Radicals derived from Lewis acid/base pairs

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While conventional approaches to stabilizing main group radicals have involved the use of Lewis acids or bases, this tutorial review focuses on new avenues to main group radicals derived from combinations of donor and acceptor molecules. Reactions involving the use of both classical Lewis acid–base adducts and frustrated Lewis pair systems are discussed and the subsequent reactivity is considered.

Key learning points
1. The development of Lewis pair chemistry has contributed to advancements in generation of persistent or transient radicals.
2. Frustrated radical pairs have been shown to cleave chemical bonds in a homolytic fashion.
3. Single electron delivery to Lewis pairs leads to transient radical anions that split a variety of chemical bonds.
4. A variety of stable radicals have been achieved via reactions involving frustrated Lewis pairs or classical Lewis adducts.

Introduction

In 1923, Gilbert N. Lewis classified electron-pair donors and electron-pair acceptors as Lewis bases (LBs) and Lewis acids (LAs) respectively. Since then, classical Lewis acid–base adducts (CLAs) derived from the two electron donation from a Lewis base (LB) to a Lewis acid (LA) were thought to be thermodynamically stable and generally unreactive. This paradigm changed in 2006 with the discovery that a reversible activation of H2 could be mediated by $p$-[Mes2P]C6F4[B(C6F5)2] (Mes = mesityl). In this case, the Lewis basic phosphorus and acidic boron centres are sterically encumbered and this precludes the dative bond formation permitting the reaction with H2. Subsequently this observation was generalized to combinations of LAs and LBs with appropriate steric hindrance to deter dative bonding. Indeed, access to dissociative equilibria has proved sufficient to such frustrated Lewis pairs (FLPs) to react with a wide variety of substrates, as well as to effect metal-free hydrogenation catalysis.

Over the last decade the above development of FLP chemistry has been predicated on the notion that the chemistry results from two-electron processes in which the Lewis bases and acids act as two electron donors and acceptors respectively. However, a number of recent studies have either inferred or demonstrated the role of radical pathways in reactions involving Lewis acids and bases, both in FLP chemistry and beyond. At the same time, carbon-based radicals have an extended history dating from the landmark work of Gomberg more than one century ago. In contrast, main group radicals have received much less attention. The conventional approaches to stabilizing main group radicals has involved the use of LAs or LBs. For example, LA-complexation of a radical donor has been known for some time and the reactivity of such species has been exploited more recently. The complementary approach in which LBs are used to stabilize radicals has also been employed. For example, several recent studies have used singlet carbenes to stabilize main group radicals derived from combinations of donor and acceptor molecules. Reactions involving the use of both CLA and FLP systems are discussed and the subsequent reactivity of the derived radicals is considered.

Donor–acceptor induced homolysis

A unique approach to the generation of a main group radical involves base induced homolysis of an element–element bond. In 2016, Li, Zhu and co-workers described such a strategy involving the transient formation of a donor–acceptor adduct derived from the addition of two equivalents of 4-cyanopyridine to B2(pin)2. This prompted homolytic cleavage of the B–B bond affording the pyridine-ligated boryl radical [NCC5H4NBpin] (Scheme 1).
The donor 4-cyanopyridine behaves as a one-electron acceptor, reminiscent of homolytic cleavage reactions of a base stabilized diborane (4).\textsuperscript{16}

In extending this approach Jiao and Zhang showed that the combination of B\textsubscript{2}(pin)\textsubscript{2}, MeOK and 4-phenylpyridine afforded the novel pyridine-boryl species [PhC\textsubscript{5}H\textsubscript{4}NBpin(OMe)]\textsubscript{2} and [(PhC\textsubscript{5}H\textsubscript{4}N)\textsubscript{2}Bpin]K\textsubscript{3} (Scheme 2).\textsuperscript{17} In the absence of MeOK, no radical was observed, inferring that the pyridine-boryl adduct reacts with MeOK to prompt the homolytic B–B bond cleavage to produce 2 and 3. These species behave as super electron donors, and can be used in catalytic radical borylation reactions and reductive cleavage reactions.\textsuperscript{17,18}

Recently, Erker, Grimme, Warren et al. prepared a novel type of aminoxyl radical 4 via the reaction of an intramolecular FLP Mes\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} with NO (Scheme 3).\textsuperscript{19,20} Compound 4 was fully characterized including single crystal X-ray diffraction. The Mulliken spin densities of O and N atoms in 4 are 0.54 and 0.34 a.u., respectively. Shortly thereafter, Erker and co-workers reported analogous reactions leading to a variety of related aminoxyl radicals 5–10 (Scheme 3).\textsuperscript{20–22}

**Scheme 1** Synthesis of a pyridine-ligated neutral boryl radical 1 via a homolytic cleavage of the B–B bond in B\textsubscript{2}(pin)\textsubscript{2}.

**Scheme 2** Synthesis of 2 and 3.

**Scheme 3** Examples of aminoxyl radicals derived from reactions of FLPS with NO.
These aminoxyl radicals were shown to engage readily in H-atom abstraction reactions (Scheme 4). For example, compounds 4 and 8 rapidly reacted with 1,4-cyclohexadiene to afford the corresponding diamagnetic products 11 and 12, respectively, along with the formation of benzene. Compound 7 underwent abstraction of H-atoms with cyclohexene to give 13 and a pair of diastereoisomers of 14 and 15.

**Frustrated radical pairs**

**A triarylamine radical cation**

Although the one-electron oxidation of transition-metal complexes by B(C6F5)3 has been described,23,24 Wang et al. reported the first example of a one-electron oxidation of a triarylamine (C6H3CMe2)3N 16 by B(C6F5)3, in 2013 (Scheme 5),25 affording the deep blue triarylamine radical cation. Although the salt of the weakly coordinating anionate [Al(ORF)4](ORF=OC(F3)2) was isolated, the formation of the boron centred radical anion in the reaction with B(C6F5)3 was not confirmed as this species decomposes rapidly (vide infra).26

**Phosphine/Lewis acid frustrated radical pairs (FRPs)**

Stephan and co-workers have recently reported evidence for a mechanism for FLP reactivity that involves a radical pathway.27 Upon dissolving Mes3P and E(C6F5)3 (E = B or Al) in very dry toluene or chlorobenzene, the formation of a trace amount of a triarylamine radical cation (E = B, 18; Al, 19) was observed. Although the EPR spectrum of the purple solution generated from Mes3P/B(C6F5)3 displayed a weak signal, the solution generated from the corresponding Al reaction revealed a room-temperature doublet EPR resonance with a g value of 2.0089 and a hyperfine coupling constant of 238 G. This confirmed the presence of [Mes3P]+, however, the presumed radical anion [E(C6F5)3]− was not observed as it was rapidly quenched by reactions with solvent.25,26 Nonetheless, these data support the notion of single-electron transfer (SET) equilibria between the FLP and FRP of the form [Mes3P]+ [E(C6F5)3]. Generation of these FRPs in the presence of tetrachloro-1,4-benzoquinone (p-O2C6Cl4) prompts the formation of the radical salt [Mes3P]+[(Mes3P)OC6Cl4OE(C6F5)]3 (E = B, 18; Al, 19) (Scheme 6).

These species react further with p-O2C6Cl4 to give the 1,6-addition products [Mes3P]OC6Cl4OE(C6F5)]3 (E = B, 20; Al, 21) (Scheme 6). Alternatively, the FRPs homolytically split the Sn–H bond in Ph3SnH to give [Mes3P][HB(C6F5)3] 22 or [Mes3P][µ-H][Al(C6F5)3] 23, respectively (Scheme 6), along with (Ph3Sn)2. In sharp contrast, the combination of tBu3P/E(C6F5)3 shows no evidence of radical formation. Indeed, addition of Sn–H to these FLPs prompts heterolytic Sn–H cleavage affording [tBu3PSn][HB(C6F5)3] 24 and [tBu3PSn][µ-H][Al(C6F5)3] 25, respectively (Scheme 6). This contrasting behaviour demonstrates that FLPs can react either via consecutive one-electron steps or via a classic two-electron process.

In a recent and related study, the reactivity of the Mes3P/ B(C6F5)3 pair with benzyl peroxide derivatives was shown to proceed to efficiently split the O–O bond in a homolytic fashion, giving radical salts [Mes3P]+[PhCOOB(B(C6F5)3)] 26, [Mes3P]+[Br-C6H4COOB(C6F5)3] 27 and [Mes3P]+[MeC6H4COOB(C6F5)3] 28 (Scheme 7).28 Control experiments showed that the combination of B(C6F5)3 with the peroxides gave an adduct mixture. These reactions represent the first examples where FLPs react via a SET process affording the homolytic cleavage of a homodiatomic bond. It is also noteworthy that related phosphoniumyl radical cations [Tipp]2+ (Tipp = 2,4,6-trisopropylpheny) and [Tipp2Mes3P]2+ were prepared and structurally characterized by Wang et al. employing the weakly coordinating anions such as [Al(ORF)4]− (ORF=OC(F3)2) and [Al(ORMe)4]− (ORMe=OC(F3)Me)
In 2018, Müller, Klare et al. demonstrated that a SET as a viable reaction pathway for silylium ion/phosphine Lewis pairs (Scheme 8). For example, in solution, both FLPs consisting of $R_3 P \{[(Me_5 C_6)_3 Si] [B(C_6 F_5)_4] \}$ ($R = TipP$ or Mes) and CLAs derived from the combination of $R_3 P \{[iPr_3 Si(odcb)] [B(C_6 F_5)_4] \}$ ($odcb = 1,2$-dichlorobenzene) promote the establishment of a SET equilibrium mixture with the corresponding radical pairs $29–31$, indicating that complete frustration of the Lewis pairs is not necessarily a prerequisite for such SET processes.

Single electron transfer in a Lewis acid–base reaction

More recently, the group of Müller disclosed that a Lewis acid–base reaction between the nucleophilic hafnocene-based germylene $32$ and $B(C_6 F_5)_3$ leading to a Ge-B CLA $33$ is initiated by a SET process (Scheme 9). $30$ The radical salt $34$ generated by a SET from the germylene to $B(C_6 F_5)_3$ was identified by EPR and UV-vis spectroscopy. In addition, the nature of the radical cation was confirmed via independent synthesis of the $[B(C_6 F_5)_3]$ salt via the reaction of $32$ with $[Ph_C][B(C_6 F_5)_3]$. This work provided evidence for a SET in CLA formation reactions.

Electron transfer in FLP-reactions

C–H activation by FRPs

Prior to the recognition of the possibility of a radical pathway for FLP reactivity, it was noted that combination of $B\{C_6 F_5\}_3$ and PMe$_3$ generated a faintly purple solution. While early efforts to support a radical pathway were unsuccessful, in 2013, unequivocal evidence of highly reactive transient FRPs of the form $[R_3 P]^+ \cdot [O\{Al(C_6 F_5)_3\}]$ ($R = tBu$ or Nap, Nap = naphthyl) was obtained. $31$ Generated from the reactions of $R_3 P$ and $Al\{C_6 F_5\}_3$ in a molar ratio of 1:2 with $N_2 O$ (1 atm) (Scheme 10), these FRPs were shown to effect C–H bond activation. In the case of $R = tBu$, a C–H bond of the $tBu$ group was readily activated to form $[Bu_PMe(C(CH_3)_3)-Me][[μ-OH]Al\{C_6 F_5\}_3]_2$ $35$, whereas for $R = Nap$, the intermolecular activation of toluene or bromobenzene afforded $[Nap_PCH_Br][[μ-OH]Al\{C_6 F_5\}_3]_2$ $36$ or $[Nap_PCH_Br][[μ-OH]Al\{C_6 F_5\}_3]_2$ $37$, respectively (Scheme 10). These reactions proceeded via the corresponding FLP-$N_2 O$ adducts, as supported by isolation of the species $tBu_P[N_2 O]Al\{C_6 F_5\}_3$, using the equal molar portion of $tBu_P$ and $Al\{C_6 F_5\}_3$. The H atom in the anion $[μ-OH]Al\{C_6 F_5\}_3$ was derived from hydrogen atom abstraction from the toluene solvent by the transient radical anion $[[μ-O^*]Al\{C_6 F_5\}_3]$.

Borocyclic radicals via $H_2$ activation

It is well known that carbonyl–oxygen atoms form adducts with Lewis acids. $32$ Nonetheless, the equilibrium access to Lewis pairs provides a pathway to reaction with $H_2$ resulting in carbonyl hydrogenation. $33$ In a similar sense, Stephan et al. in 2016 reported that the reaction of phenanthrene-9,10-dione with $B\{C_6 F_5\}_3$ in toluene led to formation of a Lewis acid–base adduct $\{C_6 F_5\}_2 B(O_2 C_14 H_8)$ featuring a tetracoordinated boron centre. $34$ Remarkably, treating the above reaction mixture with $H_2$ (4 atm) at 110 $^\circ$C resulted in the formation of two products, the major one being $\{C_6 F_5\}_2 B(O_2 C_14 H_8)^- 38$ together with the minor product $\{C_6 F_5\}_B(O_2 C_14 H_8)$ $39$ (Scheme 11). The paramagnetic nature of $38$ was confirmed by EPR spectroscopy which revealed hyperfine coupling to the $^{11}$B atom ($a_B = 2.58$ G) and to hydrogen atoms with $a_H = 3.39, 0.00, 2.43$, and 1.01 G. These data were...
consistent with DFT calculations of the spin density showing the delocalization of the unpaired electron over the phenanthrene backbone.

A mechanistic study showed that initially the FLP-hydrogenation of the dione proceeds giving phenanthrene-9,10-diol. This diol reacts with the dione to afford 9,10-phenanthrenequinhydrone radical that readily coordinates B(C₆F₅)₃ to form a paramagnetic Lewis acid–base adduct, followed by protonation of one of the C₆F₅ rings affording 38 and HC₆F₅. Alternatively, if the reduced diol reacts with B(C₆F₅)₃, double protodeborylation affords the minor product 39.

The analogous reactions of B(C₆F₅)₃ with pyrene-4,5-dione, N-(2,6-dimethylphenyl)-phenanthreno-iminoquinone or N,N-di-p-tolylphenanthrene-9,10-dimine under the atmosphere of H₂ (4 atm) at 110 °C led to the formation of the related stable borocyclic radical 40–42, respectively (Scheme 12). Notably, the borocyclic radicals 38 and 40–42 are stable towards moisture and oxygen, presumably due to the delocalization of the unpaired electron over the aromatic backbone.

In an ensuing work, the reactivity of 38 with a variety of nucleophiles was probed (Scheme 13). The LUMO of 38 primarily involves π*-antibonding orbitals over the phenanthrene backbone, prompting a reaction with Ph₃P to give two regioisomeric zwitterions, 1-[Ph₃P]C₁₄H₇O₂B(C₆F₅)₂ 43 and 3-[Ph₃P]C₁₄H₇O₂B-(C₆F₅)₂ 44, coupled with the related boronic ester 39 and HC₆F₅. Similarly, the reaction of 38 with tBu₃P afforded the zwitterion 3-[tBu₃P]C₁₄H₇O₂B(C₆F₅)₂ 45 and the salt [tBu₃PH][C₁₄H₇O₂B(C₆F₅)₂] 46, while reaction with N-heterocyclic carbene IMes or quinuclidine gave 3-(IMes)C₁₄H₇O₂B(C₆F₅)₂ 47 and [IMesH][C₁₄H₇O₂B(C₆F₅)₂] 48 or 3-(C₇H₁₃N)C₁₄H₇O₂B-(C₆F₅)₂ 50, respectively (Scheme 13). In contrast, treatment of 38 with DMAP led to attack at the carbonyl carbon atoms, affording [9,10-(DMAP)₂C₁₄H₇O₂B(C₆F₅)₂][C₁₄H₇O₂B(C₆F₅)₂] 51 (Scheme 13).

A neutral aminyl radical from disulfide activation

The FLP system consisting of the nitrogen based Lewis acidic nitrenium cation 52 with tBu₃P has been shown to react (PhS)₂ to afford the persistent neutral aminyl radical, [(p-ClC₆H₄)₂N⁺(PhBu₃)]⁻ 53 and the salt [PhSPBu₃][BF₄] 54 (Scheme 14). This is reminiscent of the dione/borane reaction with H₂ described above, suggesting that the concerted FLP action on the disulfide prompts electron transfer. It is noteworthy that the radical 53 was also accessible via a more conventional reduction of 52 with cobaltocene or PhSNa.

Transient donor–acceptor radicals

In 2016, the Erker group described the selective oxidation of the intramolecular amine/borane FLP, [C₅H₆Me₄N(CH₃)₂]B(C₆F₅)₃,
with dioxygen (Scheme 15). In this case, the resulting tetrahydroisoxazolium borate salt \([\text{C}_5\text{H}_6\text{Me}_4\text{N}(\text{CH}_2)_3\text{O}]\) \([\text{C}_5\text{H}_6\text{Me}_4\text{N}(\text{CH}_2)_3\text{B(}\text{C}_6\text{F}_5\text{)}_2\text{OB(}\text{C}_6\text{F}_5\text{)}_3\text{]}\] 56 was formed via a series of transient radical intermediates. Initially an endergonic generation of alkyl radicals prompts the propagation step generating a borylperoxide intermediate, leading to the formation of 56 in an overall thermodynamically favourable process \((\Delta G^\text{f} = 59.5 \text{ kcal mol}^{-1})\) (Scheme 15).

A related work described by Erker, Studer et al. described that the reaction of the boryldiene \(\text{CH}_2\text{Q}\text{C}(\text{Me})\text{CH}_2\text{Q}\text{CHB(}\text{C}_6\text{F}_5\text{)}_2\text{]} 57 with two equivalents of TEMPO yielded species 58 featuring a zwitterionic four-membered ring, in which two TEMPO radicals added to the boryldiene starting material (Scheme 16). The authors proposed that the initial coordination of TEMPO to the Lewis acidic boron centre affords a transient radical that undergoes cyclization and then couples a second TEMPO to give the product 58. Trapping of TEMPO at the terminal position is presumably sterically driven. Similarly, the cyclopropyl-substituted alkenyl borane, \(\text{C}_3\text{H}_5\text{CH}_2\text{Q}\text{CHB(}\text{C}_6\text{F}_5\text{)}_2\text{]} 59 was shown to react with two equivalents of TEMPO affording the ring-opening product 60 (Scheme 16). This observation supported the generation of the analogous radical intermediates. Indeed the scope of analogous reaction with TEMPO radical was extended in 2017. In a recent work, the FLP derived from a nitrogen-centered LA, namely a cyclic (alkyl)(amino)nitrenium cation, \([\text{C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{tBu}]\) \([\text{BF}_4]\) 61 and \(\text{tBu}_3\text{P}\) was shown to react with dipropyl disulfide \((\text{PrS})_2\). One product is the salt \([\text{tBu}_3\text{PSPr}][\text{BF}_4]\). The other product derived from the heterolytic S–S cleavage, \([\text{C}_6\text{H}_4\text{HN}(\text{tBu})\text{N(SPr)CPh}_2\text{]}\) was not observed but instead, the reaction affords a mixture of \((\text{tBuS})_2\), \((\text{tBuSSPr})\), \(\text{Pr}_2\text{S}\), \([\text{C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{tBu}]\) 62 and \([\text{C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{Ph}]\) 63, consistent with a radical chain pathway (Scheme 17).

**Scheme 17** FLP reactivity of \(\text{tBu}_3\text{P}/61\) with \((\text{PrS})_2\) leading to a spontaneous radical chain degradation.

**Electron transfer to an acid/base adduct**

**Ferrocene/Lewis pair systems**

Another approach to reactive radicals is derived from the addition of a one-electron donor with a Lewis donor/acceptor combination. This concept was first demonstrated by Agapie and Henthorn who reported reactions of ferrocene/B(\text{C}_6\text{F}_5\text{)}_3 pairs with dioxygen which afforded \([\text{Cp}^*\text{Fe}]_2\text{[(C}_6\text{F}_5\text{)}_3\text{BOOB(}\text{C}_6\text{F}_5\text{)}_3\text{]}\) \((\text{Cp}^* = \text{Cp 64 or Cp}^* 65)\); the first examples of dianionic boron peroxide salts (Scheme 18). Although B(\text{C}_6\text{F}_5\text{)}_3 is inert to \(\text{O}_2\) over 24 h, the presence of B(\text{C}_6\text{F}_5\text{)}_3 appeared to facilitate the reduction of \(\text{O}_2\) by ferrocenes. A cyclic voltammetry (CV) study suggested the reaction proceeded via the transient B(\text{C}_6\text{F}_5\text{)}_2 superoxide intermediate although attempts to access this intermediate were unsuccessful.

Exploiting a related strategy, Stephan and co-workers exploited such single electron delivery from \(\text{Cp}^*\text{Fe}\) in the presence of a Lewis acid \([\text{E(}\text{C}_6\text{F}_5\text{)}_3, \text{E} = \text{B or Al}]\) for small
molecule activation. In this fashion, O–O, S–S, Se–Se, Te–Te, C–H, C–O and Sn–H bonds were cleaved in a homolytic fashion, affording a variety of ferrocenium salts featuring novel B- and Al-containing anions (Scheme 19). For example, exposure of a solution of Cp* 2 Fe/Al(C 6 F 5 ) 3 to dry 3 O 2 immediately resulted in the O–O bond cleavage, giving the salt [Cp* 2 Fe] 2 [(C 6 F 5 ) 3 -AlOAl(C 6 F 5 ) 2 ] 72 with a dianionic Al 2 O 2 core. This stands in contrast to the corresponding reaction of Cp* 2 Fe/B(C 6 F 5 ) 3 that yields 65 in which the O–O bond remains intact (Scheme 18).

The corresponding reactions of Cp* 2 Fe/E(C 6 F 5 ) 3 with elemental Te and S 8 afford a unique tricyclic Al 3 Te 2 anion and a dianion in which two boron centers are linked by seven sulfur atoms, respectively (Scheme 19).

Control reactions showed the slow generation of ferrocenium cation in the absence of substrate molecules, consistent with SET from Cp* 2 Fe to E(C 6 F 5 ) 3, suggesting that the generated [*E(C 6 F 5 ) 3 ] + reacts with substrate. Alternatively, SET to the Lewis acid-substrate adduct is also possible. It is noteworthy that Chen also proposed the generation of the fleeting [*Al(C 6 F 5 ) 3 ] + that was followed by decomposition during thermolysis of a C 6 D 5 Br solution of Al(C 6 F 5 ) 3 with Cp 2 Fe at 100 °C for 3 days, although the radical anion [*Al(C 6 F 5 ) 3 ] − was not observed.

In a recent work, this concept of SET was extended to systems based on the transition-metal-based LA; Zn(C 6 F 5 ) 2 (Scheme 20). In this case, the combination of Zn(C 6 F 5 ) 3 and [(PhC(S)S) 2 ] gave a weak CLA, while the cleavage of the S–S bond of [(PhC(S)S) 2 ] was immediately upon mixing the substrate with Zn(C 6 F 5 ) 2 and Cp* 2 Fe, leading to a salt [Cp* 2 Fe][PhCS 2 Zn(C 6 F 5 ) 3 ] 76. No SET reaction from Cp* 2 Fe to Zn(C 6 F 5 ) 3 was observed in the absence of [(PhC(S)S) 2 ], inferring that single electron delivery from Cp* 2 Fe to the CLA prompts the rapid cleavage of the S–S bond.

More recently, the group of Severin reacted Cp' 2 Fe/Al(C 6 F 5 ) 3 (Cp' = Cp* or Cp) with N 2 O (Scheme 21), affording salts [Cp' 2 Fe][µ-HO][Al(C 6 F 5 ) 2 ] 77; Cp, 79. At the same time, neutral species 78 and 80 involving the C–H activation of the metallocenes were isolated. These observations indicated the formation of the transient oxyl radical anion [*OAl(C 6 F 5 ) 3 ] − that spontaneously abstracts hydrogen atoms from the metallocenes. The ensuing metallocene-based radicals underwent radical/radical coupling reactions leading to 78 and 80. This is further evidenced by the reaction of Ph 3 C*/[Al(C 6 F 5 ) 3 ] with N 2 O, wherein [*OAl(C 6 F 5 ) 3 ] − was trapped by the excess Ph 3 C* to give the salt [Ph 3 C][Ph 3 COAl(C 6 F 5 ) 3 ] 81.

Zinc-containing radical anions

In 2018, related zinc-dione-containing radical anions were prepared via a single electron transfer to donor–acceptor system consisting of dione/Zn(C 6 F 5 ) 3 (Scheme 22). Specifically, the phenanthen-9,10-dione or pyrene-4,5-dione donor–acceptor adduct [(C 14 H 10 O 2 )Zn(C 6 F 5 ) 3 ] 82 or [(C 16 H 8 O 2 )Zn(C 6 F 5 ) 3 ] 83 was shown to feature low-lying LUMOs relative to those of the corresponding free diones. One-electron reduction of these...
adducts with Cp*₂Fe gave the persistent zinc-cyclic radical anions 84 and 85 with counterions of the ferrocenium cation. These salts proved labile undergoing reaction with DMAP to give [Zn(C₆F₅)₂(DMAP)₂] with the regeneration of Cp*Fe and the free corresponding dione (Scheme 22).

**Semiquinone radical anions**

In a recent and related work, Erker et al. reported that, in the presence of two molar equivalents of B(C₆F₅)₃, p-benzoquinone, 9,10-anthraquinone, acenaphthenequinone or 9,10-phenanthrenequinone reacted with a one-electron donor such as TEMPO, Gomberg dimer and Cp*₂Fe, leading to the formation of a series of isolable doubly O-borylated semiquinone radical anion salts 86–93 (Scheme 23). In the absence of B(C₆F₅)₃, the corresponding reaction of the studied quinones with TEMPO, Gomberg dimer or Cp*₂Fe did not react. The presence of B(C₆F₅)₃ appeared to facilitate the reduction of the quinones.

**Bis(borane)superoxide radicals**

In 2017, the group of Erker demonstrated that electron transfer can be effected from TEMPO to boranes in the presence of O₂ (Scheme 24), affording the salts of the bis(borane)superoxide radical anion [C₅H₆Me₄N≡O][O₂(B(C₆F₅)₃)₂] 94 and [C₅H₆Me₄N≡O][O₂(B(p-C₆F₄H)₃)₂] 95 respectively. These species are analogous to the [Cp*₂Fe]⁺ salts reported by Agapie and Henthorn (Scheme 18) (vide supra). Interestingly, the Gomberg dimer of the trityl radical reacted in a similar fashion to give the salt [Ph₃C][O₂(B(p-C₆F₄H)₃)₂] 96 (Scheme 24). These results showcase the advantage of application of TEMPO or the trityl radical for the isolation of these bis(borane)superoxide radical salts.

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**Scheme 20** Reaction of Cp*₂Fe/Zn(C₆F₅)₂ with [PhC(S)S]₂.

**Scheme 21** Reaction of Cp*₂Fe/Al(C₆F₅)₃ or Ph₃C⁺/Al(C₆F₅)₃ with N₂O.

**Scheme 22** Synthesis and reactivity of zinc-containing radicals.

**Scheme 23** Synthesis of semiquinone radical anions.

**Scheme 24** Reaction of Cp*₂Fe/Al(C₆F₅)₃ or Ph₃C⁺/Al(C₆F₅)₃ with N₂O.
anions. Interestingly, THF or DMSO reacted with 94 prompted the regeneration of TEMPO and O₂ and formation of (THF)B(C₆F₅)₃ or (DMSO)B(C₆F₅)₃, respectively. This observation indicates that displacement of B(C₆F₅)₃ moiety from the anion alters the redox potential of the transient superoxide radical prompting electron transfer to the oxoammonium cation to generate TEMPO and liberating O₂.

**Conclusion and perspectives**

The generation and characterization of radical species in main group chemistry has become more prevalent in the literature recently. Indeed, this tutorial has described a number of strategies involving the combinations of Lewis acids and bases that result in radical reactants or products. These include the induction of element–element bond homolysis, electron transfer between donor and acceptor molecules, the use of FLPs to stabilize or generate reactive radicals, and electron transfer to donor–acceptor adducts. The systems presented herein, also offering new routes and strategies for the exploitation of main group chemistry in reactivity and synthesis.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**