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 LAs 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 \([\text{NCC}_5\text{H}_4\text{NBpin}^-]\) (Scheme 1).

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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}K\textsubscript{2} and [(PhC\textsubscript{5}H\textsubscript{4}N)\textsubscript{2}Bpin]\textsubscript{2}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}P\textsubscript{CH\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}

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Douglas W. Stephan began independent career at the University of Windsor (1982). In 2008 he moved to the University of Toronto as a Professor and Canada Research Chair. A highly successful researcher in inorganic chemistry/catalysis, he is best known for articulating the concept of “frustrated Lewis pairs”. Stephan has received a number of awards. He was named a Fellow of the Royal Society of Canada (2005), a Fellow of the Royal Society (2013, London), a Corresponding Member of North-Rhein-Westfaelia Academy (2014, Germany), and an Einstein Visiting Professor at the Technical University of Berlin (2016–2019) and made the Thomson Reuters Highly Cited List (2014–2018).
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 described²³,²⁴ 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 coordinating alanate 17. Although the salt of the weakly coordinating anions such as [Mes₃POC₆Cl₄]⁺Œ(C₆F₅)₃,²⁶ these species react further with p-O₂C₆Cl₄ to give the 1,6-addition [Mes₃POC₆Cl₄]⁺Œ(C₆F₅)₃OE(C₆F₅)₃ (E = B, 18; Al, 19) (Scheme 6).

These species react further with p-O₂C₆Cl₄ to give the 1,6-addition products [Mes₃POC₆Cl₄OE(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 tetrachloro-1,4-benzoquinone ([p-O₂C₆Cl₄]) with the peroxides gave an adduct mixture. These species react further with benzyl peroxide derivatives was shown to proceed to efficiently split the O–O bond in a homolytic fashion, [Bu₃PSnPh₃][HB(C₆F₅)₃] [24 and [Bu₃PSnPh₃][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(C₆F₅)₃] 26, [Mes₃P⁺][p-BrC₆H₄COOB(C₆F₅)₃] 27 and [Mes₃P⁺][p-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 with peroxides affording the homolytic cleavage of a homodiatomic bond. It is also noteworthy that related phosphoniumyl radical cations [Tipp⁺]⁺ (Tipp = 2,4,6-trisopropylphenyl) and [Tipp₂MesP⁺]⁺ were prepared and structurally characterized by Wang et al.²⁹ employing the weakly coordinating anions such as [Al(OR₉)₃]⁻ (OR₉ = OC(CF₃)₃) and [Al(OR₉Me)₃]⁻ (OR₉Me = OC(CF₃)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 R₃P/[(Me₅C₆)₃Si][B(C₆F₅)₄] (R = Tipp or Mes) and CLAs derived from the combination of R₃P/[iPr₃Si(odcb)][B(C₆F₅)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 SET as a viable reaction pathway for silylium ion/phosphine Lewis pairs (Scheme 9). For example, in solution, both FLPs consisting of R₃P/[(Me₅C₆)₃Si][B(C₆F₅)₄] (R = Tipp or Mes) and CLAs derived from the combination of R₃P/[iPr₃Si(odcb)][B(C₆F₅)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.

**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(C₆F₅)₃ and PMes₃ 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 [R₃P]-[*O(Al(C₆F₅)₃)]⁺ (R = tBu or Nap, Nap = naphthyl) was obtained. Generated from the reactions of R₃P and Al(C₆F₅)₃ in a molar ratio of 1:2 with N₂O (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 [Bu₂PMe(C(CH₃)-Me)][[μ-OH](Al(C₆F₅)₃)]₃, whereas for R = Nap, the intermolecular activation of toluene or bromobenzene afforded [Nap₃PCH₂Br][μ-HO][Al(C₆F₅)₃]₃, respectively (Scheme 10). These reactions proceeded via the corresponding FLP·N₂O adducts, as supported by isolation of the species tBu₃P(N₂O)Al(C₆F₅)₃. The H atom in the anion [[μ-O](Al(C₆F₅)₃)]⁻ was derived from hydrogen atom abstraction from the toluene solvent by the transient radical anion [[μ-O]*][Al(C₆F₅)₃]⁻.

**Borocyclic radicals via H₂ activation**

It is well known that carbonyl–oxygen atoms form adducts with Lewis acids. Nonetheless, the equilibrium access to Lewis pairs provides a pathway to reaction with H₂ resulting in carbonyl hydrogenation. In a similar sense, Stephan et al. in 2016 reported that the reaction of phenanthrene-9,10-dione with B(C₆F₅)₃ in toluene led to formation of a Lewis acid–base adduct (C₆F₅)₃B(O₂C₄H₈) featuring a tetracoordinated boron centre. Remarkably, treating the above reaction mixture with H₂ (4 atm) at 110 °C resulted in the formation of two products, the major one being [(C₆F₅)₂B(O₂C₄H₈)]⁻ 38 together with the minor product (C₆F₅)B(O₂C₄H₈) (Scheme 11). The paramagnetic nature of 38 was confirmed by EPR spectroscopy which revealed hyperfine coupling to the ¹¹B atom (aₑ = 2.58 G) and to hydrogen atoms with a₁₁ = 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, 34 N-(2,6-dimethylphenyl)-phenanthrene-iminoquinone 35 or N,N-di-p-tolylphenanthrene-9,10-dimine 35 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. Nevertheless, the one-electron chemical reduction of 38 or 40 with cobaltocene generated the corresponding cobaltocenium borate salts. 34

In an ensuing work, the reactivity of 38 with a variety of nucleophiles was probed (Scheme 13). 36 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][C₁₄H₈O₂B(C₆F₅)₂] 46, while reaction with N-heterocyclic carbene IMes or quinuclidine gave 3-[IMes]C₁₄H₇O₂B(C₆F₅)₂ 47 and [IMesH][C₁₄H₈O₂B(C₆F₅)₂] 48 or 3-[C₇H₁₃N]C₁₄H₇O₂B(C₆F₅)₂ 45 and [H(NC₇H₁₃)₂][C₁₄H₈O₂B-(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)₂C₁₄H₈O₂B(C₆F₅)₂][C₁₄H₈O₂B(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)N₂-(PhBu₃)]⁺ 53 and the salt [Ph₅PBU₃][BF₄] 34 (Scheme 14). 37 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 $\text{[C}_5\text{H}_6\text{Me}_4\text{N(CH}_2\text{)}_3\text{O]}\text{[C}_5\text{H}_6\text{Me}_4\text{N(CH}_2\text{)}_3\text{-B(C}_6\text{F}_5\text{)}_2\text{OB(C}_6\text{F}_5\text{)}_3\text{]}$ 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 ($\Delta G^\circ = -59.5$ kcal mol$^{-1}$) (Scheme 15). A related work described by Erker, Studer et al. described that the reaction of the boryldiene $\text{CH}_2\text{Q}\text{C(Me)CHQ}\text{CHB(C}_6\text{F}_5\text{)}_2\text{57}$ 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, $\text{C}_3\text{H}_5\text{CHQ}\text{CHB(C}_6\text{F}_5\text{)}_2\text{59}$ 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, $\text{[C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{tBu]}\text{[BF}_4\text{]}\text{61}$, and $\text{tBu}_3\text{P}$ was shown to react with dipropyl disulfide $(\text{PrS})_2$. One product is the salt $\text{[tBu}_3\text{PSPr][BF}_4\text{]}$. The other product derived from the heterolytic S–S cleavage, $\text{[(C}_6\text{H}_4\text{)(N(tBu)]N(SPr)CPh}_2\text{]}$, was not observed but instead, the reaction affords a mixture of $\text{(tBuS)}_2$, $\text{(tBuSSPr)}$, $\text{Pr}_2\text{S}$, $\text{[C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{]}\text{62}$ and $\text{[C}_6\text{H}_4\text{CPh}_2\text{N}_2\text{Ph}]\text{63}$, consistent with a radical chain pathway (Scheme 17).

**Scheme 15** Oxidation of an intramolecular amine/borane FLP with dioxygen. Free energies are given in kcal mol$^{-1}$.

**Scheme 16** Synthesis of 58 and 60 via transient radicals.

**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 $\text{[Cp}_2\text{Fe]}\text{[(C}_6\text{F}_5\text{)}_3\text{BOOB(C}_6\text{F}_5\text{)}_3\text{]}$ (Cp$^* = \text{Cp 64 or Cp}^*\text{65}$); the first examples of dianionic boron peroxide salts (Scheme 18). Albeit $\text{B(C}_6\text{F}_5\text{)}_3$ is inert to $^3\text{O}_2$ over 24 h, the presence of $\text{B(C}_6\text{F}_5\text{)}_3$ appeared to facilitate the reduction of $^3\text{O}_2$ by ferrocenes. A cyclic voltammetry (CV) study suggested the reaction proceeded via the transient $\text{B}_2\text{O}_2$ superoxide intermediate although attempts to access this intermediate were unsuccessful.

Exploiting a related strategy, Stephan and co-workers exploited such single electron delivery from Cp$^*$Fe in the presence of a Lewis acid $\text{E(C}_6\text{F}_5\text{)}_3$, $\text{E = B or Al}$ 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*2Fe/Al(C6F5)3 to dry O2 immediately resulted in the O–O bond cleavage, giving the salt \([\text{Cp}^*\text{Fe}]_2\{[(\text{C6F5})_3\text{AlO(Al(C6F5)3)}]_2\}\) 72 with a dianionic Al2O2 core. This stands in contrast to the corresponding reaction of Cp*2Fe/B(C6F5)3 that yields 65 in which the O–O bond remains intact (Scheme 18).

The corresponding reactions of Cp*2Fe/E(C6F5)3 with elemental Te and S8 afford a unique tricyclic Al3Te2 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*2Fe to E(C6F5)3, suggesting that the generated \([*E(\text{C6F5)})_3]^-\) 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 \([*\text{Al(Al(C6F5)3)}]^-\) that was followed by decomposition during thermolysis of a C6D5Br solution of Al(C6F5)3 with Cp2Fe at 100 °C for 3 days, although the radical anion \([*\text{Al(Al(C6F5)3)}]^-\) was not observed.

In a recent work, this concept of SET was extended to systems based on the transition-metal-based LA; Zn(C6F5)2 (Scheme 20). Specifically, the combination of Zn(C6F5)2 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(C6F5)2 and Cp*2Fe, leading to a salt \([\text{Cp}^*\text{Fe}][\text{PhCS2Zn(C6F5)3}]\) 76. No SET reaction from Cp*2Fe to Zn(C6F5)2 was observed in the absence of [(PhC(S)S)2], inferring that single electron delivery from Cp*2Fe to the CLA prompts the rapid cleavage of the S–S bond.

More recently, the group of Severin reacted Cp’2Fe/Al[Cn(C6F5)3] (Cp’ = Cp* or Cp) with N2O (Scheme 21), affording salts \([\text{Cp}^*\text{Fe}][\mu-\text{HO}][\text{Al(Cn(C6F5)3)}]_2\] \([\text{Cp}^* = \text{Cp}, 77; \text{Cp}, 79]\). 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 \([*\text{OAl(Cn(C6F5)3)}]^-\) 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 Ph3C*/Al(Cn(C6F5)3) with N2O, wherein \([*\text{OAl(Cn(C6F5)3)}]^-\) was trapped by the excess Ph3C* to give the salt \([\text{Ph3C}][\text{Ph3COAl(Cn(C6F5)3)}]\) 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(C6F5)2 (Scheme 22). Specifically, the phenanthrene-9,10-dione or pyrene-4,5-dione donor–acceptor adduct \([[(\text{C14H9O2})\text{Zn(Cn(C6F5)3)}]_2] \) 82 or \([(\text{C14H8O2})\text{Zn(Cn(C6F5)3)}]_3 \) 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 \([\text{Zn(C}_6\text{F}_5)_2(\text{DMAP})_2]\) 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(C\(_6\)F\(_5\))\(_3\), \(p\)-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).\(^{47}\) In the absence of B(C\(_6\)F\(_5\))\(_3\), the corresponding reaction of the studied quinones with TEMPO, Gomberg dimer or Cp*₂Fe did not react. The presence of B(C\(_6\)F\(_5\))\(_3\) 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 \(O_2\) (Scheme 24),\(^{48}\) affording the salts of the bis(borane)superoxide radical anion \([\text{C}_5\text{H}_6\text{Me}_4\text{N}=\text{O}]^-\text{[B(C}_6\text{F}_5)_3]_2\) \(94\) and \([\text{C}_5\text{H}_6\text{Me}_4\text{N}=\text{O}]^-\text{[B(p-C}_6\text{F}_4\text{H}_3)_3]_2\) \(95\) respectively. These species are analogous to the \([\text{Cp}^*\text{Fe}]^-\) salts reported by Agapie and Henthorn (Scheme 18) (\textit{vide supra}).\(^{42}\) Interestingly, the Gomberg dimer of the trityl radical reacted in a similar fashion to give the salt \([\text{Ph}_3\text{C}]^-\text{[B(p-C}_6\text{F}_4\text{H}_3)_3]_2\) \(96\) (Scheme 24). These results showcase the advantage of application of TEMPO or the trityl radical for the isolation of these bis(borane)superoxide radical...
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 stabilize or generate reactive radicals, and electron transfer to donor–acceptor adducts. The systems presented herein, also offer 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