant impact. First, the formation the bridging hydride [Ph₃SnH–SnPh₃]⁺ is now endothermic (ΔE°¹TS = 14.1, ΔE = 9.5 kcal mol⁻¹; Figure 2, in blue) and the subsequent deprotonation faces a sizeable barrier (ΔE°¹TS = 30.9, ΔE = −0.2 kcal mol⁻¹). The near thermoneutral reaction profile and high barrier accounts for the slow and modest formation of [{Bu₃P}[HB(CF₃)₃]] and explains why the [{Bu₃P–SnPh₃}[HB(CF₃)₃]] intermediate can be isolated after short reaction times and immediate work-up.²⁰

To support the intermediacy of the bridging [Ph₃SnH–SnPh₃]⁺ cation, we combined [{P(C₆H₄)₃C}[B(CF₃)₃]] with 2 equiv of Ph₃SnH in C₂H₂Cl 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 downfield shift of the aromatic ¹H nuclei of the Ph₃Sn species in combination with a broadening of the hydride peak at 6.91 ppm was observed by ¹H NMR spectroscopy (Supporting Information, Figures S20, S21).²¹ In addition, the spectrum evidenced formation of triphenylmethane (δH = 5.55)²². As predicted by DFT, subsequent addition of PMes₂ led to formation of [{Mes₂PH}[B(CF₃)₃]] by

![Figure 1. Computed structure for the adducts of Ph₃SnH with B(CF₃)₃ (left) and Ph₃Sn⁻ (right) featuring a bridging hydride (DFT: ωB97X-D/def2-TZVP). Selected bond lengths and angles: Ph₃SnH–B(CF₃)₃: Sn–H 1.83 Å, B–H 1.37 Å; Sn–H in B(CF₃)₃: Sn–H 1.87 Å; Sn–H in B(CF₃)₃: 147°.](image1.jpg)

![Figure 2. Proposed reaction mechanism based on DFT calculations at the ωB97X-D/def2-TZVP level of theory. R = iPrB (blue, dashed) or Mes (green, dotted). [HB(CF₃)₃]⁻ anion has been omitted for clarity. Energies in kcal mol⁻¹.](image2.jpg)

![Scheme 4. Hydride abstraction from Ph₃SnH using [P(C₆H₄)₃C][B(CF₃)₃] and subsequent reaction with PMes₂.](image3.jpg)
deprotonation, as observed by $^1$H- and $^{31}$P-NMR spectroscopy (Supporting Information, Figure S23, S24), and the formation of Ph$_3$Sn-SnPh$_3$, evidenced by $^{119}$Sn NMR spectroscopy (Supporting Information, Figure S25). Addition of PrBu$_3$ instead of PMes$_3$ afforded both $[\text{Bu}_3\text{PH}][\text{B}(\text{C}_3\text{F}_3)_2]$ and $[\text{Bu}_3\text{P-SnPh}_3][\text{B}(\text{C}_3\text{F}_3)_2]$ according to $^{31}$P-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 $[\text{R-P-SnPh}_3][\text{HB}(\text{C}_3\text{F}_3)_2]$, subsequent bond metathesis leads to formation of $[\text{R-PH}][\text{HB}-(\text{C}_3\text{F}_3)_2]$ via a bridging hydride intermediate and highlights that the complete reaction of PMes$_3$/B(C$_3$F$_3)_2$ and PrBu$_3$/B(C$_3$F$_3)_2$ with Ph$_3$SnH is accessible via heterolytic polar pathways.

Next, we set out to analyze the reaction of PMes$_3$/B(C$_3$F$_3)_2$ with tetrachloro-1,4-benzoquinone (TCQ) for which Stephan et al. detected radical formation (PMes$_3$)$_2^+$, and PrBu$_3$/B(C$_3$F$_3)_2$ with Ph$_3$SnH instead of PMes$_3$. They postulated that this proceeds via SET from A to form the corresponding radical ion pair (Figure 3). Furthermore, we noted an unexplained smaller third signal, which was also reported by Müller and Klare et al. when combining PMes$_3$ with tetrachloro-1,4-benzoquinone (TCQ) for which Stephan et al. detected radical formation (PMes$_3$)$_2^+$. We performed this reaction in the absence of light and found that the reaction still proceeds rapidly, forming a deep purple solution for which EPR spectroscopy confirmed the formation of PMes$_3^+$ (two-line signal simulated with $g_{iso}=2.0050$, $A_{iso}=670.00$ MHz) but also showed for the first time a featureless signal ($g_{iso}=2.0058$) that we attribute to a TCQ centered radical anion, most likely TCQ-B(C$_3$F$_3)_2^-$ (Figure 3). Furthermore, we noted an unknown smaller third signal, which was also reported by Müller and Klare et al. when combining PMes$_3$ and the strongly accepting silyl and trityl cations.

So, how is it possible that radicals are formed in the dark? Clearly, a strong electron acceptor is required to oxidise PMes$_3$ ($E_0=5.25$ eV; SCRF$^{[15]}$/G97X-D/6–311 + G(d,p), solvent = chlorobenzene) and neither B(C$_3$F$_3)_2$ nor TCQ are suitable ($E_a=3.31$ and 4.45 eV, respectively)$^{[15]}$ to accommodate the needed thermal SET. Yet, B(C$_3$F$_3)_2$ can coordinate to one of the carbonyl moieties of TCQ, affording the corresponding Lewis adduct TCQ-B(C$_3$F$_3)_2$, which has an increased electron affinity ($E_a=5.57$ eV) and therefore should be capable of oxidizing PMes$_3$. 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(C$_3$F$_3)_2$ is weak ($\Delta E=-4.6$, $\Delta G^{\circ}_{298K}=-\Delta H^{\circ}_{298K}=-\Delta S^{\circ}_{298K}=-\Delta H^{\circ}_{298K}$).

**Scheme 5.** a) Orbitals involved in the SET between PMes$_3$ and the TCQ-B(C$_3$F$_3)_2$ adduct. b) Reactivity, featuring all possible pathways for the reaction of TCQ, B(C$_3$F$_3)_2$, and PMes$_3$. Figure 3. Experimental EPR spectrum (bottom) for reaction of PMes$_3$, B(C$_3$F$_3)_2$, and TCQ (2:2:1) and simulated spectra for PMes$_3^+$, TCQ-B(C$_3$F$_3)_2^-$ and the third smaller signal. See the Supporting Information for experimental and simulation parameters. HFI = hyperfine interaction.
10.7 kcal mol\(^{-1}\) leading to an equilibrium featuring low concentrations of the TCO-B(C\(\text{F}_3\))\(_3\) adduct, which supports the notion of Stephan et al. that no interaction between B(C\(\text{F}_3\))\(_3\) and TCO is observable by NMR spectroscopy.[26] However, in presence of PMes\(_5\), the transient TCO-B(C\(\text{F}_3\))\(_3\) adduct will undergo SET from the PMes\(_5\) HOMO to the TCO-B(C\(\text{F}_3\))\(_3\) LUMO (Scheme 5, left) generating the radical ion pair \([\text{PMes}_5]^+;\text{TCO}-\text{B}(\text{C}\text{F}_3)_3\)\(^-\) 3, which drives the equilibrium towards the TCO-B(C\(\text{F}_3\))\(_3\) adduct (Scheme 5b, blue). Subsequent radical coupling of PMes\(_5^+\) and TCO-B(C\(\text{F}_3\))\(_3\)\(^-\) via a computed 8 kcal mol\(^{-1}\) \(\Delta G^\circ_{298K}\) barrier leads to the formation of Mes\(_5\)P-TCO-B(C\(\text{F}_3\))\(_3\) 4 as observed experimentally by Stephan et al. (Scheme 5b, black).[2b] This mechanism highlights that, rather than directly participating in SET, B(C\(\text{F}_3\))\(_3\) is facilitating the process by increasing the electron affinity of the quinone acceptor.

As TCO features two carbonyl moieties, coordination of two B(C\(\text{F}_3\))\(_3\) molecules can also occur prior to SET (\(2\rightarrow5\) \(\Delta E = -16.0,\ \Delta G^\circ_{298K} = -2.9\) kcal mol\(^{-1}\); coordination after SET is unlikely; \(3\rightarrow6\) \(\Delta E = 2.7,\ \Delta G^\circ_{298K} = 18.8\) kcal mol\(^{-1}\)), yielding radical ion pair \([\text{PMes}_5]^+; (\text{C}\text{F}_3)_3\text{B-TCO-B}(\text{C}\text{F}_3)_3\)\(^-\) 6 (Scheme 5b, green). The radical anion of 6 has a high electron affinity \(E_A = 6.11\) eV, which allows another SET from a second equiv of PMes\(_5\) to generate dianion 7.[2b] To complete the picture, dianion 7 is in equilibrium with TCO-B(C\(\text{F}_3\))\(_3\)\(^-\) radical anion 3 (\(\Delta E = 5.2,\ \Delta G^\circ_{298K} = 2.3\) kcal mol\(^{-1}\) Scheme 5b, purple) that can, as noted earlier, undergo radical coupling with PMes\(_5^+\) to form 4 (\(\Delta E = -48.9,\ \Delta G^\circ_{298K} = -20.4\) kcal mol\(^{-1}\); Scheme 5b, black).

Changing the phosphate to PrBu\(_3\) was shown by Stephan et al. to only yield the PrBu\(_3\)-TCO-B(C\(\text{F}_3\))\(_3\) adduct, akin to 4, without detectable radicals or dianion 7, which could indicate a different mechanism. The ionization energy of PrBu\(_3\) (IE\(_{\text{PrBu}} = 5.54\) eV), however, suggests that SET from the phosphate to the TCO-B(C\(\text{F}_3\))\(_3\) adduct (\(E_A = 5.57\) eV) is still feasible. In this case, though, the subsequent radical coupling is barrierless[23] which leads to the immediate formation of PrBu\(_3\)-TCO-B(C\(\text{F}_3\))\(_3\) \(\Delta E = -56.5,\ \Delta G^\circ_{298K} = -20.4\) kcal mol\(^{-1}\) and prevents detection of radical species or subsequent reactivity to form dianion 7. This shows that, similar to our findings for Ph\(_3\)SnH, changing from PMes\(_5\) to PrBu\(_3\) does not alter the mechanism, but merely the energy levels along the reaction path leading to observation of radical intermediates for PMes\(_5\), but not in case of PrBu\(_3\).

Since the groups of Melen and Ooi recently reported FLP type reactions featuring radical formation when using B(C\(\text{F}_3\))\(_3\) 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 Melen et al. (Scheme 1c),[6] we found that B(C\(\text{F}_3\))\(_3\) forms an adduct (\(\Delta E = -16.3,\ \Delta G^\circ_{298K} = 0.9\) kcal mol\(^{-1}\); SCRF/\(\text{b97x-d/6-311} + \text{G(d,p)}\), 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 (IE\(_D = 5.11\) eV; R = Me; Scheme 1d) and methylvinylketone acceptor pair to the corresponding radical ion pair [amine\(^-\); MVK-B(C\(\text{F}_3\))\(_3\)\(^-\)] from 6.8 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(C\(\text{F}_3\))\(_3\) (\(\Delta E = -19.1,\ \Delta G^\circ_{298K} = -0.2\) kcal mol\(^{-1}\); SCRF/\(\text{b97x-d/6-311} + \text{G(d,p)}\), solvent = THF) increases the electron affinity from 2.31 to 3.56 eV (Scheme 7, right) bringing the energy required for SET (with PMes\(_5\), 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

Scheme 6. Lewis acid coordination to a carbonyl moiety facilitating SET. LB = Lewis base.

Scheme 7. Change in electron affinity when B(C\(\text{F}_3\))\(_3\) coordinates and the resulting LUMO for two different B(C\(\text{F}_3\))\(_3\)-coordinated substrates.
LED) will be beneficial. These results, in combination with the transient nature of the highly reactive B(C₆F₅)₂⁻ species in solution,[6,24] make it highly plausible that also for these systems, B(C₆F₅)₂ is facilitating SET through binding to the substrate and increasing its electron affinity, instead of participating directly in SET.

Conclusion

Although the archetypal PMes₂/B(C₆F₅)₂ and PrBu₃/B-(C₆F₅)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 PhSnH, 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 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.

Acknowledgements

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.), NWA Idea Generator grant (J.C.S.) and a VENI grant (A.R.J.).

Conflict of interest

The authors declare no conflict of interest.

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


Note that the conversion values are based on the relative integrals of the \( \text{iBu}_3\text{P} \) and \( \text{iBu}_3\text{PH} \) 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.


See the Supporting Information.


The third signal corresponds to either a radical species which shows hyperfine coupling with two \( \text{^{31}P} \) nuclei, or a species featuring two uncoupled (that is, non-interacting) unpaired electrons, for which one shows hyperfine coupling to a \( \text{^{31}P} \) nucleus. One possible assignment would be \( \text{Mes}_3\text{P} - \text{PMes}_3^+ \), 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.


The computed barrier (\( \Delta G^\circ_{\text{swk}} = -0.4 \text{ kcalmol}^{-1} \)) is less than the error margin and can thus be considered approximately equal to zero.


Manuscript received: July 14, 2020
Accepted manuscript online: August 25, 2020
Version of record online: October 1, 2020