Single-Electron Transfer in Frustrated Lewis Pair Chemistry

Holtrop, F.; Jupp, A.R.; Kooij, B.J.; van Leest, N.P.; de Bruin, B.; Slootweg, J.C.

DOI
10.1002/ange.202009717
10.1002/anie.202009717

Publication date
2020

Document Version
Final published version

Published in
Angewandte Chemie

License
CC BY-NC-ND

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)
Single-Electron Transfer in Frustrated Lewis Pair Chemistry

Flip Holtrop, Andrew R. Jupp, Bastiaan J. Kooij, Nicolaas P. van Leest, Bas de Bruin und J. Chris Slootweg*

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-benzozquinone (TCQ) both experimentally and computationally to determine the nature of the single-electron transfer (SET) event; that is, being direct SET to B(C₆F₅)₃ or not. The reactions of H₂ and Ph₃SnH 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.[2c,3] Stephan et al. reported the detection of a weak radical signal by electron paramagnetic resonance (EPR) spectroscopy for the archetypal FLP PMes₃/B(C₆F₅)₃ (Mes = 2,4,6-trimethylphenyl), and after switching the Lewis acid to Al(C₆F₅)₃ found a similar, yet much clearer, EPR signal that could be unambiguously attributed to the phosphine radical cation (PMe₃⁺).[2b] Furthermore, reaction of PMes₃/B(C₆F₅)₃ with Ph₃SnH resulted in formation of [Mes,P][HB(C₆F₅)₃] and Ph₃SnPh₂, instead of the [Mes,P,SnPh₂][HB(C₆F₅)₃] product that would be expected for heterolytic cleavage of the Sn–H bond.[2d] In the case of PhBu₃/B(C₆F₅)₃, for which no radicals were detected in the reaction mixture, indeed [tBu,P,SnPh₂][HB(C₆F₅)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 Ph₃SnH as a probe for determining the mechanistic nature of FLP reactions.[2c,4] Furthermore, Stephan et al. determined that reacting PMes₃/B(C₆F₅)₃ with tetrachloro-1,4-benzozquinone (TCQ) leads to radical forma-

Scheme 1. a) Different pathways proposed by Stephan et al. for reactions of FLPs with Ph₃SnH. b) Reactivity observed by Stephan et al. for Mes₃/P/B(C₆F₅)₃ with tetrachloro-1,4-quinone (TCQ). c) Reactivity observed by Melen et al. (ArF = Ph, p-F-Ph or fluorene; Ar = variety of ary groups, see Ref. [6]. d) Reactivity observed by Ooi et al. utilizing catalytic B(C₆F₅)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).
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 [MesP][HB(C$_6$F$_5$)$_3$]. We previously showed that this combination of donor (PMes$_3$) and acceptor (B(C$_6$F$_5$)$_3$) forms a violet 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). 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 presence or absence 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 [MesP][HB(C$_6$F$_5$)$_3$], and showed that for common ortho-deuterated hydrogen splitting, the photo-stationary concentration of the radical ion pair is insignificantly contributing factor in hydrogen splitting, as determined 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 [PMes$_3^+$, B(C$_6$F$_5$)$_3^-$.] is too low and/or its lifetime is too short to significantly influence the reaction rate. Indeed, this charge-separated state lies much higher in energy (54.4 kcal mol$^{-1}$) than the neutral donor-acceptor pair [PMes$_3$, B(C$_6$F$_5$)$_3$] 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 PMes$_3$ and B(C$_6$F$_5$)$_3$ proceeds via a two-electron, heterolytic pathway, even when the reaction is performed in ambient light.[2c–e]

Next, we probed the reaction between PMes$_3$/B(C$_6$F$_5$)$_3$ and Ph$_3$SnH (2 equiv) to analyse whether light affects the formation of phosphonium borate [MesP][HB(C$_6$F$_5$)$_3$] and Ph$_3$Sn–SnPh$_3$. We found that the reaction proceeds rapidly in both darkness and ambient light and, in both cases, within minutes full conversion to [MesP][HB(C$_6$F$_5$)$_3$] and Ph$_3$Sn–SnPh$_3$ was observed under multi-nuclear NMR spectroscopy (δ$_{31}$P = −28.6, δ$^1$B = −26.1, δ$^{11}$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 [MesP][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$_6$ at room temperature instantly led to heterolytic cleavage of the Sn–H bond and the formation of [Bu$_3$P-SnPh$_3$][HB(C$_6$F$_5$)$_3$] (δ$_{31}$P = 65.8, $^1$J$_{PhSn} = 90$ Hz; Scheme 3; Supporting Information, Figure S10), supporting the observations by Stephan et al.[2e] We noted, however, that when more Ph$_3$SnH (up to 2.5 equiv) was used, the reaction continued and after 20 hours [Bu$_3$P][HB(C$_6$F$_5$)$_3$] (δ$_{31}$P = 58.1, $^1$J$_{PhSn} = 410$ 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$_3$, B(C$_6$F$_5$)$_3$] (400 nm, 2.2 W LED). These findings show that for both phosphines R$_2$P (R = Mes and Bu) a polar, heterolytic mechanism is operative and that the initial product [R$_2$P-
SnPh₃][HB(C,F₃)₃] can convert into [R,P][HB(C,F₃)₃] in the presence of Ph₃SnH.

To elucidate the heterolytic splitting of Ph₃SnH in more detail, we first combined it with B(C,F₃)₃ in calculations and found the formation of an adduct with a bridging hydride [Ph₃Sn−H−B(C,F₃)₃] (ΔE = -21.3; ΔG°₂₉₈ = -1.9 kcal mol⁻¹; Figure 1, left), which is analogous to the key, transient intermediate in the B(C,F₃)₃-catalyzed hydrosilylation.[14] We also observed the [Ph₃Sn−H−B(C,F₃)₃] adduct in C₆H₆Cl₄ solution by ²⁹F-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, ¹¹⁹Sn-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(C,F₃)₃, making it more susceptible to nucleophilic attack by a phosphine in an Sn,-fashion to produce the initial [R,P−SnPh₃][HB(C,F₃)₃] species.

To investigate the subsequent reaction steps and determine the influence of the P-substituent (Mes vs. tBu), we again employed computational chemistry (oB97X-D/def2-TZVP; [HB(C,F₃)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.[17] When using PMes₂ (Figure 2, in green), [Mes,P−SnPh₃]⁺ undergoes a facile reaction with Ph₃SnH to afford the bridging hydride [Ph₃Sn−H−SnPh₃]⁺ (ΔE°₉₈ ≈ 9, ΔE = -4.9 kcal mol⁻¹),[18] akin to the tin hydride-B(C,F₃)₃ adduct (Figure 1). Subsequent deprotonation by the liberated phosphine, which induces Sn−Sn bond formation (ΔE°₉₈ ≈ 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(C,F₃)₃] is a transient, unobserved intermediate in the formation of [Mes,PH][HB(C,F₃)₃].[19]

Changing the phosphine to PbBu₃ has a significant impact. First, the formation the bridging hydride [Ph₃Sn−H−SnPh₃]⁺ is now endothermic (ΔE°₉₈ = 14.1, ΔE = 9.5 kcal mol⁻¹; Figure 2, in blue) and the subsequent deprotonation faces a sizeable barrier (ΔE°₉₈ = 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(C,F₃)₃] and explains why the [Bu₃P−SnPh₃][HB(C,F₃)₃] intermediate can be isolated after short reaction times and immediate work-up.[19]

To support the intermediacy of the bridging [Ph₃Sn−H−SnPh₃]⁺ cation, we combined [Ph₃C][B(C,F₃)₃] with 2 equiv of Ph₃SnH in C₆H₂Cl 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 ^{1}H nuclei of the Ph₃Sn 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).[18] In addition, the spectrum evidenced formation of triphenylmethane (δH = 5.55).[19] As predicted by DFT, subsequent addition of PMes₂ led to formation of [Mes,PH][B(C,F₃)₃]₁ by deprotonation, as observed by ^{1}H- and ^{³¹}P-NMR spectroscopy (Supporting Information, Figure S23, S24), and the formation of Ph₃Sn−SnPh₃.
of Ph₃Sn–SnPh₃, evidenced by ¹¹¹Sn NMR spectroscopy (Supporting Information, Figure S25). Addition of Ph₄Bu instead of PMes₂ afforded both [Bu₄PH][B(C₆F₅)₃] and [Bu₄P–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 [R₂P-SnPh₃][HB(C₆F₅)₃], subsequent bond metathesis leads to formation of [R₂PH][HB(C₆F₅)₃] via a bridging hydride intermediate and highlights that the complete reaction of PMes₂/B(C₆F₅)₃ and Ph₄Bu/B(C₆F₅)₃ with Ph₃SnH is accessible via heterolytic polar pathways.

Next, we set out to analyze the reaction of PMes₂/B(C₆F₅)₃ with tetrachloro-1,4-benzoquinone (TCQ) for which Stephan et al. detected radical formation (PMes₂⁺⁺) by EPR spectroscopy.[24] They postulated that this proceeds via SET from PMes₂ to B(C₆F₅)₃ to form the corresponding radical ion pair [PMes₂⁺⁺, 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 rapidly, forming a deep purple solution for which EPR spectroscopy confirmed the formation of PMes₂⁺⁺ (two-line signal simulated with glosures = 2.0050, A₁₁₁ = 670.00 MHz)[24,19] but also showed for the first time a featureless signal (glosures = 2.0058) that we attribute to a TCQ centered radical anion, most likely TCQ-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 PMes₂ and the strongly accepting silyl and trityl cations.[20,21]

So, how is it possible that radicals are formed in the dark? Clearly, a strong electron acceptor is required to oxidize PMes₂⁺⁺ (IE₂ = 5.25 eV; SCRF[15]/ωB97X-D/6–311 + G(d,p), solvent = chlorobenzene) and neither B(C₆F₅)₃ nor TCQ are suitable (E₄ = 3.31 and 4.45 eV, respectively)[25] 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 (E₆ = 5.57 eV) and therefore should be capable of oxidizing PMes₂⁺⁺.[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 (∆E = −4.6, ∆G°298K = 10.7 kcal mol⁻¹) leading to an equilibrium featuring low concentrations of the TCQ-B(C₆F₅)₃ adduct, which supports the formation of the TCQ-centered radical anion TCQ-B(C₆F₅)₃⁻⁻.

![Image](image-url)
Changing the phosphine to PrBu3 was shown by Stephan et al. to only yield the PrBu3P-TCQ-B(CF3)3 adduct, akin to 4, without detectable radicals or dianion 7, which could indicate a different mechanism. The ionization energy of PrBu3P (IEP = 5.54 eV), however, suggests that SET from the phosphine to the TCQ-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 PrBu3P-TCQ-B(CF3)3, (ΔE = −56.5, ΔG°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 Ph5SnH, 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-(C5F5)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(C5F5)3 forms an adduct (ΔE = −16.3, ΔG°298K = 0.9 kcal mol⁻¹; SCRF/oB97X-D/6–311 + 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 (IEO₂ = 5.11 eV, R = Me; Scheme 1d) and methylvinylketone acceptor pair to the corresponding radical ion pair [amine•⁻, MVK-B(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(C5F5)3 (ΔE = −19.1, ΔG°298K = −0.2 kcal mol⁻¹; SCRF/oB97X-D/6–311 + 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 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(C5F5)3•⁻ species cannot be studied by NMR spectroscopy.[24] However, in presence of Pmes, the transient TCQ-B(CF3)3 adduct will undergo SET from the Pmes HOMO to the TCQ-B(CF3)3 LUMO (Scheme 5, left) generating the radical ion pair [Pmes•⁺, TCQ-B(CF3)3•⁻] 3, which drives the equilibrium towards the TCQ-B(CF3)3 adduct (Scheme 5b, blue). Subsequent radical coupling of Pmes•⁺ and TCQ-B(CF3)3•⁻ via a computed 8 kcal mol⁻¹ (ΔG°298K) barrier leads to the formation of Mes,P-TCP-B(CF3)3, 4 as observed experimentally by Stephan et al. (Scheme 5b, black).[25] This mechanism highlights that, rather than directly participating in SET, B-(C5F5)3 is facilitating the process by increasing the electron affinity of the quinone acceptor.

As TCQ features two carbonyl moieties, coordination of two B(C5F5)3 molecules can also occur prior to SET (2→5 ΔE = −16.0, ΔG°298K = −2.9 kcal mol⁻¹; coordination after SET is unlikely; 3→6 ΔE = 2.7, ΔG°298K = 18.8 kcal mol⁻¹), yielding radical ion pair [Pmes•⁺, (C5F5)3B-TCQ-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 dianion 7.[26] To complete the picture, dianion 7 is in equilibrium with TCQ-B(CF3)3•⁻ radical anion 3 (ΔE = 5.2, ΔG°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, ΔG°298K = −20.4 kcal mol⁻¹; Scheme 5b, black).

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

**Scheme 7.** Change in electron affinity when B(CF3)3 coordinates and the resulting LUMO for two different B(CF3)3-coordinated substrates.
in solution make it highly plausible that also for these systems, B(C,F) is facilitating SET through binding to the substrate and increasing its electron affinity, instead of participating directly in SET.

**Conclusion**

Although the archetypal PMes/B(C,F) and PrBu/B(C,F) 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 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.

**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 tBuP and tBuPH+ 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 $\text{Mes}_3\text{P}^+\text{PMes}_3^-$, 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.


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