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Photoinduced and Thermal Single-Electron Transfer to Generate Radicals from Frustrated Lewis Pairs

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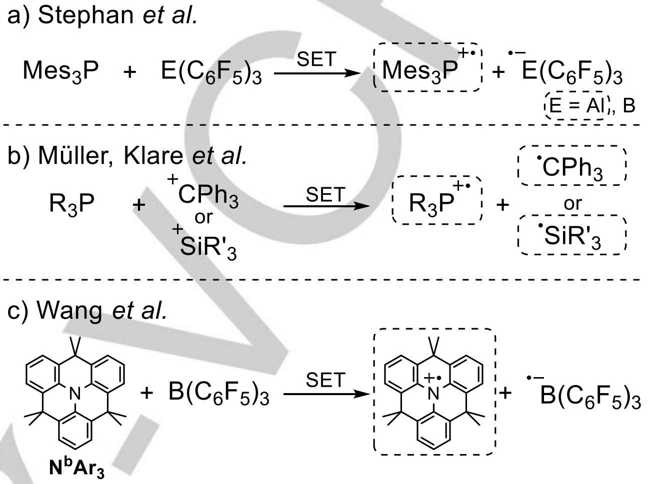
Abstract: Archetypal phosphine/borane frustrated Lewis pairs are famed for their ability to activate small molecules. The mechanism is generally believed to result from two-electron processes. However, detection of radical intermediates indicates that single-electron transfer generating frustrated radical pairs could also play an important role. These highly reactive radical species typically lie significantly higher in energy, which prompted this investigation into their formation. Herein, we provide evidence that the classical phosphine/borane combinations $PMes_3/B(C_6F_5)_3$ and $PtBu_3/B(C_6F_5)_3$ both form an electron donor-acceptor (charge-transfer) complex, which undergoes visible light induced single-electron transfer (SET) to form the corresponding highly reactive radical ion pairs. Subsequently, we show that by tuning the properties of the Lewis acid and base pair, the energy required for SET can be reduced to become thermally accessible.



Scheme 1. Literature examples of detected radicals (highlighted in boxes) in cooperative main-group Lewis acid/base chemistry.[2c,4b,7] R = Mes, Tipp, C_6F_5, C_6Me_5, *t*Bu (only in case of CPh_3^+). $SiR'_3{}^+$ = $Si\textit{i}Pr_3{}^+$, $Si(C_6Me_5)_3{}^+$, $Si\textit{t}BuMe_2{}^+$, $SiEt_3{}^+$

Frustrated Lewis pair (FLP) chemistry is useful for the activation of a variety of small molecules, most notably dihydrogen and carbon dioxide.[1] However, activation of less reactive substrates, such as dinitrogen or methane, remains a challenge. It is generally accepted that FLP reactivity proceeds via association of the electron donor (D; Lewis base) and electron acceptor (A; Lewis acid) to form an encounter complex ([D--A]), which features a reactive pocket in which heterolytic bond cleavage of the substrate occurs.[2] Interestingly, recent studies have revealed evidence for the formation of radicals within such systems indicating that single-electron transfer can also play an important role in Lewis acid/base chemistry.[2b,c, 3] Such highly reactive radical species could be key to the activation of inert substrates, which we were keen on investigating.

A single-electron transfer mechanism within FLP chemistry was first suggested by Piers *et al.*,[3b] as $B(C_6F_5)_3$ (BCF) is also known to act as single-electron oxidant.[4] However, it was noted that the disparity in redox potentials between $PtBu_3$ and BCF would limit the presence of radicals to subnanomolar concentrations for this archetypal FLP.[3b] When combining $PMes_3$ with BCF, Stephan and co-workers noted detection of a very weak signal by EPR spectroscopy in chlorobenzene which they postulated to be the $PMes_3{}^{\bullet+}$ radical cation. Switching to the more Lewis acidic $Al(C_6F_5)_3$ resulted in significantly larger signals which could be accredited to the $PMes_3{}^{\bullet+}$ radical cation (Scheme 1a).[2c] Absence of the radical anions ($BCF^{\bullet-}$ and $Al(C_6F_5)_3{}^{\bullet-}$) was attributed to the known rapid degradation of these species via solvolytic pathways.[3a,5,6] Further indications for a radical pathway was provided by the reaction of $PMes_3/B(C_6F_5)_3$ with Ph_3SnH that afforded $[Mes_3PH][HB(C_6F_5)_3]$ and $Ph_3Sn–SnPh_3$, instead of the expected $[Mes_3PH][Ph_3SnB(C_6F_5)_3]$.[2c] Müller, Klare and colleagues also observed radical formation when combining trityl (CPh_3^+) and silylium cations (SiR_3^+) with phosphines ($PMes_3$, $P(C_6F_5)_3$, $P(C_6Me_5)_3$ and $PTipp_3$, Tipp = 2,4,6-triisopropylphenyl; Scheme 1b).[7] In the case of trityl, both radical species are persistent, allowing the detection of both components of the radical pair in solution.

Interestingly, when the analogous reactions using BCF, $Al(C_6F_5)_3$ and SiR_3^+ were carried out with $PtBu_3$ as the Lewis base, no radical reactivity was observed. Müller, Klare *et al.* accredited this to the higher ionization potential of $PtBu_3$ compared to $PMes_3$ (Table S1). Another challenge comes from the fact that the $PtBu_3{}^{\bullet+}$ radical is far less stable than its mesityl analogue, decomposing rapidly at room temperature.[7,8] In addition to phosphines, amines are also potent electron donors for which the amine radical cations, e.g., formed by visible light photoredox catalysis, have been well explored recently.[9] Indeed, Wang *et al.* reported on the one-electron oxidation of cyclic triarylamine N^bAr_3 by $B(C_6F_5)_3$ and isolated the corresponding radical cation (Scheme 1c).[4b] Furthermore, while this manuscript was under revision, Ooi *et al.* reported on the photoinduced SET between $B(C_6F_5)_3$ and N,N-

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dialkylanilines.[10] In both cases, again the BCF$^{\bullet-}$ radical anion was not detected.[3a,5]

$$D + A \rightleftharpoons \left[D\text{--}A\right] \underset{\text{BET}}{\overset{\text{SET}}{\rightleftharpoons}} \left[D^{+\bullet}\text{---}A^{\bullet-}\right] \rightleftharpoons D^{+\bullet} + A^{-\bullet}$$

Scheme 2. Electron donor-acceptor complex formation and subsequent single-electron transfer to generate the corresponding radical ion pair.

These findings prompted us to focus on understanding single-electron-transfer processes (versus the established concerted, polar pathways) in frustrated Lewis pair chemistry,[11] ultimately allowing the rational design of reactive main-group radical ion pairs from the corresponding Lewis acid/base combinations by a single-electron shift.[12,3c] Mulliken theory describes how interactions between donors and acceptors can lead to formation of electron donor-acceptor (EDA) complexes [D--A] that exhibit characteristic absorption bands resulting from promotion of an electron from the donor component to the acceptor component in the EDA complex (Scheme 2).[13] It is worth noting that these EDA complexes are analogous to the encounter (or van der Waals) complexes proposed in FLP mechanistic pathways. Kochi et al. showed that such EDA complexes can be formed by mixing tetracyanoethylene and anthracenes, and utilized picosecond laser-spectroscopy to demonstrate that specific irradiation of the charge-transfer (CT) band indeed induces single-electron transfer, generating the corresponding radical ion pairs [D$^{\bullet+}$--A$^{\bullet-}$].[14,15] Note that these radical species often undergo rapid back-electron transfer (BET) to regenerate the starting donor-acceptor complex [D--A].

In applying this knowledge to frustrated Lewis pairs, we first calculated the ionization potential (I_D) and electron affinity (EA_A)[7] for the archetypal FLP systems P*t*Bu$_3$/BCF and PMes$_3$/BCF at the SCRF/ωB97X-D/6-311+G(d,p) level of theory (solvent = toluene).[16] This highlighted that there is a large disparity between the EA_A of BCF (–3.03 eV) and the I_D of P*t*Bu$_3$ (5.95 eV) and PMes$_3$ (5.54 eV) affording energy differences of 2.92 eV (67.2 kcal·mol^{-1}) and 2.51 eV (57.8 kcal·mol^{-1}), respectively, between the Lewis acid/base pairs and the corresponding radical ion pairs (Figure 1). Overcoming such a large energy gap to generate these main-group radicals by single-electron transfer is, therefore, unlikely to be a thermal process. This prompted us to further investigate, employing both TD-DFT calculations and a range of spectroscopic techniques, to shed light on the process of radical formation.[17]

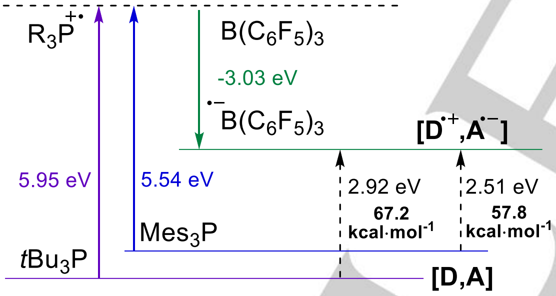

Figure 1. Calculated (DFT) energy needed to access radical ion pairs from frustrated Lewis pair systems P*t*Bu$_3$ / PMes$_3$ and BCF.[7]

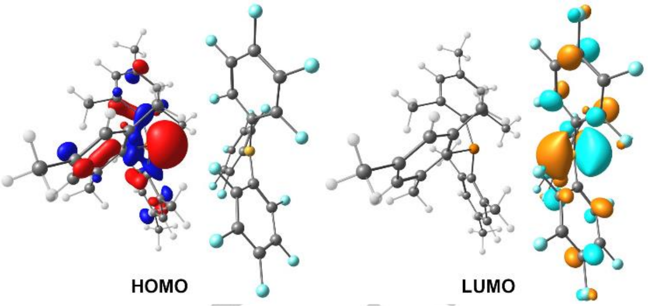

Figure 2. Frontier molecular orbitals of the PMes$_3$/BCF encounter complex (ωB97X-D/6-311G(d,p)). Iso-value = 0.05.

It is known that mixing colourless solutions of PMes$_3$ and BCF yields a violet solution,[2c,18] indicating that interaction with visible light (λ = 400–800 nm, Δ*E* = 71.4 to 35.7 kcal·mol^{-1}) is occurring. Although the violet colour has previously been suggested to result from formation of radical species (PMes$_3^{\bullet+}$)[2c], we postulated that this colour change is more likely to result from the formation of a visible-light-absorbing electron donor–acceptor (EDA) complex, generated in the ground state upon association of the electron-rich phosphine and the electron-deficient borane. Computed absorption spectra at the TD-DFT ωB97X-D/6-311++G(d,p) level of the phosphine–borane encounter complex (PMes$_3$/BCF) indeed feature an additional absorption band at a longer wavelength than the individual components (λ = 439 nm; Figure S1),[19] which is indicative of a charge-transfer band.[13] Analysis of the encounter complex frontier molecular orbitals clearly shows this charge transfer is from the phosphorus lone pair (HOMO; Figure 2) to the formally vacant p-orbital on boron (LUMO; Figure 2).[20] UV-vis

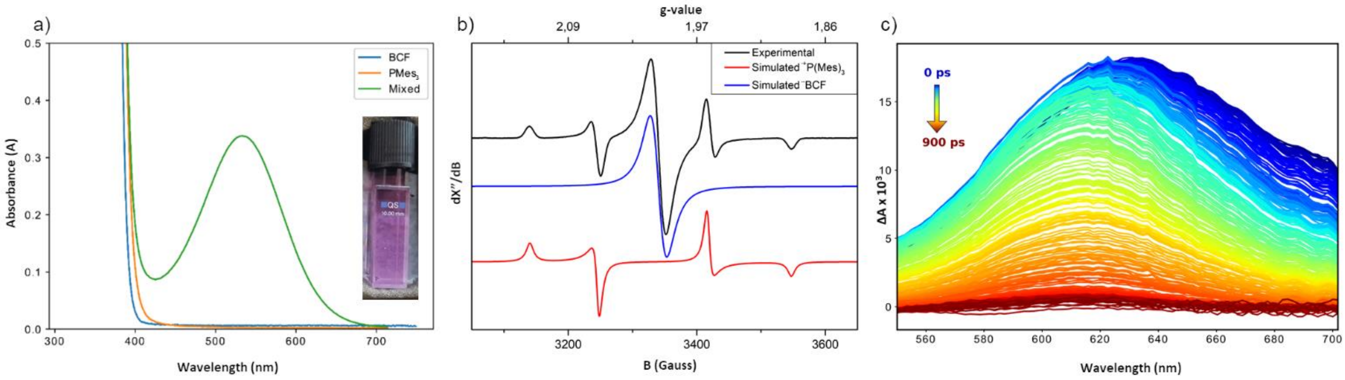

Figure 3. a) UV-Vis spectrum of PMes$_3$/BCF (both components: 1.5 x 10^{-2} M in toluene) compared to the separate components (1.5 x 10^{-2} M). b) Experimental EPR spectrum of PMes$_3$/BCF in toluene measured at 30K during irradiation with visible light (390–500 nm) and simulated EPR spectrum. c) Transient absorption spectrum measured after pulsed excitation of PMes$_3$/BCF with 530 nm light.

spectroscopy of the violet solution of $\mathrm{PMes_3}$/BCF in toluene (0.015 M) confirmed this hypothesis and revealed an absorption band in the visible spectrum (λ_{max} = 534 nm; Figure 3a), which corresponds to a vertical excitation energy of 53.5 kcal·mol^{-1} ($S_0 \rightarrow S_1$ transition).

To investigate whether irradiation of the coloured EDA complex induces single-electron transfer, we designed an electron paramagnetic resonance (EPR) experiment with a light source within the spectrometer. Low temperature (30 K) analysis of a violet $\mathrm{PMes_3}$/BCF frozen toluene (0.06 M) solution prepared in the dark showed no radical formation, clearly evidencing the violet colour is not generated by radicals. During a 90-second irradiation with visible light (390–500 nm) an intense EPR signal corresponding to a superposition of two radical species was observed (Figure 3b). The broad signal at g = 2.005 is attributed to the $\mathrm{BCF^{\bullet-}}$ radical anion, with a featureless signal at 30 K that shows no resolved hyperfine coupling interactions.[16] The other four lines stem from the axially symmetric $\mathrm{PMes_3^{\bullet+}}$ radical cation ($g_\perp$ = 2.0055 and $g_\parallel$ = 2.0015) exhibiting hyperfine coupling ($A_\perp$ = 550, $A_\parallel$ 1170 MHz) with the I = ½ phosphorus nucleus; similar spectra have been previously reported in nitrile solvents ($A_\perp$ = 427–480, $A_\parallel$ = 1128–1157 MHz).[21] When we stopped irradiating the EPR sample, both radicals remain visible with the signal intensity only decaying by ~25% after 6 minutes at 30 K. We postulate that this relative longevity can be ascribed to the formation of separate $\mathrm{PMes_3^{\bullet+}}$ and $\mathrm{BCF^{\bullet-}}$ radical ions via electron tunneling through the frozen solvent.[22] Upon removal of the sample from the EPR spectrometer, an intense dark purple colour could be observed, which quickly reverted back to violet as the sample thawed.

Next, we employed transient absorption spectroscopy[23] to determine both the absorption spectrum and the lifetime of the $\mathrm{PMes_3^{\bullet+}}$/$\mathrm{BCF^{\bullet-}}$ radical ion pair. Using the $\mathrm{PMes_3}$/BCF toluene solution (0.04 M) at room temperature, short laser pulse (<200 fs; λ = 530 nm) excitation of the CT-band and subsequent time-resolved picosecond spectroscopy allowed us to detect a broad absorption band (λ_{max} = 620 nm; Figure 3c), which we assign to a superposition of individual absorption spectra of $\mathrm{PMes_3^{\bullet+}}$ and $\mathrm{BCF^{\bullet-}}$ (lit. values: $\lambda \approx$ 600 nm in PhCN[24] and $\lambda \approx$ 600 nm in THF,[5] respectively). Decay analysis of this transient absorption showed that the photo-generated radical ion pair has a lifetime[25] of 237 ps at room temperature, due to rapid back-electron transfer to the ground-state EDA complex in solution. Formally, CT-band excitation gives optical electron transfer, *i.e.* direct population of the CT-state ($[\mathrm{D^{\bullet+}}\text{--}\mathrm{A^{\bullet-}}]$) within the laser pulse.[26] These findings evidence, for the first time, unequivocally that visible light is a necessity to access the $\mathrm{PMes_3^{\bullet+}}$/$\mathrm{BCF^{\bullet-}}$ radical ion pair. Note that the instability of $\mathrm{BCF^{\bullet-}}$ in combination with the light dependence and short lifetime of the radical ion pair indicates that the $\mathrm{PMes_3^{\bullet+}}$/$\mathrm{BCF^{\bullet-}}$ pair will be available in minute quantities and, thus, is unlikely to account for the follow-up chemistry reported recently.[2c,3d,11] Since for a series of donors interacting with a common acceptor, the energies of the charge transfer transitions $h\nu_{CT}$ vary proportionally with the donor ionization potentials (I_D; Figure 1),[14b] we expect the same SET process for the $\mathrm{P}t\mathrm{Bu_3}$/BCF combination to be feasible using light, albeit of higher energy.[2c] Indeed, mixing the two colourless FLP components $\mathrm{P}t\mathrm{Bu_3}$ and BCF (0.015 M in toluene) resulted directly in a pale yellow solution[27] for which UV-vis spectroscopy also revealed an additional broad absorption band ($\lambda \approx$ 400 nm; Figure 4a) that partly overlaps with the absorptions of the separate species; the charge-transfer band of the $\mathrm{P}t\mathrm{Bu_3}$/BCF EDA complex is expected in this region. However, it is also known that $\mathrm{P}t\mathrm{Bu_3}$ and $\mathrm{B(C_6F_5)_3}$ slowly react to form the yellow (λ = 372 nm) para-addition product,[27] which, although not visible by ^{19}F-NMR spectroscopy, could also be present in low concentrations in this region hampering unambiguous assignment of the new absorption band. EPR spectroscopy at 30 K of a $\mathrm{P}t\mathrm{Bu_3}$/BCF frozen toluene (6 x 10^{-5} M) solution, freshly prepared in the dark, showed no radicals. Yet to our delight, during a 90-second irradiation with visible light (390–500 nm) EPR signals corresponding to $\mathrm{P}t\mathrm{Bu_3^{\bullet+}}$ and $\mathrm{BCF^{\bullet-}}$ radical ions were observed (Figure 4b) confirming the existence of a CT-band in the visible region. Again the $\mathrm{BCF^{\bullet-}}$ radical comprises a featureless broad signal at g = 2.005 and the remaining four lines result from the axially symmetric $\mathrm{P}t\mathrm{Bu_3^{\bullet+}}$ radical cation ($g_\perp$ = 2.0065 and $g_\parallel$ = 2.0012) with hyperfine coupling ($A_\perp$ = 580, $A_\parallel$ = 1365 MHz) to the I = ½ P nucleus.[8] This time, after irradiation, the EPR signals decay notably faster when compared to $\mathrm{PMes_3}$/BCF, with a 50% decline in intensity after 6 minutes at 30 K. Similarly, faster decay is observed when the sample is removed from the EPR spectrometer, as the dark purple colour instantly reverts back to pale yellow upon thawing. Ultra-fast transient absorption spectroscopy confirms these observations and showed that excitation of the CT-band (<200 fs laser pulse; λ = 400 nm) affords the absorption bands of the $\mathrm{P}t\mathrm{Bu_3^{\bullet+}}$/$\mathrm{BCF^{\bullet-}}$ radical ions (λ_{max} = 680 nm; Figure 4c) that

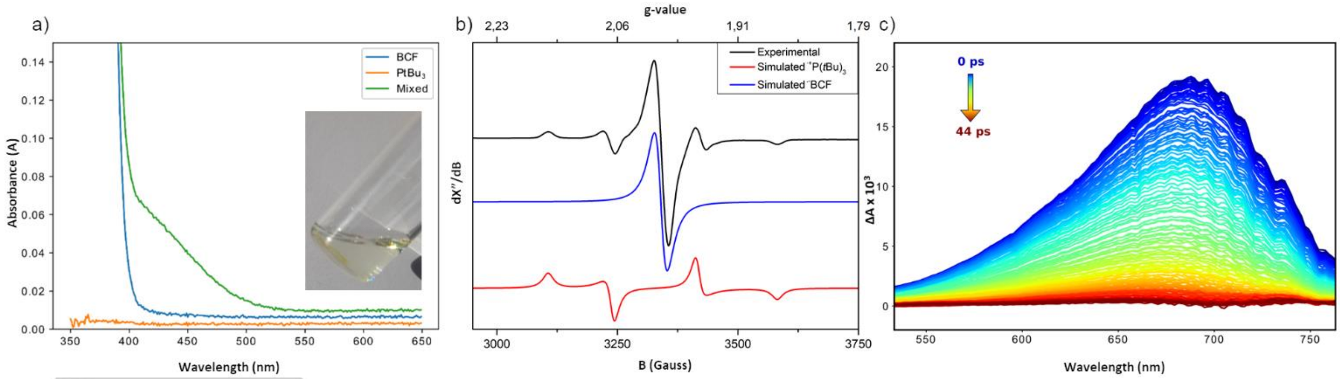

Figure 4. a) UV-Vis spectrum of $\mathrm{P}t\mathrm{Bu_3}$/BCF (both components: 1.5 x 10^{-2} M in toluene) compared to the separate components (1.5 x 10^{-2} M). Inset shows colour of the solution. b) Experimental EPR spectrum of $\mathrm{P}t\mathrm{Bu_3}$/BCF in toluene measured at 30K during irradiation with visible light (390–500 nm) and simulated EPR spectrum. c) Transient absorption spectrum measured after pulsed excitation of $\mathrm{P}t\mathrm{Bu_3}$/BCF with 530 nm light.

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disappear rapidly (lifetime = 6 ps) after the laser pulse. This short lifetime, resulting from facile back-electron transfer, prevents significant contribution of diffusive separation and subsequent chemistry,[14c,23] which accounts for the lack of radical chemistry observed for this FLP system.

Intrigued by the formation of the stable, deep blue $N^bAr_3^{\bullet+}$ radical cation when the bridged triphenylamine N^bAr_3 is reacted with BCF in DCM at room temperature for 72 hours (Scheme 1c),[4b,28] we expanded our studies by varying the Lewis base to incorporate triphenylamine (NPh_3) and tri-*p*-tolylamine (N*p*Tol_3). Calculation of their ionization potentials (I_D NPh_3 = 5.94 eV, N*p*Tol_3 = 5.67 eV) with ωB97X-D/6-311+G(d,p) showed again a large disparity with the EA_A of BCF (–3.03 eV), affording energy gaps of 2.91 eV (67.1 kcal·mol^{-1}) and 2.64 eV (60.7 kcal·mol^{-1}), respectively, between the Lewis acid/base pairs and the corresponding radical ions, which indicates that the needed single-electron transfer again requires visible light. Indeed, the CT-band of the electron donor–acceptor (EDA) complex was detected by UV-vis spectroscopy for both NPh_3/BCF and N*p*Tol_3/BCF in toluene (0.015 M; λ_{max} = 500 and 420 nm, respectively; Figures S17-S19). Interestingly, for N*p*Tol_3/BCF the UV-vis spectrum changed over time and after 5 hours at room temperature the absorptions of the stable *p*$Tol_3N^{\bullet+}$ radical cation were also observed (λ_{max} = 590 and 690 nm; Figure S19).[29,30] EPR analysis confirmed that mixing NPh_3 or N*p*Tol_3 with BCF yields no SET in the dark, though irradiation with visible light (390–500 nm) promoted photoinduced SET to generate the corresponding radical ion pair, of which the amine radical cations were observed at room temperature (Figure S27-28).[31] Absence of the $BCF^{\bullet-}$ is attributed to its known rapid degradation in solution a room temperature,[3a,5] which is the driving force for the build-up of the amine radical cation as it prevents regeneration of the ground-state EDA complex by BET (Scheme 3). Since the computed ionization potential for the bridged triarylamine N^bAr_3 (5.67 eV) is equal to that of N*p*Tol_3 (5.67 eV),[16] these findings strongly suggest that the SET reported[4b] by Wang *et al*. between triarylamine N^bAr_3 and BCF also proceeds photochemically, and that performing this reaction in broad daylight (or using a high-power LED) will be beneficial.

Next, we selected the bulky tris(3,5-dinitro-2,4,6-trimethylphenyl)borane as the Lewis acid (abbreviated as $B(NO_2\text{-}Mes)_3$; EA_A = –3.04 eV; Figure 5), which has a similar electron affinity to the archetypal borane $B(C_6F_5)_3$ (EA_A = –3.03 eV; Figure 5). The former can be reduced with Na metal[32] to afford the persistent radical anion $B(NO_2\text{-}Mes)_3^{\bullet-}$.[33] We postulated that this borane radical anion should also be accessible from an EDA complex by photoinduced SET, when a suitable Lewis base is used. For this, we selected P*t*Bu_3 (I_D = 5.95 eV),[29] since the corresponding FLP has an energy gap of 2.91 eV (I_D + EA_A, 66.9 kcal·mol^{-1}) with the P*t*$Bu_3^{\bullet+}$/$B(NO_2\text{-}Mes)_3^{\bullet-}$ radical ion pair. We could not detect a CT-band by UV-vis spectroscopy; the appearance of a small band corresponding to the dark red $B(NO_2\text{-}Mes)_3^{\bullet-}$ radical anion (510 nm) was the only peak observable that was not attributable to the separate phosphine or borane (Figure S14). However, we proceeded to irradiate a pale yellow solution of P*t*Bu_3/$B(NO_2\text{-}Mes)_3$ in DCM (0.03 M) with 455 nm light (2.2 W, LED), avoiding excitation of the separate Lewis acid and base (λ < 420 nm), and were delighted to see that facile SET took place within 3 hours at room temperature to generate a dark red solution of $B(NO_2\text{-}Mes)_3^{\bullet-}$ (confirmed by EPR spectroscopy, Figure S24; Scheme 3), which is facilitated by the degradation of the highly unstable P*t*$Bu_3^{\bullet+}$ radical cation (70% conversion, Figure S25). This is a proof of principle for the use of Lewis bases as sacrificial one-electron donors in the photochemical reduction of boranes.

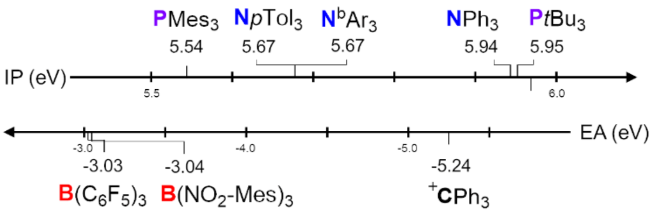
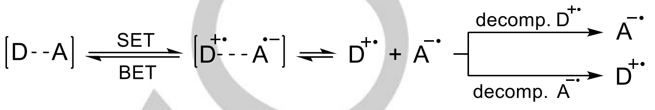


Figure 5. Calculated ionization potentials (I_D; top) and electron affinities (EA_A; bottom) of donors and acceptors typical for FLP chemistry at the SCRF/ωB97X-D/6-311+G(d,p) level of theory.



Scheme 3. Single-electron transfer to afford the high energy radical ion pair, which via decomposition of either the radical cation or the radical anion forms the corresponding stable radical ion selectively.

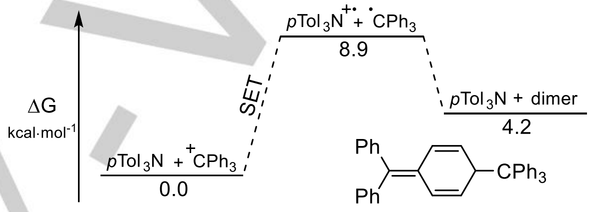


Figure 6. Energy diagram showing thermal single-electron-transfer equilibrium for the N*p*Tol_3/$^+CPh_3$ EDA pair. For computational details, see figure 5.

In light of the foregoing findings, we were also keen on targeting the generation of radical pairs from Lewis acids and bases via thermal SET by using FLPs for which the energy difference between donor-acceptor and radical pair is smaller to show that this generates a fundamentally different situation involving equilibria. The combination of $PTipp_3$ or $PMes_3$ with the strongly Lewis acidic trityl cation ($^+CPh_3$), previously reported by Müller, Klare and co-workers, serves as an ideal starting point (Scheme 1b).[7] In these cases, both radicals obtained by SET at room temperature ($PR_3^{\bullet+}$ and $^{\bullet}CPh_3$) were detected by EPR spectroscopy,[7] and we were keen to elucidate if this process is general and also occurs in the dark. Note that the high sensitivity of EPR spectroscopy allows for detection of persistent radicals in concentrations as low as 10^{-8} M. For a 0.06 M solution, this corresponds to an equilibrium with an energy gap (ΔG) of ~9 kcal·mol^{-1} (0.4 eV) between the ground-state EDA complex and the radical pair leading to the formation of measurable amounts of radicals (according to its Boltzmann distribution).[16] Indeed, combining $PMes_3$ with $[Ph_3C][B(C_6F_5)_4]$ (I_D + EA_A = 7.0 kcal·mol^{-1}; Figure 5) in toluene in the absence of light resulted in facile SET and detection of the corresponding phosphoniumyl $PMes_3^{\bullet+}$/$^{\bullet}CPh_3$ radical pair by EPR spectroscopy (Figure S29-30).[7] As the trityl radical is in equilibrium with its quinoid-type dimer, Gomberg dimerization provides an additional driving force towards the radical side of the equilibrium (ΔG = –4.7 kcal·mol^{-1}; Figure 6).[34]

Finally, we were curious if we also could design the one-electron oxidation of amines via a thermal SET, simply by using the trityl cation as the Lewis acid in the dark. Although the energy gap between the levels of the EDA pairs formed by combining the arylamines NPh$_3$ or N*p*Tol$_3$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] and corresponding radical pairs (ΔG (ΔE) = 14.4 (16.3) and 8.9 (10.0) kcal·mol^{-1}, respectively; Figure 5) are close or exceeding the threshold to be detectable by EPR spectroscopy, Gomberg dimerisation drives the equilibrium to the right allowing for observation of the radical species (Figure 6). As the trityl radical is mostly present as Gomberg's dimer, the EPR spectrum is dominated by the amine radical cations (Figure S32-33).

In summary, we have shown that the encounter complexes in FLP chemistry can also be described as EDA complexes, which are susceptible to undergo photo-induced single-electron transfer to form the corresponding radical pairs. This knowledge has resulted, for the first time, in the controlled generation and detection of the radical ion pairs of the archetypal FLPs PMes$_3$/BCF and P*t*Bu$_3$/BCF via visible light induced single-electron transfer. This study allows us to directly probe any FLP type reaction facilitated by these systems, and determine whether it proceeds via radical pair formation. Furthermore, we demonstrated that the energy gap between EDA complex and the corresponding radical pair can be readily tuned to proceed thermally by changing the Lewis acid and base components. It is therefore possible to predict the nature of single-electron-transfer between two donor-acceptor species by simple analysis of their ionization potential and electron affinity. In addition, this work grants important insight for understanding and controlling the generation of highly reactive radical pairs by photoinduced or thermal single-electron transfer, which we are currently applying to the design of new radical ion pairs with photophysical properties tuned for exploiting radical reactivity. We envision such systems could be highly beneficial for designing FLPs suitable for the activation of inert substrates as well as the development of main-group photo-redox catalysis.[35]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: frustrated Lewis pair • radicals • single-electron transfer • charge transfer complex • photoinduced

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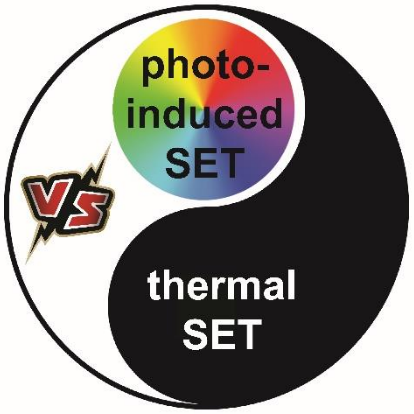
Entry for the Table of Contents

COMMUNICATION

Exciting FLPs! – Radicals pairs of archetypal frustrated Lewis pair (FLP) systems $PMes_3/B(C_6F_5)_3$ and $P\textit{t}Bu_3/B(C_6F_5)_3$ are accessed via visible light-induced single-electron transfer. Varying the FLP system shows this process is general for a range of donor-acceptor combinations and can be tuned to proceed thermally.



*Flip Holtrop, Andrew R. Jupp, Nicolaas P. van Leest, Maximilian Paradiz Dominguez, René M. Williams, Albert M. Brouwer, Bas de Bruin, Andreas W. Ehlers and J. Chris Slootweg**

Page No. – Page No.

Photoinduced and Thermal Single-Electron Transfer to Generate Radicals from Frustrated Lewis Pairs