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■ **Lewis Acid/Base Pairs**

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

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

Dedicated to Professor Peter Chen on the occasion of his 60th birthday

Abstract: Archetypal phosphine/borane frustrated Lewis pairs (FLPs) are famed for their ability to activate small molecules. The mechanism is generally believed to involve two-electron processes. However, the detection of radical intermediates indicates that single-electron transfer (SET) generating frustrated radical pairs could also play an important role. These highly reactive radical species typically have significantly higher energy than the FLP, 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 that undergoes visible-light-induced SET to form the corresponding highly reactive radical-ion pairs. Subsequently, we show that by tuning the properties of the Lewis acid/base pair, the energy required for SET can be reduced to become thermally accessible.

Introduction

Frustrated Lewis pair (FLP) chemistry is useful for the activation of a variety of small molecules, most notably dihydrogen and carbon dioxide.[1] However, the activation of less reactive substrates, such as dinitrogen or methane, remains a challenge. It is generally accepted that FLP reactivity stems from the association of the electron donor (D; Lewis base) and the electron acceptor (A; Lewis acid) to form an encounter complex ([D–A]) that 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 sys-

tems, which indicates that single-electron transfer (SET) may 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 to investigate.

A SET 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 a 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 detected a very weak signal by EPR spectroscopy in chlorobenzene, which they postulated to be the $PMes_3^{·+}$ radical cation. Switching to the more Lewis acidic $Al(C_6F_5)_3$ resulted in significantly larger signals accredited to the $PMes_3^{·+}$ radical cation (Scheme 1 a).[2c] The absence of radical anions ($BCF^{·-}$ and $Al(C_6F_5)_3^{·-}$) was attributed to the known rapid degradation of these species through solvolytic pathways.[3a,5,6] Further indications for a radical pathway were provided by the reaction of $PMes_3/B(C_6F_5)_3$ with Ph_3SnH, which 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] Klare, Müller and co-workers also observed radical formation when combining trityl (CPh_3^+) or 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 1 b).[7] In the case of trityl, both radical species (·CPh_3 and $R_3P^{·+}$) were persistent, allowing the detection of both components of the radical pair in solution.
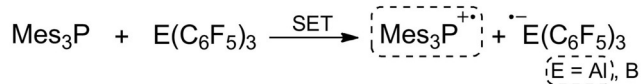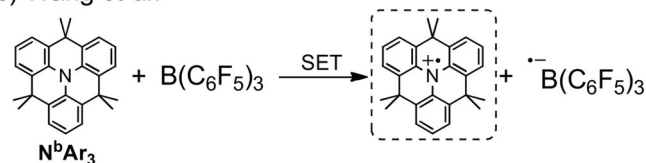
Interestingly, when the analogous reactions of BCF, $Al(C_6F_5)_3$ and SiR_3^+ were carried out with $PtBu_3$ as the Lewis base, no radical reactivity was observed. Klare, Müller and co-workers

[a] F. Holtrop, Dr. A. R. Jupp, N. P. van Leest, M. Paradiz Dominguez, Dr. R. M. Williams, Prof. Dr. A. M. Brouwer, Prof. Dr. B. de Bruin, Dr. A. W. Ehlers, Prof. Dr. J. C. Slootweg
Van't Hoff Institute for Molecular Sciences
University of Amsterdam, PO Box 94157
1090 GD Amsterdam (The Netherlands)
E-mail: j.c.slootweg@uva.nl

[b] Dr. A. W. Ehlers
Department of Chemistry, Science Faculty
University of Johannesburg, PO Box 254, Auckland Park
Johannesburg (South Africa)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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a) Stephan *et al.*

$$Mes_3P \ + \ E(C_6F_5)_3 \ \xrightarrow{SET} \ \boxed{Mes_3P^{+\bullet}} \ + \ {}^{\bullet-}E(C_6F_5)_3$$
$$E = Al, B$$

b) Müller, Klare *et al.*

$$R_3P \ + \ {}^{+}CPh_3 \ \text{or} \ {}^{+}SiR'_3 \ \xrightarrow{SET} \ \boxed{R_3P^{+\bullet}} \ + \ \boxed{{}^{\bullet}CPh_3 \ \text{or} \ {}^{\bullet}SiR'_3}$$

c) Wang *et al.*

$$N^bAr_3 \ + \ B(C_6F_5)_3 \ \xrightarrow{SET} \ [\text{radical cation}] \ + \ {}^{\bullet-}B(C_6F_5)_3$$

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 the case of CPh_3^+); $SiR'_3^+ = SiiPr_3^+$, $Si(C_6Me_5)_3^+$, Sit-$BuMe_2^+$, $SiEt_3^+$.

accredited this to the higher ionisation energy of P*t*Bu$_3$ compared with PMes$_3$ (see Table S1 in the Supporting Information). Another challenge comes from the fact that the P*t*Bu$_3{}^{\bullet+}$ radical cation 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, with the amine radical cations, for example, formed by visible-light photoredox catalysis, having 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 and co-workers reported on the photoinduced SET between $B(C_6F_5)_3$ and *N*,*N*-dialkylanilines.[10] Again, the BCF$^{\bullet-}$ radical anion was not detected in either case.[3a, 5]

These findings prompted us to focus on understanding SET 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.[3c,12] Mulliken theory describes how interactions between donors and acceptors can lead to the formation of electron donor–acceptor (EDA) complexes [D–A] that exhibit characteristic absorption bands resulting from the 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 and co-workers showed that such EDA complexes can be formed by mixing tetracyanoethylene and anthracenes, and used picosecond laser spectroscopy to demonstrate that spe-

cific irradiation of the charge-transfer (CT) band indeed induces SET to generate 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].
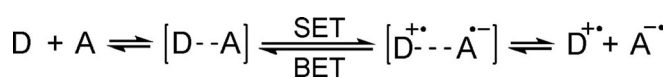
Results and Discussion

In applying this knowledge to frustrated Lewis pairs, we first calculated the ionisation energy (IE$_D$) 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 the fact that there is a large disparity between the EA$_A$ of BCF (-3.03 eV) and the IE$_D$ 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 SET is, therefore, unlikely to be a thermal process. This prompted us to further investigate these systems, employing both time-dependent DFT (TD-DFT) calculations and a range of spectroscopic techniques, to shed light on the process of radical formation.[17]
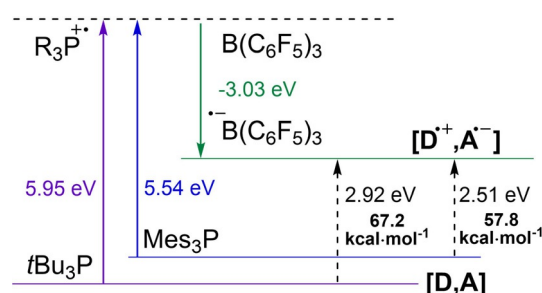
Figure 1. DFT-calculated energy needed to access the radical-ion pairs from the FLP systems P*t*Bu$_3$/PMes$_3$ and BCF.[7]

It is known that mixing colourless solutions of PMes$_3$ and BCF yields a violet solution,[2c,18] which indicates that interaction with visible light ($\lambda = 400$–800 nm, $\Delta E = 71.4$–35.7 kcal mol^{-1}) is occurring. Although the violet colour has previously been suggested to result from the 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 EDA complex, generated in the ground state upon association of the electron-rich phosphine and the electron-deficient borane. The absorption spectrum of the phosphine–borane encounter complex PMes$_3$–BCF, computed by TD-DFT at the ωB97X-D/6-311++G(d,p) level of theory indeed features an additional absorption band at a longer wavelength than the individual components ($\lambda = 439$ nm; see Figure S1 in the Supporting Information),[19] which is indicative of a CT band.[12] Analysis of the frontier molecular orbitals of this encounter complex clearly showed that this CT is from the phosphorus lone pair (HOMO; Figure 2) to the formally vacant p orbital on
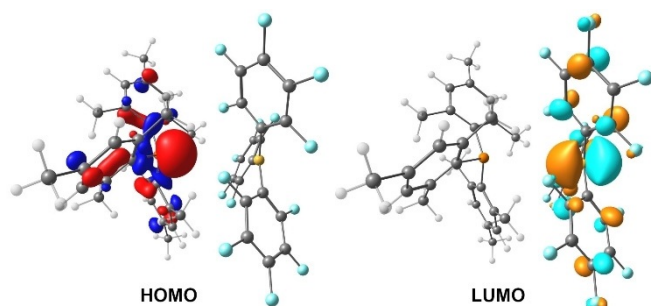
$$D + A \ \rightleftharpoons \ [D\text{-}\text{-}A] \ \underset{BET}{\overset{SET}{\rightleftharpoons}} \ [D^{+\bullet}\text{-}\text{-}A^{\bullet-}] \ \rightleftharpoons \ D^{+\bullet} + A^{\bullet-}$$

Scheme 2. Electron donor–acceptor complex formation and subsequent SET to generate the corresponding radical-ion pair.

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

boron (LUMO; Figure 2).[20] UV/Vis spectroscopic analysis of the violet solution of PMes$_3$/BCF in toluene (0.015 M) confirmed this hypothesis and revealed an absorption band in the visible spectrum at $\lambda_{max} = 534$ 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 SET, we designed an EPR experiment featuring a light source within the spectrometer. Low-temperature (30 K) analysis of a violet PMes$_3$/BCF frozen toluene (0.06 M) solution prepared in the dark showed no radical formation, clearly evidencing that the violet colour is not generated by radicals. During irradiation with visible light (390–500 nm) for 90 s, an intense EPR signal corresponding to a superposition of two radical species was observed (Figure 3b). The broad signal at $g = 2.005$, with a featureless signal at 30 K that shows no resolved hyperfine coupling interactions, is attributed to the BCF$^{\cdot-}$ radical anion.[15] The other four lines stem from the axially symmetric PMes$_3$$^{\cdot+}$ radical cation ($g_\perp = 2.0055$, $g_\parallel = 2.0015$) exhibiting hyperfine coupling ($A_\perp = 550$ MHz, $A_\parallel = 1170$ MHz) with the $I = 1/2$ phosphorus nucleus; similar spectra have been previously reported in nitrile solvents ($A_\perp = 427–480$ MHz, $A_\parallel = 1128–1157$ MHz).[21] When we stopped irradiating the sample, both radicals remained visible with the signal intensity having only decayed by about 25 % after 6 min at 30 K. We postulate that this relative longevity can be ascribed to the formation of separate PMes$_3$$^{\cdot+}$ and BCF$^{\cdot-}$ radical ions by electron tunnelling 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 record the absorption spectra of the PMes$_3$$^{\cdot+}$/BCF$^{\cdot-}$ radical-ion pair and determine its lifetime. Using a toluene solution of PMes$_3$/BCF (0.04 M) at room temperature, short laser pulse (< 200 fs; $\lambda = 530$ nm) excitation of the CT band and subsequent time-resolved picosecond spectroscopy allowed us to detect a broad absorption band ($\lambda_{max} = 620$ nm; Figure 3c), which we assign to a superposition of the individual absorption spectra of PMes$_3$$^{\cdot+}$ and BCF$^{\cdot-}$ ($\lambda \approx 600$ nm in PhCN[24] and $\lambda \approx 600$ nm in THF,[5] respectively). Decay analysis of this transient absorption showed that the photogenerated radical-ion pair has a lifetime[25] of 237 ps at room temperature, due to rapid BET to the ground-state EDA complex in solution. Formally, CT-band excitation produces optical electron transfer, that is, direct population of the CT state ([D$^{\cdot+}$–A$^{\cdot-}$]) within the laser pulse.[26] These findings evidence, for the first time, unequivocally that visible light is a necessity to access the PMes$_3$$^{\cdot+}$/BCF$^{\cdot-}$ radical-ion pair. Note that the instability of BCF$^{\cdot-}$ in combination with the light-dependence and short lifetime of the radical-ion pair indicates that the PMes$_3$$^{\cdot+}$/BCF$^{\cdot-}$ pair will be available in minute quantities and thus is unlikely to account for the follow-up chemistry reported recently.[2c, 3d, 10]

Because for a series of donors interacting with a common acceptor, the energies of the CT transitions ($h\nu_{CT}$) vary proportionally with the donor ionisation energies (IE$_D$; Figure 1),[13b] we expect the same SET process for the PtBu$_3$/BCF combination to be feasible using light, albeit of higher energy.[2c] Indeed, mixing the two colourless FLP components PtBu$_3$ and BCF (0.015 M in toluene) resulted directly in a pale-yellow solution,[27] UV/Vis spectroscopic analysis of which also revealed an additional broad absorption band ($\lambda \approx 400$ nm; Figure 4a) that partly overlaps with the absorptions of the separate species; the CT band of the PtBu$_3$/BCF EDA complex is expected in this region. However, it is also known that PtBu$_3$ and B(C$_6$F$_5$)$_3$ slowly react to form the yellow ($\lambda = 372$ nm) para-addition product,[26] 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 PtBu$_3$/BCF frozen toluene (6×
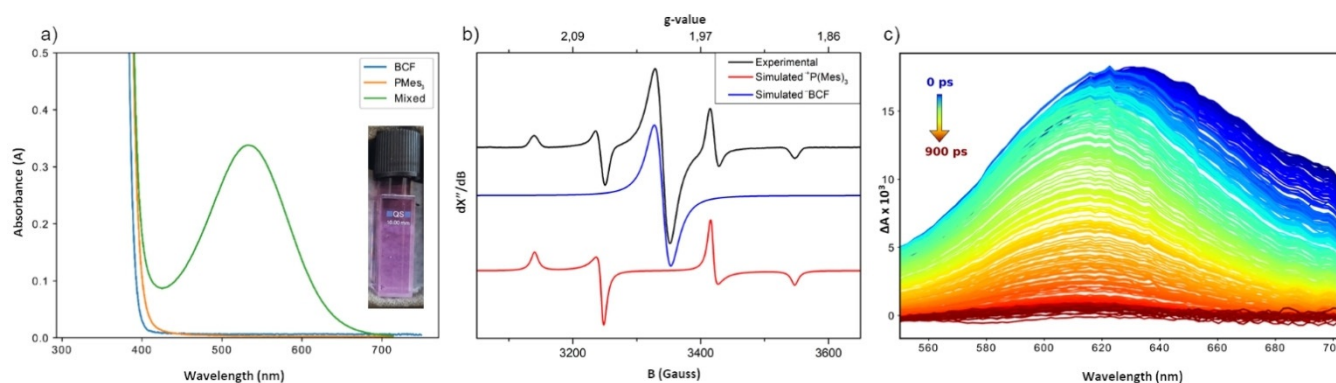

Figure 3. a) UV/Vis spectrum of PMes$_3$/BCF (both components: 1.5×10^{-2} M in toluene) compared with the spectra of the separate components (1.5×10^{-2} M). b) Experimental EPR spectrum of PMes$_3$/BCF in toluene measured at 30 K during irradiation with visible light (390–500 nm) and simulated EPR spectra of PMes$_3$$^{\cdot+}$ and BCF$^{\cdot-}$. c) Transient absorption spectra measured after pulsed excitation of PMes$_3$/BCF with 530 nm light.
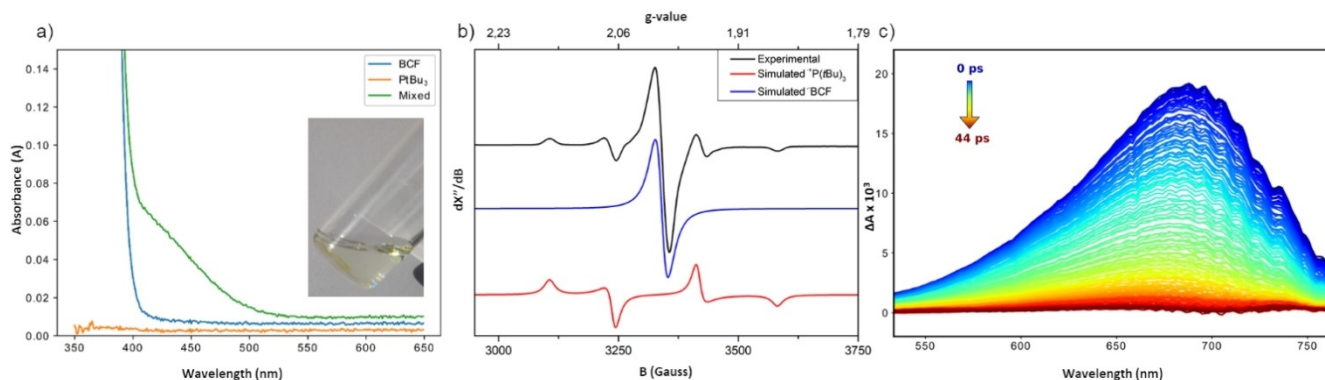
Figure 4. a) UV/Vis spectrum of PtBu$_3$/BCF (both components: 1.5×10^{-2} M in toluene) compared with the spectra of the separate components (1.5×10^{-2} M). Inset shows the colour of the solution. b) Experimental EPR spectrum of PtBu$_3$/BCF in toluene measured at 30 K during irradiation with visible light (390–500 nm) and simulated EPR spectra of PtBu$_3$$^{\cdot+}$ and BCF$^{\cdot-}$. c) Transient absorption spectra measured after pulsed excitation of PtBu$_3$/BCF with 530 nm light.

10^{-5} M) solution, freshly prepared in the dark, showed no radicals. Yet, to our delight, during irradiation with visible light (390–500 nm) for 90 s, EPR signals corresponding to PtBu$_3$$^{\cdot+}$ and BCF$^{\cdot-}$ radical ions were observed (Figure 4 b), thereby confirming the existence of a CT band in the visible region. Again, the BCF$^{\cdot-}$ radical ion comprises a featureless broad signal at $g=2.005$, and the remaining four lines result from the axially symmetric PtBu$_3$$^{\cdot+}$ radical cation ($g_\perp=2.0065$, $g_\parallel=2.0012$) with hyperfine coupling ($A_\perp=580$ MHz, $A_\parallel=1365$ MHz) with the $I=\frac{1}{2}$ phosphorus nucleus.[8] This time, after irradiation, the EPR signals decay notably faster than those of PMes$_3$/BCF, with a 50% decline in intensity after 6 min at 30 K. Similarly, faster decay was observed when the sample was removed from the EPR spectrometer, as the dark-purple colour instantly reverted back to pale yellow upon thawing. Ultrafast transient absorption spectroscopy confirmed these observations and showed that excitation of the CT band (<200 fs laser pulse; $\lambda=400$ nm) affords the absorption bands of the PtBu$_3$$^{\cdot+}$/BCF$^{\cdot-}$ radical ions ($\lambda_{max}=680$ nm; Figure 4 c) that disappear rapidly (lifetime $=6$ ps) after the laser pulse. This short lifetime, resulting from facile BET, prevents significant diffusive separation and subsequent chemistry,[13c, 22] which accounts for the lack of radical chemistry observed for this FLP system.

Intrigued by the formation of the stable, deep-blue N^{b}Ar$_3$$^{\cdot+}$ radical cation when the bridged triphenylamine N^{b}Ar$_3$ was treated with BCF in DCM at room temperature for 72 h (Scheme 1 c),[4b, 28] we expanded our studies by varying the Lewis base to incorporate triphenylamine (NPh$_3$) and tri-p-tolylamine (NpTol$_3$). Calculation of their ionisation energies (IE$_D=5.94$ eV for NPh$_3$ and 5.67 eV for NpTol$_3$) at the ωB97X-D/6-311+G(d,p) level of theory 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 SET again requires visible light. Indeed, the CT band of the EDA complex was detected by UV/Vis spectroscopy for both NPh$_3$/BCF and NpTol$_3$/BCF in toluene (0.015 M; $\lambda_{max}=500$ and 420 nm, respectively; see Figures S17–S19 in the Supporting Information). Interestingly, for NpTol$_3$/BCF, the UV/Vis spectrum changed over time and after

5 h at room temperature the absorption bands of the stable pTol$_3$N$^{\cdot+}$ radical cation were also observed ($\lambda_{max}=590$ and 690 nm; see Figure S19).[29,30] EPR analysis confirmed that mixing NPh$_3$ or NpTol$_3$ with BCF yields no SET in the dark, although irradiation with visible light (390–500 nm) promoted photoinduced SET to generate the corresponding radical-ion pair, the amine radical cations being observed at room temperature (see Figures S27 and S28).[31] The absence of BCF$^{\cdot-}$ is attributed to its known rapid degradation in solution at 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). Because the computed ionisation energy for the bridged triarylamine N^{b}Ar$_3$ (5.67 eV) is equal to that of NpTol$_3$ (5.67 eV),[15] these findings strongly suggest that the SET reported[4b] by Wang et al. between the triarylamine N^{b}Ar$_3$ and BCF also proceeds photochemically, and that performing this reaction in broad daylight (or by using a high-power light-emitting diode (LED)) will be beneficial.
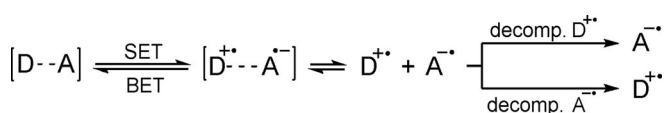
Scheme 3. SET to afford the high-energy radical-ion pair, which, by decomposition of either the radical cation or radical anion, forms the stable complementary radical ion selectively.

Next, we selected the bulky tris(3,5-dinitro-2,4,6-trimethylphenyl)borane as the Lewis acid (abbreviated as B(NO$_2$-Mes)$_3$, EA$_A=-3.04$ eV; Figure 5), which has a similar electron affinity to the archetypal borane B(C$_6$F$_5$)$_3$ (EA$_A=-3.03$ eV; Figure 5). The former can be reduced with sodium metal[32] to afford the persistent radical anion B(NO$_2$-Mes)$_3$$^{\cdot-}$.[33] We postulated that this borane radical anion should also be accessible from an EDA complex by photoinduced SET when a suitable Lewis base is used. For this, we selected PtBu$_3$ (IE$_D=5.95$ eV),[27] because the energy gap between the corresponding FLP and the PtBu$_3$$^{\cdot+}$/B(NO$_2$-Mes)$_3$$^{\cdot-}$ radical-ion pair is 2.91 eV (IE$_D$+EA$_A$,

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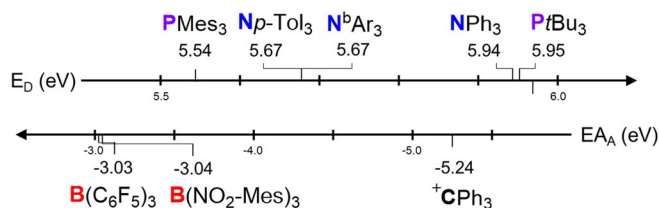**Chemistry Europe**
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Figure 5. Ionisation energies (IE$_D$, top) and electron affinities (EA$_A$, bottom) of donors and acceptors typical in FLP chemistry calculated at the SCRF/ωB97X-D/6-311+G(d,p) level of theory (solvent = toluene).

Figure 6. Energy diagram showing the thermal SET equilibrium for the NpTol$_3$/$^+$CPh$_3$ EDA pair. For computational details, see Figure 5.

66.9 kcal mol^{-1}). We could not detect a CT band by UV/Vis spectroscopy; the appearance of a small band corresponding to the dark-red B(NO$_2$-Mes)$_3$$^{·-}$ radical anion (510 nm) was the only peak observable that was not attributable to the separate phosphine or borane (see Figure S14 in the Supporting Information). However, we irradiated a pale-yellow solution of PtBu$_3$/B(NO$_2$-Mes)$_3$ in DCM (0.03 M) with 455 nm light (2.2 W, LED), avoiding excitation of the separate Lewis acid and base (λ < 420 nm), and were delighted to see that facile SET took place within 3 h at room temperature to generate a dark-red solution of B(NO$_2$-Mes)$_3$$^{·-}$ (confirmed by EPR spectroscopy, see Figure S24), facilitated by the degradation of the highly unstable PtBu$_3$$^{·+}$ radical cation (70% conversion, Scheme 3 and 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.

In light of the foregoing findings, we were also keen to target the generation of radical pairs from Lewis acids and bases through 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 Klare, Müller and co-workers, serves as an ideal starting point (Scheme 1b).[7] In both these cases, the radicals obtained by SET at room temperature (PR$_3$$^{·+}$ and $^·$CPh$_3$) were detected by EPR spectroscopy,[7] and we were keen to elucidate whether this process is general and also occurs in the dark. Note that the high sensitivity of EPR spectroscopy allows for detection of persistent radicals in concentrations as low as 10^{-8} M. For a 0.06 M solution, this corresponds to an equilibrium with an energy gap (ΔG) of around 9 kcal mol^{-1} (0.4 eV) between the ground-state EDA complex and the radical pair, leading to the formation of measurable amounts of radicals (according to its Boltzmann distribution).[15] Indeed, combining PMes$_3$ with the trityl source [Ph$_3$C][B(C$_6$F$_5$)$_4$] (IE$_D$+EA$_A$ = 0.3 eV (7.0 kcal mol^{-1}); Figure 5) in toluene in the absence of light resulted in facile SET and detection of the corresponding phosphoniumyl PMes$_3$$^{·+}$/$^·CPh_3$ radical pair by EPR spectroscopy (see Figures S29 and S30).[7] As the trityl radical is in equilibrium with its quinoid-type dimer, Gomberg dimerisation 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 as to whether we also could achieve the one-electron oxidation of amines through thermal SET
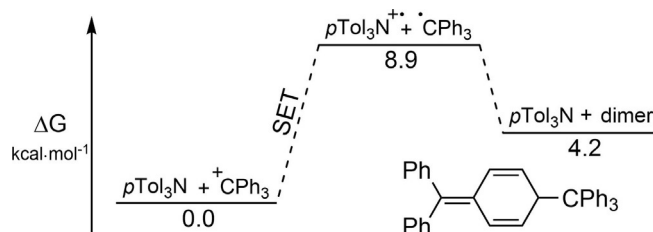
simply by using the trityl cation as the Lewis acid in the dark. Although the energy gap between the EDA pairs formed by combining the arylamines NPh$_3$ or NpTol$_3$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] and the corresponding radical pairs (ΔG (ΔE) = 14.4 (16.3) and 8.9 (10.0) kcal mol^{-1}, respectively; Figure 6) are close to or exceed the threshold for detection 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 (see Figures S32 and S33).

Conclusion

We have shown that the encounter complexes in FLP chemistry can also be described as EDA complexes, and are susceptible to photoinduced SET 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 PtBu$_3$/BCF through visible-light-induced SET. This study will allow us to directly probe any FLP-type reaction facilitated by these systems and determine whether they proceed via radical-pair formation. Furthermore, we have demonstrated that the energy gap between the 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 the SET between two donor–acceptor species by simple analysis of their ionisation energy and electron affinity. In addition, this work has provided important insights for understanding and controlling the generation of highly reactive radical pairs by photoinduced or thermal SET, 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 photoredox catalysis.[35]

Conflict of interest

The authors declare no conflict of interest.

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