Frustrated Radical Pairs: Insights from EPR Spectroscopy
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Keywords:
electron paramagnetic resonance · frustrated Lewis pair · main group chemistry · radicals · single-electron transfer

How to cite: Angew. Chem. Int. Ed. 2021, 60, 53–65
International Edition: doi.org/10.1002/anie.202010633
German Edition: doi.org/10.1002/ange.202010633
Progress in frustrated Lewis pair (FLP) chemistry has revealed the importance of the main group elements in catalysis, opening new avenues in synthetic chemistry. Recently, new reactivities of frustrated Lewis pairs have been uncovered that disclose that certain combinations of Lewis acids and bases undergo single-electron transfer (SET) processes. Here an electron can be transferred from the Lewis basic donor to a Lewis acidic acceptor to generate a reactive frustrated radical pair (FRP). This minireview aims to showcase the recent advancements in this emerging field covering the synthesis and reactivities of frustrated radical pairs, with extensive highlights of the results from Electron Paramagnetic Resonance (EPR) spectroscopy to explain the nature and stability of the different radical species observed.

1. Introduction

The combination of a Lewis acid (LA) and a Lewis base (LB) bearing sterically encumbered groups leads to the formation of frustrated Lewis adducts in which the unquenched reactivities of Lewis acidic and basic sites are capable of reversibly activating H₂.[1] The seminal work from Stephan and co-workers[2] in 2006 demonstrated that a metal-free compound Mes₂P(C₆F₅)Br(C₆F₅)₂ was active in reversible H₂ binding. The donor–acceptor ability of archetypal frustrated Lewis pairs (FLPs) makes them competitive with transition metal catalysts towards H₂ heterolysis. Since its inception in 2006, a range of FLPs are now known in the literature,[3] comprising a variety of different Lewis acidic and basic components, including transition metal[4] or chiral[5] components,[6] that may be both intramolecular or intermolecular. Vast efforts have already been made to demonstrate the further applications of FLPs towards the activation of other small molecules including olefins, alkynes, CO₂, SO₂, N₂O, and NO.[5] Extensive studies later disclosed that FLPs can be used as alternatives to transition metal systems and have successfully been employed for a plethora of organic transformations.[6] Until recently, it was believed that the mode of small molecule activation was a heterolytic process.[7] However, more recently it has been observed that certain combinations of Lewis acid and Lewis base enable competitive donation of a single electron from the donor Lewis base to the empty p-orbital of the acceptor Lewis acid to afford a frustrated radical pair (FRP).[8-9] This phenomenon was in sharp contrast with the conventional FLP mechanism, where the donor Lewis base donates two electrons to the H–X σ*-orbital, followed by heterolytic cleavage of the H–X α-bond and subsequent donation of two electrons to the empty p-orbital of the acceptor Lewis acid (Scheme 1). Conversely, FRPs are proposed to cleave the H–X bond in a homolytic fashion. This minireview aims to highlight this new direction of single-electron reactivity in FLP chemistry with recent examples of different LB/LA combinations including phosphorus–alane (P/Al), phosphorus–borane (P/B), nitrogen–borane (N/B) and carbon–borane (C/B) FRPs. In particular, we will focus on results from Electron Paramagnetic Reso-
B(C6F5)3 (−1.17 V vs. CpFex2+/3- in THF),[10] and the oxidation potential of tBu3P (0.90 V vs. CpFex2+/3-) in MeCN)[11] (Table 2), the concentration of the radical ion Lewis pair is expected to be insignificant in comparison to the Lewis pair responsible for heterolytic dihydrogen cleavage. Shortly after this report, Stephan and co-workers[12] noticed that FLPs bearing the more Lewis acidic alane [Al(C6F5)3] and tBu3P react readily with N2O (1 atm) to afford tBu3P[N2O]Al(C6F5)3 (yield 91%). This complex further reacts with an additional equivalent of Al(C6F5)3 and releases N2 to generate a proposed transient FRP [tBu3P=O](Al(C6F5)3)2 (Scheme 2, top). C–H bond activation of one of the tert-butyl groups affords the salt [tBu3PMe(C2H5)CH3][(μ-O)(Al(C6F5)3)2] (yield 62%) as the product (Scheme 2, bottom). Alternatively, if Mes3P is allowed to react with [Al(C6F5)3]tol in toluene, C–H bond activation of the solvent is observed affording [Mes3P]+·[(μ-O)(Al(C6F5)3)2]−. While EPR studies on the reactive intermediate [R,P]+[(μ-O)(Al(C6F5)3)2]− were not undertaken, the solution-phase X-band EPR spectrum of the dissolved crystals of the product [Mes3P]+·[(μ-O)(Al(C6F5)3)2]− in bromobenzene revealed a doublet (giso = 2.0056, aD(P) = 239 G (670 MHz)) for the suggested generation of the phosphonium radical cation, Mes3P+= (I) (Figure 1 and Table 1). Alternatively when Nap3P (Nap = naphthyl) was employed in the reaction, C–H activation of the solvent (toluene or bromobenzene) led to [(Nap)3P]·[Al(C6F5)3] (R = CH2Ph, C6H4Br) (Scheme 2, bottom). A few years later, Stephan et al.[13] reported distinctly different reaction pathways when FLPs, tBu3P/E(C6F5)3, and Mes3P/E(C6F5)3 (E = B, Al), were employed in the reaction with p-P2O2Cl2 and Ph2SnH.

Stephan et al.[13] reported that an equimolar mixture of Mes3P/B(C6F5)3 afforded the radical ion pair [Mes3P]+·[B(C6F5)3]+ but in an insignificantly low concentration because

\[ \text{Bu}_3\text{P} + 2 \text{Al}(\text{C}_6\text{F}_{13})_3 \rightarrow \text{N}_2 \text{O} \]
Table 1: Spin Hamiltonian parameters for radical species generated during FLP reactions.\[^{[a]}\]

| Radical                             | \(g_{zz} \) | \(a_{ee} \) [MHz]$^{[b]}$ | Reference |
|-------------------------------------|-------------|-----------------------------|-----------|
| Phosphorus                          |             |                             |           |
| Mes$_3$P$^+$                        | 2.012; \(g_z = 2.010; g_{xx} = 2.013\) | 678; \(A_z = 1135; A_x = 450\) | [18, 37]  |
| tBu$_3$P$^+$                        | 2.0047; \(g_z = 2.0012; g_{xx} = 2.0065\) | 842; \(A_z (^{13}P) = 1365; A_x (^{13}P) = 580\) | [14]     |
| (Mes$_3$P)$_2$$^+$                  | 2.014; \(g_z = 2.009; g_{xx} = 2.017\) | 470; \(A_z = 761; A_x = 125\) | [38, 39]  |
| (Et$_3$P)$_2$$^+$                   | 2.008; \(g_z = 2.00; g_{xx} = 2.012\) | 1277; \(A_z = 1511; A_x = 1160\) | [27]      |
| (Bu$_3$P)$_2$$^+$                   | 2.008; \(g_z = 2.00; g_{xx} = 2.012\) | 1298; \(A_z = 1540; A_x = 1177\) | [27]      |
| Dipp$_3$P$^+$                       | 2.008       | 672                         | [37]      |
| Tipp$^+$                            | \(g_z = 2.002; g_{xx} = 2.009\) | \(A_z = 1168; A_x = 366\) | [37]      |
| Xy$_3$P$^+$                         | 2.0052      | 685                         | [37]      |
| Nitrogen                            |             |                             |           |
| \((p\text{-bromo-N},N\text{-dimethylaniline})^+\) (8) | 2.0029 | $^{14}$N: 92.25; $^{1}$H$_{\text{aryl}}$: 60.72; $^{1}$H$_z$: 32.55; $^{1}$H$_x$: 16.12 | [27]    |
| \((4\text{-bromo-N-methyl-N-((trimethylsilyl)methyl)aniline})^+\) (8-TMS) | 2.0033 | $^{14}$N: 23.1; $^{1}$H$_{\text{aryl}}$: 3.73; $^{1}$H$_z$: 9.68; $^{1}$H$_x$: 27.8; $^{2}$H$_{\text{aryl}}$: 20.7; $^{23}$Si: 8.78 | [21]     |
| \((C(CH$_3$)$_2$C$_6$H$_3$)$_2$N$^+$ (7) | 2.002      | $^{14}$N: 26.34; $^{1}$H$_{\text{aryl}}$: 8.52; $^{1}$H$_z$: 1.99 | [21]      |
| Boron                               |             |                             |           |
| \(B(C_6F_5)$_3^+$                   | 2.0114      | B: 31; F$_{zz}$: 12.94; F$_{xx}$: 3.66; F$_{yy}$: 14.9 | [20]      |
| \(K[Me,C(CONMes)$_2$CCF$_3$BF(C_6F$_5$)$_2$C]^- (9a) | 2.022      | B: 1.41; N$_z$: 4.25; F$_{xx}$: 5.66; F$_{yy}$: 11.88 | [22]      |
| \(K[Me,C(CONMes)$_2$CCF$_3$BFH(C_6F$_5$)$_2$C]^- (9b) | 2.003      | B: 0.82; N$_z$: 4.53; F$_{xx}$: 5.34; F$_{yy}$: 11.02 | [22]      |
| \(K[Me,C(CONMes)$_2$CCF$_3$BF(OTT)(C_6F$_5$)$_2$C]^- (9c) | 2.003      | B: 1.01; N$_z$: 4.04; F$_{xx}$: 12.41; F$_{yy}$: 0.68; F$_{zz}$: 0.43 | [22]      |
| \(Me,C(CONMes)$_2$CCF$_3$BF(C_6F$_5$)$_2$^- (10) | 2.004      | B: 1.46; N$_z$: 2.61; F$_{xx}$: 14.16; F$_{yy}$: 2.94; F$_{xx}$: 4.48; F$_{yy}$: 0.09; F$_{zz}$: 1.98 | [22]      |
| Aluminium                           |             |                             |           |
| \([tBu$_3$Me$_3$Al]$^+$ (2)     | 2.005       | Al: 173.99                  | [16]      |
| Gallium                             |             |                             |           |
| \([tBu$_3$Me$_3$Ga]$^+$ (3)      | 2.015       | $^{69}$Ga: 346.89; $^{70}$Ga: 442.78 | [16]      |
| Germanium                           |             |                             |           |
| [BCHGe]$^+$ (11)                   | 1.9881      | $^{177,179}$Hf: 236.5       | [23]      |
| Carbon                              |             |                             |           |
| Ph$_3$C (12)                        | 1.999       | H$_z$: 7.29; H$_x$: 3.08; H$_y$: 7.83 | [23]      |
| [Me$_3$C(CONMes)$_2$CCF$_3$CPh$_3$]$^+$ (13) | 1.993 | N$_z$: 0.56; H$_x$: 7.31; H$_y$: 7.56; H$_z$: 7.48; F$_{xx}$: 4.06; F$_{yy}$: 6.29 | [22]      |
| Di-phenyl-methlene                  | 2.0030      | H$_z$: 23.43; H$_y$: 8.55; H$_x$: 3.42 | [40, 41]  |
| Fluorenyl (4)                       | 2.002       | H$_z$: 38.96; H$_y$: 11.15; H$_x$: 2.55; | [42]      |
|                                       |             | H$_z$: 10.54; H$_y$: 1.79; |           |
| Styril                              | 2.0023      | H$_z$: 116; H$_y$: 17; H$_x$: 16.8 | [43]      |
| phenylacetylene                     | 2.0021      | H$_z$: 7.71; H$_y$: 2.38; | [44]      |
| Aminoxyl                            |             |                             |           |
| P/B-FLP-NOC$^+$ (16)                | 2.0089      | $^{14}$N: 18.5; $^{13}$P: 48.5; $^{11}$B: 9.1 | [30]      |

[a] Subscript numbers are formatted as number of equivalent nuclei, followed by nucleus position, for example, F$_{xx}$ reads 6 equivalent nuclei in the ortho position. [b] For conversion to field units, \(a/\text{MHz} = 10^9 \times (\mu_b g \mu_n) \times a/\text{MHz}\), where \(g = g\)-factor, \(h =\) Planck constant, \(\mu_b =\) Bohr magneton.

of its short lifetime, determined as 237 ps via transient absorption spectroscopy (TAS) measurements by Slootweg et al.\[^{[14]}\] Whilst Stephan et al.\[^{[15]}\] postulated a 1 e$^-$ transfer process was operative upon reaction of Mes$_3$P/B(C$_6$F$_5$)$_3$ with Ph$_3$SnH to afford the corresponding phosphonium borate (EDA) complex at 534 nm and tBu$_3$P/B(C$_6$F$_5$)$_3$ (EDA complex at 400 nm) with H$_2$ and Ph$_3$SnH remained constant in the dark and during irradiation, indicating that a 2 e$^-$ transfer process dominates in these systems.

However, upon a dark reaction of Mes$_3$P/B(C$_6$F$_5$)$_3$ with tetrachloro-1,4-benzoquinone (TCQ), Slootweg et al. detected several EPR signals, indicating radical formation despite unfavourable electron donor–acceptor characteristics that should prevent thermodynamic SET. This result was explained via weak coordination of B(C$_6$F$_5$)$_3$ to a carbonyl moiety of the quinone acceptor to form a TCQ–B(C$_6$F$_5$)$_3$ adduct with an increased electron affinity, therefore enabling facile SET from the Mes$_3$P HOMO. This generates the
resulting PMes₃⁺/[TCO–B(C₆F₅)₃]⁻ radicals observed via EPR (in addition to an unassigned radical; Scheme 3, bottom).

Evidence for SET between Mes₃P and Al(C₆F₅)₃ was provided in the form of EPR measurements, which revealed the presence of a doublet resonance with 𝑎_ₑ₀^{(13)P} = 238 G (669 MHz) centered on 𝑔_{iso} = 2.0089, assigned to the known radical cation Mes₃P⁺. The corresponding [Al(C₆F₅)₃]⁻ was not detected in the EPR measurements because of its short lifetime. It is noted that introduction of the bulkier R = SiMe₃Bu₂ group has previously facilitated isolation of stable radical anions of Al₂′⁻ and R₂Ga⁻, enabling characterization by EPR spectroscopy (see Table 1). The large steric bulk of the R = SiMe₃Bu₂ group enforces a planar π-type radical anion structure, with only small hyperfine couplings arising from the unpaired electron localized in the 3pπ orbital of the central Group 13 atom.

The equimolar mixture of the Mes₃P and B(C₆F₅)₃ FLP was also found to form radical salts [Mes₃P⁺][RCOOB(C₆F₅)₃]⁻ (R = Ph, p-BrC₆H₄, p-CH₂C₆H₄) when reacted with benzoyl peroxide and derivatives (Scheme 4). Again the phosphonium radical cation (1) could be observed by EPR spectroscopy. These radical salts further react with Ph₃SnH as above to produce the salt [Mes₃PH][RCOOB(C₆F₅)₃] and (Ph₃Sn)₂. Recently, we have demonstrated the same FLP system can be utilized as a powerful metal-free tool for C–H bond formation which we propose takes place via a single-electron transfer reaction in which B(C₆F₅)₃ first coordinates to the substrate to initiate the single-electron transfer. An equimolar mixture of B(C₆F₅)₃ and Mes₃P in the presence of a fluoro-substituted benzhydryl ester derivative gave rise to the well characterized isotropic EPR signal of Mes₃P⁺ (1), resulting from a SET process. In addition, a much weaker and poorly resolved signal was observed centered at 𝑔_{iso} = 2.0066, whose intensity could be increased upon heating the reaction solution to 70°C in situ in the EPR cavity. When the 9H-fluorenyl ester was employed in the reaction, a weak EPR signal centered on 𝑔_{iso} = 2.0045 with a complex multiplet ¹H hyperfine pattern was observed.

Table 2: Oxidation potentials, ionisation potentials and electron affinities for Lewis acids and Lewis bases

| Substrates   | Oxidation Potential [eV] | Conditions                               | Reference |
|--------------|--------------------------|------------------------------------------|-----------|
| Mes₃P        | 5.25                     | chlorobenzene; SCRF—o1B97X-D/6-311 + G(d,p)| [15]      |
| tBu₃P        | 5.55                     | chlorobenzene; SCRF—o1B97X-D/6-311 + G(d,p)| [15]      |

| Substrates   | Electron Affinities [eV] | Conditions                               | Reference |
|--------------|--------------------------|------------------------------------------|-----------|
| B(C₆F₅)₃    | 3.31                     | chlorobenzene; SCRF—o1B97X-D/6-311 + G(d,p)| [15]      |
| pC₆H₄Cl₅    | 4.45                     | chlorobenzene; SCRF—o1B97X-D/6-311 + G(d,p)| [15]      |

[a] SCE: 𝐸 = +0.241 V; [b] Ag/Ag⁺; 𝐸 = +0.197 V; [c] E1/2 (FeCp₃⁺⁻ vs. SCE)_{MeCN} = +0.40 V; [d] E1/2 (FeCp₃⁺⁻ vs. SCE)_{DCM} = +0.46 V; [e] E1/2 (FeCp₃⁺⁻ vs. SCE)_{MeCN} = +0.56 V; As noted by Jaekle et al., there is always an element of uncertainty when comparing electrode potential data recorded under different conditions (i.e., solvent, electrolyte, electrodes), hence original data are included herein.
Through simulation and comparison to literature reports, this was tentatively assigned to the fluorenyl radical $4^{[2]}$, formed upon FLP-mediated cleavage of the C(sp$^3$)/C0 bond (see Table 1). In the absence of olefins, the diaryl radicals undergo a homocoupling reaction to yield tetraarylethane derivatives. Interestingly, when other phosphines were used (e.g. tBu$_3$P, Ph$_3$P) then no homo-coupling was observed, and phosphonium borate salts resulted (Scheme 5, top). The different reactivities of these phosphines can be explained as a result of their smaller size and higher ionization energies, which leads to formation of the corresponding phosphonium borate salts, which are comparatively more stable than the mesityl phosphine analogue. In the presence of olefins an sp$^2$–sp$^3$ C–C hetero-coupling reaction was observed to generate α,β-substituted olefins (33 examples, yields up to 84%) (Scheme 5, bottom).

Whilst SET has clearly been evidenced in a series of Mes$_3$P/B(C$_6$F$_5$)$_3$ FLP reactions as demonstrated above, the driving force of this process is based on thermodynamic parameters such as ionization potentials, electron affinities and steric bulk of the participating LA/LB. Recent studies from Slootweg et al. $^{[14,15]}$ explored the relative ionization potentials and electron affinities of the Lewis acid and base to explain formation of FRPs. The authors concluded that the large energy gap to create radicals in the archetypal Mes$_3$P/B(C$_6$F$_5$)$_3$ system renders thermally activated SET unlikely.

Rather, the authors propose that a photoexcitation process akin to those observed in donor–acceptor complexes may be responsible for radical ion generation. The low-temperature EPR spectrum of violet Mes$_3$P/B(C$_6$F$_5$)$_3$ or tBu$_3$P/B(C$_6$F$_5$)$_3$ toluene solutions prepared in the dark showed no radical formation by EPR—hence, bringing into question the previous correlations made between purple-colored solutions observed when using the Lewis base Mes$_3$P and the presence of R$_3$P$^+$. Subsequent irradiation of these solutions (390–500 nm) led to the observation of two intense EPR signals in both cases. The first broad featureless signal was assigned to the boron radical anion, [B(C$_6$F$_5$)$_3$] (5). Whilst no hyperfine coupling was observed for 5 under these experimental conditions, a well-resolved EPR spectrum for this radical anion has previously been fully reported by Norton et al. $^{[19]}$ characterized by $g_{iso} = 2.0114$, $a_{iso}(10,11B) = 31$ MHz, $a_{iso}(19F_{60}) = 12.94$ MHz and $a_{iso}(19F_{3p}) = 14.9$ MHz (Table 1, Figure 2). The second axially symmetric signal was assigned to Mes$_3$P$^+$ (1) or tBu$_3$P$^+$ (6), characterized by $g_1 = 2.0015$, $g_\perp = 2.0055$, $A_{K}(31P) = 1170$ MHz, $A_{\perp}(31P) = 550$ MHz, and $g_1 = 2.0012$, $g_\perp = 2.0065$, $A_{K}(31P) = 1365$ MHz, $A_{\perp}(31P) = 580$ MHz, respectively. The signal intensity decreased by 25% 6 mins after cessation of the irradiation (at 30 K), indicating separation of the radical cations and anions in frozen solvent.

It is noteworthy that single-electron transfer from nitrogen Lewis bases to the Lewis acidic borane B(C$_6$F$_5$)$_3$ has also been investigated. Wang et al. $^{[20]}$ reported the one-electron oxidation of a methylene-bridged triphenylamine by B(C$_6$F$_5$)$_3$ (Scheme 6). The authors observed a blue solution ($\lambda_{max} = 600$ nm) that yielded an EPR spectrum (characterized by $a_{iso}(14N) = 9.4$ G (26.3 MHz); $a_{iso}(1H_{3p}) = 3.04$ G (8.52 MHz); $a_{iso}(1H_{6m}) = 0.71$ G (1.99 MHz)), which was assigned to the formation of a stable triphenylamine radical cation (7), with spin delocalization across the whole structure (Table 1, Figure 2). An

large energy gap to create radicals in the archetypal Mes$_3$P/B(C$_6$F$_5$)$_3$ system renders thermally activated SET unlikely. Rather, the authors propose that a photoexcitation process akin to those observed in donor–acceptor complexes may be responsible for radical ion generation. The low-temperature EPR spectrum of violet Mes$_3$P/B(C$_6$F$_5$)$_3$ or tBu$_3$P/B(C$_6$F$_5$)$_3$ toluene solutions prepared in the dark showed no radical formation by EPR—hence, bringing into question the previous correlations made between purple-colored solutions observed when using the Lewis base Mes$_3$P and the presence of R$_3$P$^+$. Subsequent irradiation of these solutions (390–500 nm) led to the observation of two intense EPR signals in both cases. The first broad featureless signal was assigned to the boron radical anion, [B(C$_6$F$_5$)$_3$] (5).

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identical spectrum was observed upon reaction with Ag[Al-(OC(CF3)3)4] as an alternative to B(C6F5)3. It is noteworthy to mention that the authors did not observe the formation of the boron centered radical anion, which was attributed to the possible decomposition of reactive boron intermediates into various four-coordinate borates. This work provided the first example of single-electron oxidation of an organic compound using B(C6F5)3.

Very recently, Ooi and co-workers [21] explored the description of FLPs as EDA complexes in their investigation of single-electron transfer between the Lewis acidic borane B(C6F5)3 and N,N-dialkylaniline Lewis bases including their subsequent catalytic application towards a C–C bond forming reaction (Scheme 7).

N,N-Dialkylaniline derivatives were employed for the reaction with B(C6F5)3 in the presence or absence of photo-irradiation (405 nm LED light source). Alkyl amines react with B(C6F5)3 to generate reactive α-aminoalkyl and borane radical pairs, as thoroughly investigated via EPR (Scheme 7, top and center). An equimolar mixture of 4-bromo-N,N-methyl-N-((trimethylsilyl) methyl)aniline and B(C6F5)3 in CH2Cl2 at room temperature (Scheme 7, top) yielded an EPR spectrum characterized by $g_{\text{iso}} = 2.0033$, $a_{\text{iso}}(^{14}\text{N}) = 23.1$, $a_{\text{iso}}(^{1}H_{\text{methyl}}) = 9.68$, $a_{\text{iso}}(^{1}H_{\text{methylene}}) = 27.8$, $a_{\text{iso}}(^{29}\text{Si}) = 20.7$ and $a_{\text{iso}}(^{29}\text{Si}) = 8.78$ MHz, assigned to the radical cation of 4-bromo-N-methyl-N-((trimethylsilyl) methyl)aniline, 8-TMS$^+$ (Table 1, Figure 2). The stability of this radical cation was attributed to hyper-conjugation at the Si–C bond, as evidenced by the lack of any EPR signal corresponding to the neutral radical formed upon loss of TMS$^+$.

The formation of the para-bromo-N,N-dimethylaniline radical cation was not thermally accessible in the dark, but could be photoinduced via a SET process upon irradiation with a 405 nm LED light source. Photoinduced formation of 8 (Scheme 7, middle) was detected via EPR spectroscopy ($g_{\text{iso}} = 2.0029$, $a_{\text{iso}}(^{14}\text{N}) = 92.25$, $a_{\text{iso}}(^{1}H_{\text{methyl}}) = 60.72$, $a_{\text{iso}}(^{1}H_{\text{methyl}}) = 32.55$, $a_{\text{iso}}(^{1}H_{\text{methyl}}) = 16.12$ MHz) (Scheme 7, Table 1), the signal intensity of which was rapidly attenuated after cessation of the irradiation, indicating a back-electron transfer (BET) process. These findings suggest that the generation and subsequent experimental observation of radical ion pairs is an intricate balance between the energy barriers for SET/BET (which are related to the difference between Lewis acid/base redox potentials, Table 2), and the stability of the radical ion pair (which may be determined by other degradation pathways and which are very active for some of these highly unstable radicals).

The key intermediate of this unique SET process is an EDA complex, and the nucleophilic α-aminoalkyl radicals generated can be readily exploited to react with electron deficient olefins to make new C–C bonds. In extension of their studies on photo-generated FRPs, Slootweg et al. [14] reported that upon varying the Lewis base to incorporate N-based triphenylamine (Ph3N) and tri-p-tolylamine (pTol3N), amine radical cations could be observed via EPR spectroscopy under visible light (390–500 nm) conditions (but not in the dark) at room temperature. The isotropic EPR spectrum of 8-Tol3N with B(C6F5)3 displayed a broad featureless signal centered at $g_{\text{iso}} = 2.005$, whereas that of Ph3N displayed a 3-line multiplet signal (also at $g_{\text{iso}} = 2.005$),
presumably arising from localization of the electron spin density on the $^{14}$N ($I=1$) nucleus (no hyperfine couplings were reported). These key findings demonstrate that encounter FLP complexes can also be described as electron donor–acceptor complexes which may undergo photo-induced SET to produce radical pairs.

3. Group 13/14 Frustrated Lewis Pairs

The exciting preliminary outcomes from frustrated Lewis pair chemistry has drawn considerable interest in main group chemistry. Radical chemistry of FLPs containing boron Lewis acids and Group 14 Lewis bases such as carbenes or germlylene have also been studied. Stephan et al.,[22] demonstrated the reactivities of Lewis acidic boranes towards the nucleophilic carbene $N$,$N'$-dimesityldiamidocarbene (DAC) (Scheme 8). The reaction between DAC and $B(C_6F_5)_3$ in benzene afforded a crystalline solid $Me_C-C(\text{CONMes})_2CCF_BF(C_6F_5)_2$ in $80\%$ yield via nucleophilic attack of DAC to one of the $\text{para}$ positions of a $C_6F_5$ ring of $B(C_6F_5)_3$, followed by fluoride transfer to the boron center.

Further treatment of the above crystalline compounds with $Et_3SiH$ or TMSOTf afforded zwitterionic $Me_C-C(\text{CONMes})_2CC_6F_4BX(C_6F_5)_2$ ($X=H$ or OTf) as yellow powders in $80\%$ and $96\%$ yield, respectively. Reduction of these compounds where $X=F$, $H$, or OTf with $K_C_8$ afforded the corresponding radical anions $[Me_C-C(\text{CONMes})_2CC_6F_4BX(C_6F_5)_2]^- (\text{9a–c})$, which all gave rise to complex hyperfine structure in their corresponding isotropic EPR signals centered at $g_{\text{iso}}=2.022 (\text{9a})$ and $g_{\text{iso}}=2.003 (\text{9b,c})$ (see Table 1 for details). Alternatively, if the boron-bound fluoride ion from the zwitterionic $Me_C-C(\text{CONMes})_2CCF_BF(C_6F_5)_2$ is abstracted using $[Et_3Si][B(C_6F_5)_4]$, the formation of the $[Me_C-C(\text{CONMes})_2CCF_B(C_6F_5)_3][B(C_6F_5)_3]^- $ ion pair results in $88\%$ yield. The isotropic EPR spectrum of this complex following treatment with $CoCp_2$, centered at $g_{\text{iso}}=2.004$ (Figure 2, Table 1) was assigned to the neutral radical $10$ (Scheme 8, Figure 2). The authors noted that the isolable nature of these radicals contrasts with the transient nature of the thermally unstable $B(C_6F_5)_3^- $ (5) radical anion, which was attributed to stabilization of the radical character by distribution of the unpaired electron over the $C_6F_4$ linker group and DAC substituent. These results provided rare examples of isolable electrophilic boron centers and spontaneous formation of radicals with Lewis acid/base combinations, which may be further utilized in synthetic FRP chemistry.

The generation of FRPs as opposed to formation of the polar products $LA^-/LB^+$ relies on prevention of spin-pairing, which can either be facilitated through steric bulk, or valence isomerization of the products formed after the initial SET process. This was recently exemplified by Müller et al.,[23] in an investigation of SET in a Ge/B FLP, employing a hafnocene-based germlylene as the Lewis base in the reaction with $B(C_6F_5)_3$ to afford a B–Ge-bonded species (Scheme 9). The EPR spectrum of a toluene solution of $B(C_6F_5)_3$ and a bicyclohexane-germlylene, labelled “BCHGe”, revealed an intense singlet centered at $g_{\text{iso}}=1.9881$ surrounded by weak satellite features originating from coupling to spin-active hafnium nuclei ($I(^{177}\text{Hf})=7/2, 18.6\%$ abundance; $I(^{179}\text{Hf})=9/2, 13.6\%$ abundance) characterized by $a_{\text{iso}}(\text{Hf})=85 \text{ G} (236.5 \text{ MHz})$. This signal, which decayed to zero over $3.5$ h, was attributed to a Ge$^+$/Hf$^{11+}$-based radical cation, labelled “[BCHGe]$^+$”, $11$ (Scheme 9), formed upon oxidation of BCHGe in which the total spin density is mainly localized on the $d^2$ orbital of the hafnium atom, with minimal contribution of the lone pair on germanium.
Radical behaviour of both trityl cations and silylum cations, iso-electronic and isoelectronic to B(C₆F₅)₃, have also been investigated when used as the Lewis acid component of an FLP with carbenes, germylenes or phosphines acting as the Lewis base. In Section 2, the generation of carbon-based FLP with carbenes, germylenes or phosphines acting as the Lewis acid component of an FLP with diaryl esters, although it was already known that two-electron nucleophilic addition of Bu₃P to the para position of the trityl borate [Ph₃C][B(C₆F₅)₄] leads to the formation of the cyclohexa-2,5-diene-phosphenium [B-(C₆F₅)₄] salt (Scheme 10, left), subsequent evidence subsequent evidence showed that a single-electron pathway was also operational (Scheme 10, right). Reaction in benzene or chlorobenzene solution yielded the characteristic EPR spectra of the Ph₃C trityl radical (12), characterized by $g_{iso} = 1.999$, and a rich hyperfine structure of $a_{iso}(H_{2}PH) = 7.27$ MHz, $a_{iso}(H_{2}PH) = 3.08$ MHz and $a_{iso}(H_{2}PH) = 7.83$ MHz originating from the ring protons (Figure 2). The radical cation $^{+}$Bu₃P, however could not be observed by EPR spectroscopy due to its short lifetime.

Instead of phosphines as the Lewis base, carbenes have also been employed in combination with the same Lewis acid. Recently, single-electron transfer reactions generating C-based radicals in classical Lewis pairs have been observed and highlighted by Severin et al. In the reaction between the carbene 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene (IDipp) and [Ph₃C][B(C₆F₅)₄], a single-electron transfer from the carbene to the trityl borate salt afforded the persistent radical [Ph₃C]⁺ (12), as characterized by EPR spectroscopy. (Scheme 11, top). As a series of colour changes were observed during the reaction, it was further probed via UV/Vis spectroscopy.

At the beginning of the reaction, a gradual decrease of an absorption band at 438 nm was observed, assigned to the trityl cation, and simultaneously a band at 343 nm assigned to the trityl radical began to grow. A weak band at 591 nm observed during the reaction, it was further probed via UV/Vis spectroscopy.

Stephan et al.,[22] have also investigated the reactivities of the same trityl salt [Ph₃C][B(C₆F₅)₄] with the nuclophilic DAC carbene described earlier (Scheme 11, bottom). Nucleophilic attack of DAC at one of the para-positions of the trityl cation was observed, followed immediately with $H_2$ evolution to afford a cationic radical [Me₂C(CONMes),C₆H₄CPh₂C]⁺ (13) (Scheme 11, bottom). The EPR spectrum of this species gave a $g_{iso}$ value of 1.993, with simulation of the hyperfine coupling consistent with delocalization of the radical over the trityl moiety.

Moving down Group 14, reaction of the BCHGe species described in Section 3 with the trityl cation [Ph₃C][B(C₆F₅)₄] and separation of the biphasic mixture into products also yielded EPR active solutions (Scheme 12, top).[23] The EPR spectrum of the organic phase revealed the presence of the trityl radical Ph₃C· (12) characterized by a rich hyperfine structure originating from the ring protons, centered on $g_{iso} = 1.9980$ (see Table 1), whereas [BCHGe]+ (11) was detected in the polar phase. Similarly, when a silyl arenium borate [Et₃Si(C₆H₆)][B(C₆F₅)₄] or a silylum borate [(Me₅C₆)₃Si][B-(C₆F₅)₄] was treated with BCHGe, EPR signals for 11 were observed but no EPR active signals for silyl-centered radicals were detected.

Despite the lack of observation of silyl radicals in the hafnocene-based germylene derivative, Müller et al.,[24] were able to evidence the utility of single-electron transfer reactions for different combinations of silylum ion/phosphine Lewis pairs (Scheme 13). For example, when Tipp₃P (Tipp = 2,4,6-triisopropylphenyl) was treated with [(Me₅C₆)₃Si][B-(C₆F₅)₄] the radical salt [Tipp₃P][B(C₆F₅)₄] (14) resulted along with the silyl radical [(Me₅C₆)₃Si][B-(C₆F₅)₄] (Scheme 13, top). The EPR spectrum of the reaction mixture revealed a doublet signal centered on $g_{iso} = 2.0015$ with $a_{iso}(P) = 238$ G (667 MHz), characteristic of the P-based Tipp₃P⁺ radical cation (14). Again, direct EPR evidence for the triarylsilyl radicals was not obtained as a result of their very short lifetimes. Radical scavenging using TEMPO ((2,2,6,6-tetra-
methylpiperidin-1-yl)oxyl) free radical) and cyclohexadiene also proved inconclusive. Use of the less bulky phosphine Mes₃P with [(Me₅C₆)₃Si][B(C₆F₅)₄] yielded multiple signals in the EPR spectrum. The authors assigned one of these to Mes₃P⁺ (1) and upon close inspection of their results, we suggest that the unassigned features in their EPR spectra are due to a [P(Mes)₃]₂⁺⁺ dimer, formed upon rapid reaction of the monomer radical cation with a second molecule of phosphine to produce the dimer cation radical. The EPR spectrum of [(Mes)₂]₂⁺⁺ (15) has previously been reported (Scheme 13, top, and Figure 1), and it is noted that previous literature examples of phosphine dimer cation radicals of divalent (R₂P)⁺⁺ and trivalent (R₃P)⁺⁺ systems yield very similar EPR spectra, dominated by the phosphorus hyperfine.

SET was also observed by these authors with the use of trialkylsilyle ions, stabilized in o-C₆H₄Cl₂ (Scheme 13, bottom). Thus, reaction of o-C₆H₄Cl₂-stabilized silyl borates [R₂Si][B(C₆F₅)₄] (R₂Si = iPrMe₂Si, tBuMe₂Si, Et₃Si) with different phosphines R₃P (R₃P = Tipp, Mes, tBu, o-Tol) were tested and the SET reactions between the silylum ion/phosphine were studied (Scheme 13, bottom). The experimental results indicated that the radical mechanism is not restricted to sterically encumbered triarylsilylium ion-based FLPs but may also apply to solvent-stabilized trialkylsilyle ions. Use of Lewis acids with strong electron affinities is recommended to induce one-electron oxidation to facilitate novel radical reactions.

5. FLP-NO Radicals

Development of facile and mild synthetic strategies for the synthesis of various aminoxyl (nitroxyl) radicals are exciting as these types of persistent radical compounds have diverse applications in chemistry as well as biological sciences. The formation of sterically encumbered, persistent aminoxyl radicals has been investigated with an emphasis on elucidating their stability and reactivity. Intramolecular frustrated phosphino-borane Lewis pairs have been found to be reactive towards NO and to afford FLP-NO N-oxyl radicals. N,N-cycloaddition of C₂-bridged intramolecular P/B frustrated Lewis pairs with nitric oxide has been demonstrated by Erker et al. in 2011. The authors observed that an intramolecular ethylene-bridged FLP system Mes₂PCH₂CH₂B(C₆F₅)₂ can readily react in situ with 1 equiv nitric oxide (NO gas) to form the persistent heterocyclic N-oxyl radical P/B-FLP-NO (16) in 58% yield (Scheme 14, top).

Although nitric oxide is inert towards H-atom abstraction (HNO bond strength 47 kcal mol⁻¹), the cyclic P/B-FLP-NO radical species (16) was found to be active towards H-atom abstraction from stronger C-H bonds when reacted with for example, 1,4-cyclohexadiene or ethylbenzene, to afford the diamagnetic P/B-FLP-NOH and/or P/B-FLP-NOR species (Scheme 14, top). In both cases the P/B-FLP-NOH species formed along with P/B-FLP-NOR in a 1:1 ratio. The presence of a single electron in the P/B-FLP-NOH adduct was confirmed via EPR spectroscopy, revealing νiso(14N) = 2.0089, aiso(31P) = 18.5, aiso(11B) = 48.5 and aiso(15N) = 9.1 MHz. Similar reactivity is observed when an intramolecular cyclohexylene-bridged P/B FLP or an intramolecular norbornane-bridged P/B FLP are allowed to react with NO (Scheme 14, bottom). In both cases, formation of the persistent P/B-FLP-NO radical species was observed. As in the first example, the oxygen-centered aminoxyl radicals were found to be highly reactive.
and both undergo H-atom abstraction with 1,4-cyclohexadiene to give the diamagnetic FLP-NOH product. DFT and kinetic studies, along with reaction monitoring through multinuclear NMR (\(^1\)H, \(^{19}\)F, \(^{31}\)P), have been employed to highlight the reaction mechanism. Formation of reactive radical intermediates was also monitored using UV/Vis spectroscopy and detailed EPR studies have been performed to confirm the formation of those radicals.\(^{[33]}\) The stable TEMPO radical has also been observed to act as a Lewis base towards strongly Lewis acidic B(C\(_6\)F\(_5\))\(_3\). The TEMPO-B-(C\(_6\)F\(_5\))\(_3\) adduct was found to be in equilibrium with the unquenched form and can thus act as an FLP (Scheme 15).

Indeed, while the TEMPO\(^+\) radical is inert toward dihydrogen, the TEMPO/B(C\(_6\)F\(_5\))\(_3\) FLP system was found to be active towards dehydrogenation of 1,4-cyclohexadiene (Path A) as well as dihydrogen activation under mild reaction conditions (Path B).\(^{[34]}\)

High reactivities of FLPs towards NO were demonstrated to account for the formation of reactive aminoxyl radicals. On the other hand, Slootweg and co-workers\(^{[11]}\) explored the formation of the NO\(^+\) radical using the nitrosium salt [NO][BF\(_4\)] and \(\tau\)Bu3P. Single-electron transfer between \(\tau\)Bu3P and the nitrosium salt [NO][BF\(_4\)] in acetonitrile generated [HP\(_{\tau}\)Bu\(_3\)][BF\(_4\)] as the major product (Scheme 16).

The formation of this product was proposed to proceed through the formation of the radical intermediate [\(\tau\)Bu3P]**-[\([\text{BF}_4]^\text{-}\)] and NO\(^+\). The radical salt readily abstracts a proton from the solvent to form the phosphonium borate product, whereas EPR studies suggested that the NO\(^+\) generated reacts with \(\tau\)Bu3P to give \(\tau\)Bu3P-NO\(^+\).

6. Conclusion

Frustrated Lewis pair chemistry has gained considerable interest because of its unique chemical reactivities particularly in small molecule activation. Extensive investigation on their reactivity via single-electron transfer, and the resulting structural and bonding properties, have revealed a new class of reactivities coined frustrated radial pair (FRP) chemistry. The unique behavior of FLPs/FRPs has successfully been employed in catalysis and synthetic organic chemistry, even using catalytic conditions. Providing complementarity to transition metal catalysis, FLP/FRP chemistry has rapidly garnered considerable interest from the scientific community, for which there are ample opportunities for future development. In particular, whilst it is noted that the operation of SET has currently only been experimentally observed with a small number of LA/LB pairs, it is now understood that FRP generation may be accessed for any combination of LA/LB via either thermochemical or photochemical routes, hence the generation of radical ion pairs as reactive species must continue to be further investigated in order to fully exploit their utility in organic synthesis.

As reviewed herein, the application of EPR spectroscopy is fundamental to the characterization of FRPs, via detection of short-lived radical intermediates generated under a broad range of experimental conditions, as direct experimental

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**Scheme 14.** Synthesis and reactivity of intramolecular FLP-NO radicals.

**Scheme 15.** Formation of persistent nitroxide radicals under frustrated Lewis pair conditions.

**Scheme 16.** Single-electron oxidation of \(\tau\)Bu3P by a nitrosium borate salt.
evidence of single-electron transfer events. The relative redox potentials of the LA/LB, the propensity for formation of electron-donor complexes and back donation of electrons, and the requirement for photochemical activation are all topics that must be further explored, experimentally and with supporting computational calculations. Whilst outside the immediate focus of this contribution, the reader is encouraged to refer to the excellent reviews detailing the thermodynamic and kinetic factors governing photoelectron transfer catalysis in transition metal (in)organic chemistry,[35] and redox processes in main group systems for further discussion.[36] Overall, this minireview demonstrates the synthesis of several frustrated radical pairs, which we believe opens the potential for new modes of reactivity.

Acknowledgements

We are grateful to the EPSRC for funding and the awarding for new modes of reactivity.

Conflict of interest

The authors declare no conflict of interest.

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Manuscript received: August 3, 2020
Accepted manuscript online: September 15, 2020
Version of record online: November 17, 2020