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Radicals derived from Lewis acid/base pairs

Liu Leo Liu and Douglas W. Stephan *

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.[1] 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 H_2 could be mediated by p-$(Mes_2P)C_6F_4(B(C_6F_5)_2)$ (Mes = mesityl).[2] 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 H_2. 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,[3–6] 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.[7] 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[8] and the reactivity of such species has been exploited more recently.[9,10] 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[11–14] In this tutorial review, we focus on new avenues to 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[15] described such a strategy involving the transient formation of a donor–acceptor adduct derived from the addition of two equivalents of 4-cyanopyridine to $B_2(pin)_2$. This prompted homolytic cleavage of the B–B bond affording the pyridine-ligated boryl radical $[NCC_5H_4NBpin]^\bullet$ **1** (Scheme 1).

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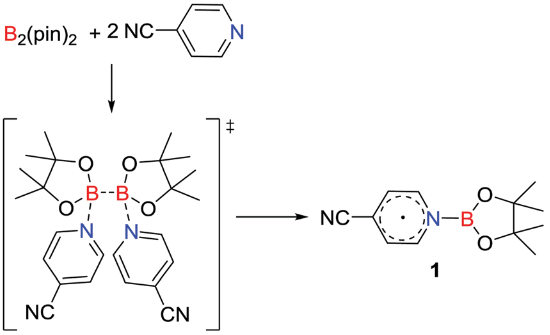
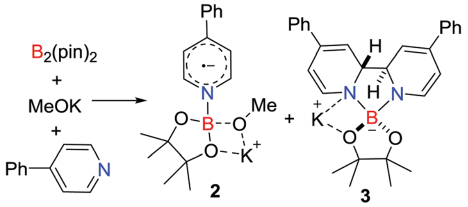


Scheme 1 Synthesis of a pyridine-ligated neutral boryl radical **1** *via* a homolytic cleavage of the B–B bond in $B_2(pin)_2$.

The donor 4-cyanopyridine behaves as a one-electron acceptor, reminiscent of homolytic cleavage reactions of a base stabilized diborane (4).[16]

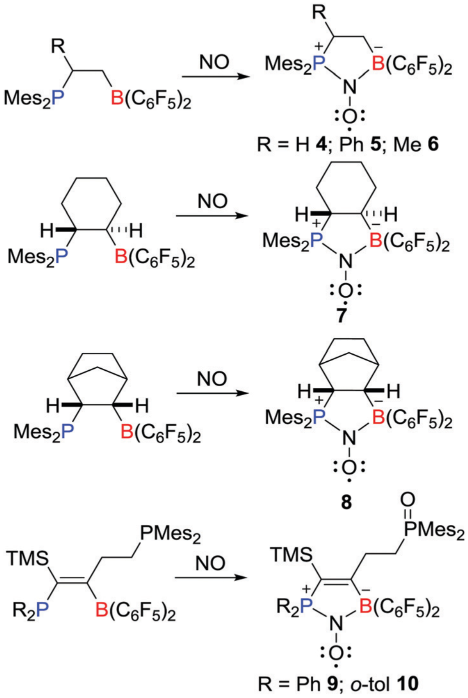
In extending this approach Jiao and Zhang showed that the combination of $B_2(pin)_2$, MeOK and 4-phenylpyridine afforded the novel pyridine-boryl species $[PhC_5H_4NBpin(OMe)^{\bullet}][K]$ **2** and $[(PhC_5H_4N)_2Bpin][K]$ **3** (Scheme 2).[17] In the absence of MeOK, no radical was observed, inferring 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.[17,18]



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

Radical capture by FLPs

Recently, Erker, Grimme, Warren *et al.* prepared a novel type of aminoxyl radical **4** *via* the reaction of an intramolecular FLP $Mes_2PCH_2CH_2B(C_6F_5)_2$ with NO (Scheme 3).[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).[20–22]



Scheme 3 Examples of aminoxyl radicals derived from reactions of FLPs with NO.

Liu Leo Liu

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Douglas W. Stephan

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).

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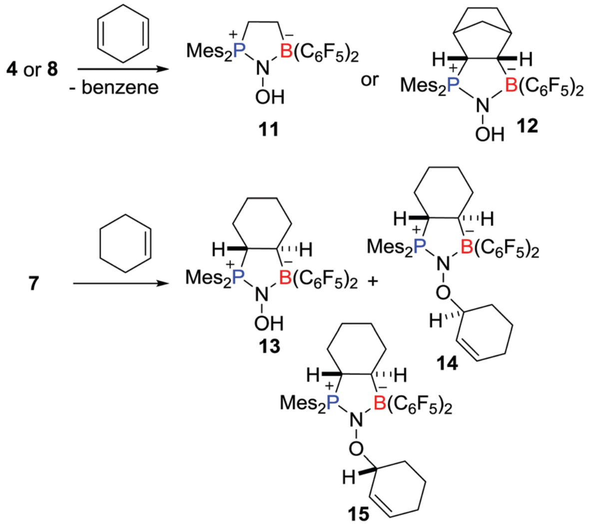


Scheme 4 Examples of hydrogen atom abstraction reactions of aminoxyl radicals.

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**.

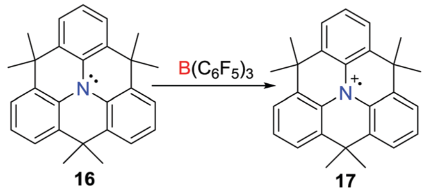
Frustrated radical pairs

A triarylamine radical cation

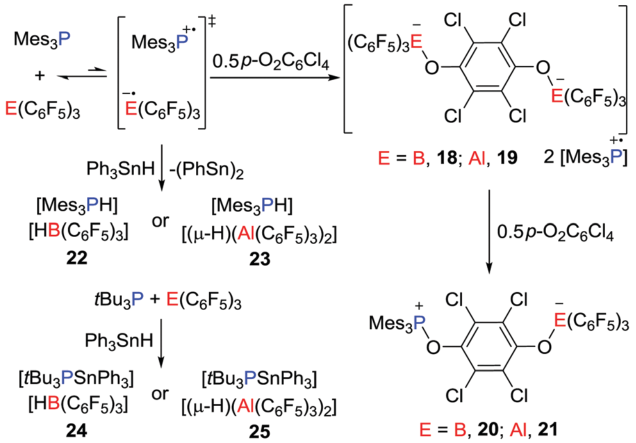
Although the one-electron oxidation of transition-metal complexes by $B(C_6F_5)_3$ has been described,[23,24] Wang *et al.* reported the first example of a one-electron oxidation of a triarylamine $(C_6H_3CMe_2)_3N$ **16** by $B(C_6F_5)_3$ in 2013 (Scheme 5),[25] affording the deep blue triarylamine radical cation **17**. Although the salt of the weakly coordinating alanate **17**$[Al(OR_F)_4]$ ($OR_F = OC(CF_3)_3$) was isolated, the formation of the boron centred radical anion in the reaction with $B(C_6F_5)_3$ 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 Mes_3P and $E(C_6F_5)_3$ (E = B or Al) in very dry toluene or chlorobenzene, the formation of a trace amount of the purple-colored $[Mes_3P^\bullet]^+$ was observed. Although the EPR spectrum of the purple solution generated from $Mes_3P/B(C_6F_5)_3$ 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 $[Mes_3P^\bullet]^+$, however, the presumed radical anion $[^\bullet E(C_6F_5)_3]^-$ 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 $[Mes_3P^\bullet][^\bullet E(C_6F_5)_3]$. Generation of these FRPs in the presence of tetrachloro-1,4-benzoquinone (p-$O_2C_6Cl_4$) prompts the formation of the radical salt $[Mes_3P^\bullet]_2[(C_6F_5)_3EOC_6Cl_4OE(C_6F_5)_3]$ (E = B, **18**; Al, **19**) (Scheme 6).



Scheme 5 Synthesis of **17** *via* a one-electron oxidation by $B(C_6F_5)_3$.



Scheme 6 Reactivity of $R_3P/E(C_6F_5)_3$ toward p-$O_2C_6Cl_4$ and Ph_3SnH.

These species react further with p-$O_2C_6Cl_4$ to give the 1,6-addition products $[Mes_3POC_6Cl_4OE(C_6F_5)_3]$ (E = B, **20**; Al, **21**) (Scheme 6). Alternatively, the FRPs homolytically split the Sn–H bond in Ph_3SnH to give $[Mes_3PH][HB(C_6F_5)_3]$ **22** or $[Mes_3PH][(\mu\text{-}H)(Al(C_6F_5)_3)_2]$ **23**, respectively (Scheme 6), along with $(Ph_3Sn)_2$. In sharp contrast, the combination of $tBu_3P/E(C_6F_5)_3$ shows no evidence of radical formation. Indeed, addition of Sn–H to these FLPs prompts heterolytic Sn–H cleavage affording $[tBu_3PSnPh_3][HB(C_6F_5)_3]$ **24** and $[tBu_3PSnPh_3][(\mu\text{-}H)(Al(C_6F_5)_3)_2]$ **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 $Mes_3P/B(C_6F_5)_3$ pair with benzyl peroxide derivatives was shown to proceed to efficiently split the O–O bond in a homolytic fashion, giving radical salts $[Mes_3P^\bullet][PhCOOB(C_6F_5)_3]$ **26**, $[Mes_3P^\bullet][p\text{-}BrC_6H_4COOB(C_6F_5)_3]$ **27** and $[Mes_3P^\bullet][p\text{-}MeC_6H_4COOB(C_6F_5)_3]$ **28** (Scheme 7).[28] Control experiments showed that the combination of $B(C_6F_5)_3$ 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 $[Tipp_3P^\bullet]^+$ (Tipp = 2,4,6-triisopropylphenyl) and $[Tipp_2MesP^\bullet]^+$ were prepared and structurally characterized by Wang *et al.*[29] employing the weakly coordinating anions such as $[Al(OR_F)_4]^-$ ($OR_F{=}OC(CF_3)_3$) and $[Al(OR_{Me})_4]^-$ ($OR_{Me}{=}OC(CF_3)_2Me$).

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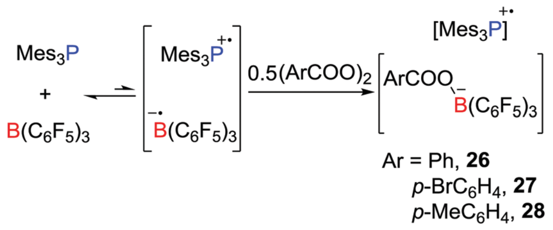
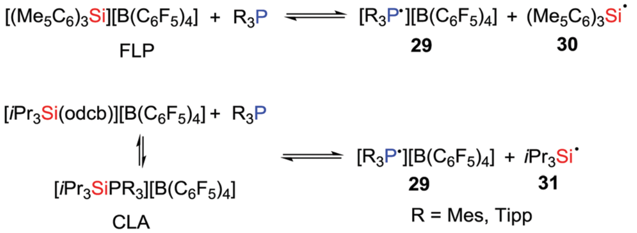


Scheme 7 Reactivity of $Mes_3P/B(C_6F_5)_3$ toward benzyl peroxide derivatives.

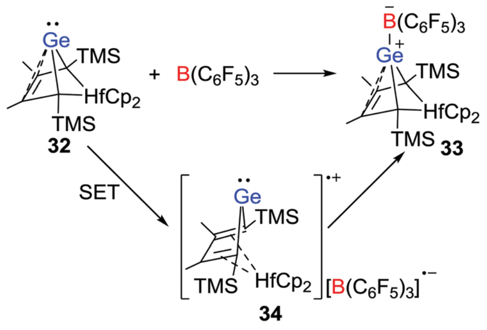


Scheme 8 One-electron oxidation of phosphines in silylium ion/phosphine Lewis pairs.

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 $R_3P/[(Me_5C_6)_3Si][B(C_6F_5)_4]$ (R = Tipp or Mes) and CLAs derived from the combination of $R_3P/[iPr_3Si(odcb)][B(C_6F_5)_4]$ (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 $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ was identified by EPR and UV-vis spectroscopy. In addition, the nature of the radical cation was confirmed *via* independent synthesis of the $[B(C_6F_5)_4]^-$ salt *via* the reaction of **32** with $[Ph_3C][B(C_6F_5)_4]$. This work provided evidence for a SET in CLA formation reactions.



Scheme 9 Synthesis of **33** *via* a radical complex **34**.

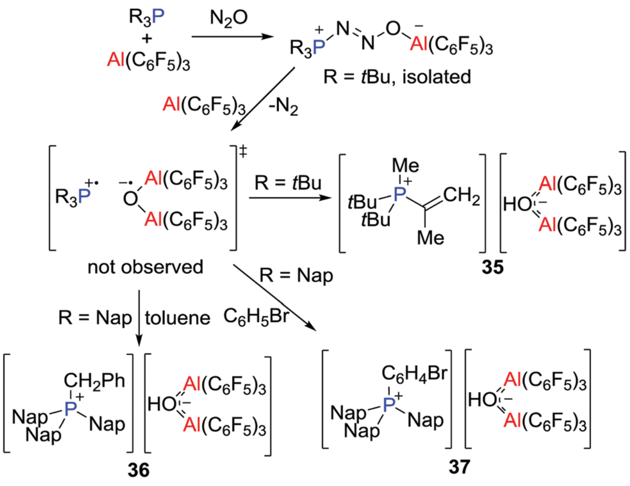
Electron transfer in FLP-reactions

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 $B(C_6F_5)_3$ and $PMes_3$ 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 $[R_3P^•][^•O(Al(C_6F_5)_3)_2]$ (R = *t*Bu or Nap, Nap = naphthyl) was obtained.[31] Generated from the reactions of R_3P and $Al(C_6F_5)_3$ in a molar ratio of 1 : 2 with N_2O (1 atm) (Scheme 10), these FRPs were shown to effect C–H bond activation. In the case of R = *t*Bu, a C–H bond of the *t*Bu group was readily activated to form $[tBu_2PMe(C(CH_2)Me)][(\mu\text{-}OH)(Al(C_6F_5)_3)_2]$ **35**, whereas for R = Nap, the intermolecular activation of toluene or bromobenzene afforded $[Nap_3PCH_2Ph][(\mu\text{-}OH)(Al(C_6F_5)_3)_2]$ **36** or $[Nap_3PC_6H_4Br][(\mu\text{-}HO)(Al(C_6F_5)_3)_2]$ **37**, respectively (Scheme 10). These reactions proceeded *via* the corresponding FLP-N_2O adducts, as supported by isolation of the species $tBu_3P(N_2O)Al(C_6F_5)_3$ using the equal molar portion of tBu_3P and $Al(C_6F_5)_3$. The H atom in the anion $[(\mu\text{-}HO)(Al(C_6F_5)_3)_2]^-$ was derived from hydrogen atom abstraction from the toluene solvent by the transient radical anion $[(\mu\text{-}O^•)(Al(C_6F_5)_3)_2]^-$.

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 $B(C_6F_5)_3$ in toluene led to formation of a Lewis acid–base adduct $(C_6F_5)_3B(O_2C_{14}H_8)$ featuring a tetracoordinated boron centre.[34] Remarkably, treating the above reaction mixture with H_2 (4 atm) at 110 °C resulted in the formation of two products, the major one being $[(C_6F_5)_2B(O_2C_{14}H_8)]^•$ **38** together with the minor product $(C_6F_5)B(O_2C_{14}H_8)$ **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



Scheme 10 C–H bond activation by transient FRPs.

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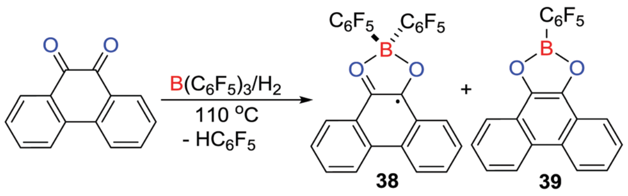
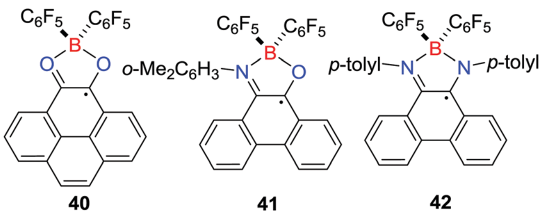


Scheme 11 Synthesis of a borocyclic radical **38** *via* an FLP hydrogenation.



Scheme 12 Stable borocyclic radicals prepared *via* FLP hydrogenations.

consistent with DFT calculations of the spin density showing the delocalization of the unpaired electron over the phenanthrene backbone.

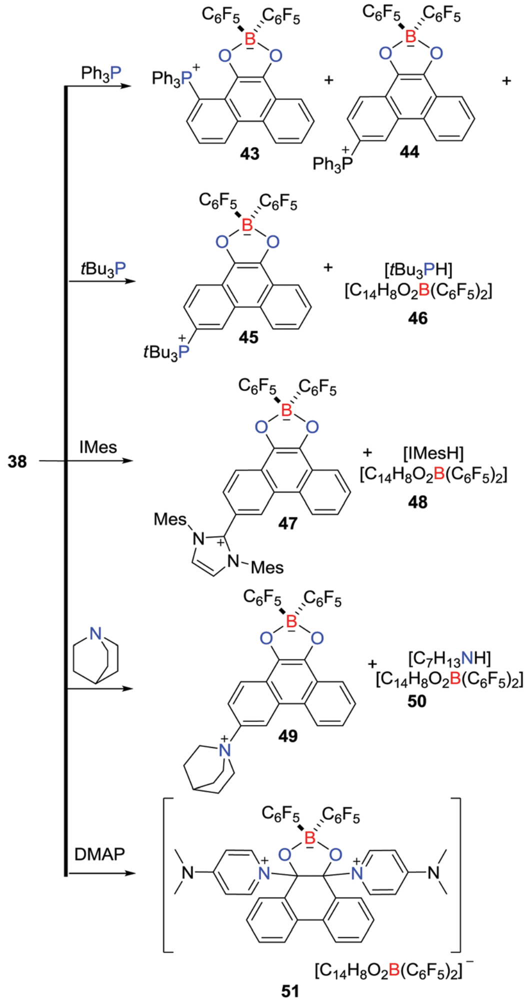
A mechanistic study showed that initially the FLP-hydrogenation of the dione proceeds giving phenanthrene-9,10-diol. This diol reacts with the dione to afford 9,10-phenanthrenequinhydrone radical that readily coordinates $B(C_6F_5)_3$ to form a paramagnetic Lewis acid–base adduct, followed by protonation of one of the C_6F_5 rings affording **38** and HC_6F_5. Alternatively, if the reduced diol reacts with $B(C_6F_5)_3$, double protodeborylation affords the minor product **39**.

The analogous reactions of $B(C_6F_5)_3$ with pyrene-4,5-dione,[34] *N*-(2,6-dimethylphenyl)-phenanthreno-iminoquinone[35] or *N*,*N*-di-*p*-tolylphenanthrene-9,10-diimine[35] under the atmosphere of H_2 (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]

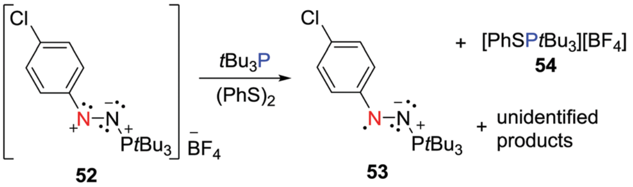
In an ensuing work, the reactivity of **38** with a variety of nucleophiles was probed (Scheme 13).[36] The LUMO of **38** primarily involves π*-antibonding orbitals over the phenanthrene backbone, prompting a reaction with Ph_3P to give two regioisomeric zwitterions, $1\text{-}(Ph_3P)C_{14}H_7O_2B(C_6F_5)_2$ **43** and $3\text{-}(Ph_3P)C_{14}H_7O_2B(C_6F_5)_2$ **44**, coupled with the related boronic ester **39** and HC_6F_5. Similarly, the reaction of **38** with $t\text{Bu}_3P$ afforded the zwitterion $3\text{-}(t\text{Bu}_3P)C_{14}H_7O_2B(C_6F_5)_2$ **45** and the salt $[t\text{Bu}_3PH][C_{14}H_8O_2B(C_6F_5)_2]$ **46**, while reaction with N-heterocyclic carbene IMes or quinuclidine gave $3\text{-}(\text{IMes})C_{14}H_7O_2B(C_6F_5)_2$ **47** and $[\text{IMesH}][C_{14}H_8O_2B(C_6F_5)_2]$ **48** or $3\text{-}(C_7H_{13}N)C_{14}H_7O_2B(C_6F_5)_2$ **45** and $[H(NC_7H_{13})_2][C_{14}H_8O_2B(C_6F_5)_2]$ **50**, respectively (Scheme 13). In contrast, treatment of **38** with DMAP led to attack at the carbonyl carbon atoms, affording $[9,10\text{-}(\text{DMAP})_2C_{14}H_8O_2B(C_6F_5)_2][C_{14}H_8O_2B(C_6F_5)_2]$ **51** (Scheme 13).

A neutral aminyl radical from disulfide activation

The FLP system consisting of the nitrogen based Lewis acidic nitrenium cation **52** with $t\text{Bu}_3P$ has been shown to react $(PhS)_2$ to afford the persistent neutral aminyl radical, $[(p\text{-ClC}_6H_4)N_2(Pt\text{Bu}_3)]^\bullet$ **53** and the salt $[\text{PhSP}t\text{Bu}_3][BF_4]$ **54** (Scheme 14).[37] This is reminiscent of the dione/borane reaction with H_2 described above, suggesting that the concerted FLP action on the disulphide prompts electron transfer. It is noteworthy that the radical **53** was also accessible *via* a more conventional reduction of **52** with cobaltocene or PhSNa.



Scheme 13 Reactivity of **38** toward nucleophiles.



Scheme 14 Synthesis of an aminyl radical **53** *via* FLP activation of diphenyl disulfide.

Transient donor–acceptor radicals

In 2016, the Erker group described the selective oxidation of the intramolecular amine/borane FLP, $[C_5H_6Me_4N(CH_2)_3B(C_6F_5)_2]$,

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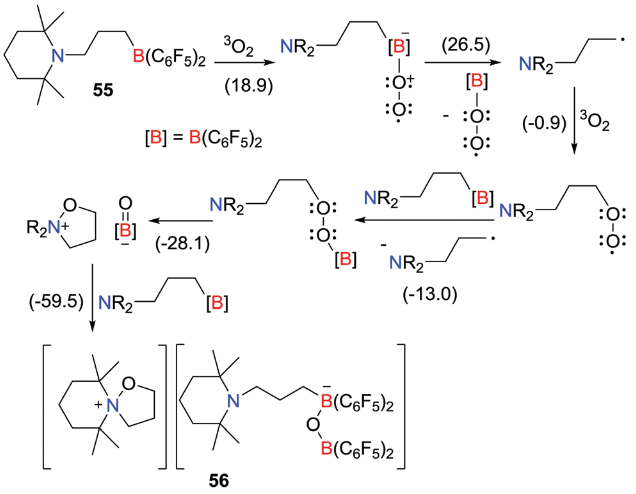
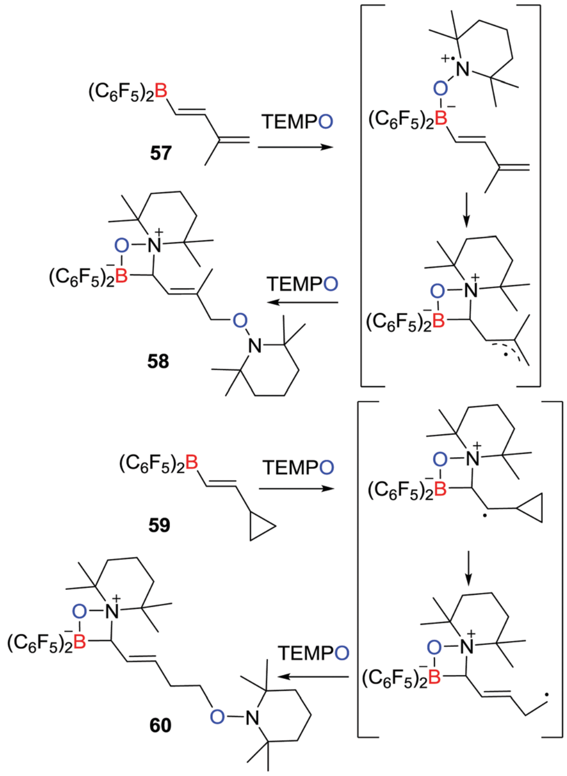
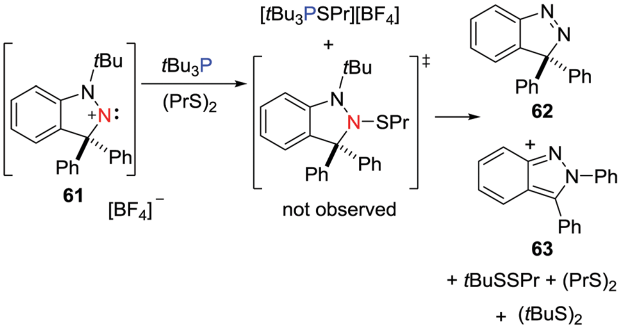


Scheme 15 Oxidation of an intramolecular amine/borane FLP with dioxygen. Free energies are given in kcal mol^{-1}.

with dioxygen (Scheme 15).[38] In this case, the resulting tetrahydroisoxazolium borate salt $[C_5H_6Me_4N(CH_2)_3O][C_5H_6Me_4N(CH_2)_3B(C_6F_5)_2OB(C_6F_5)_3]$ **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 (−59.5 kcal mol^{-1}) (Scheme 15).



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



Scheme 17 FLP reactivity of tBu_3P/**61** with $(PrS)_2$ leading to a spontaneous radical chain degradation.

A related work described by Erker, Studer *et al.* described that the reaction of the boryldiene $CH_2{=}C(Me)CH{=}CHB(C_6F_5)_2$ **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).[39] 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, $C_3H_5CH{=}CHB(C_6F_5)_2$ **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.[40]

In a recent work, the FLP derived from a nitrogen-centered LA, namely a cyclic (alkyl)(amino)nitrenium cation, $[C_6H_4CPh_2N_2tBu][BF_4]$ **61**, and tBu_3P was shown to react with dipropyl disulfide $(PrS)_2$.[41] One product is the salt $[tBu_3PSPr][BF_4]$. The other product derived from the heterolytic S–S cleavage, $[(C_6H_4)(NtBu)N(SPr)CPh_2]$, was not observed but instead, the reaction affords a mixture of $(tBuS)_2$, $(tBuSSPr)$, Pr_2S, $[C_6H_4CPh_2N_2]$ **62** and $[C_6H_4CPhN_2Ph]$ **63**, consistent with a radical chain pathway (Scheme 17).

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/$B(C_6F_5)_3$ pairs with dioxygen which afforded $[Cp'_2Fe]_2[(C_6F_5)_3BOOB(C_6F_5)_3]$ (Cp′ = Cp **64** or Cp* **65**); the first examples of dianionic boron peroxide salts (Scheme 18).[42] Although $B(C_6F_5)_3$ is inert to $^3O_2$ over 24 h, the presence of $B(C_6F_5)_3$ appeared to facilitate the reduction of $^3O_2$ by ferrocenes. A cyclic voltammetry (CV) study suggested the reaction proceeded *via* the transient B_2O_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^*_2Fe in the presence of a Lewis acid ($E(C_6F_5)_3$, E = B or Al) for small

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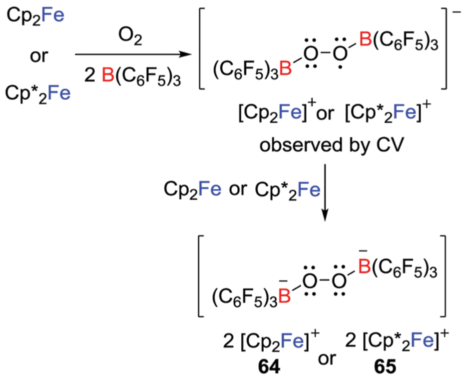


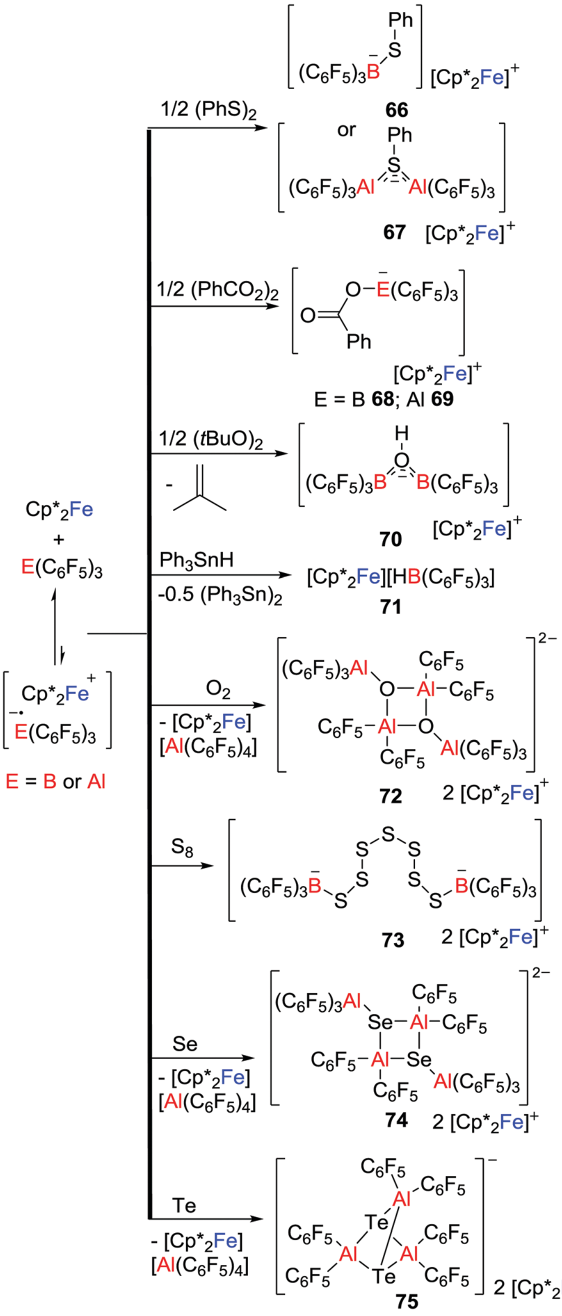
Scheme 18 Reactivity of ferrocene/$B(C_6F_5)_3$ toward dioxygen.

molecule activation.[43] 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 **66–75** featuring novel B- and Al-containing anions (Scheme 19). For example, exposure of a solution of $Cp^*_2Fe/Al(C_6F_5)_3$ to dry $^3O_2$ immediately resulted in the O–O bond cleavage, giving the salt $[Cp^*_2Fe]_2[((C_6F_5)_3AlOAl(C_6F_5)_2)_2]$ **72** with a dianionic Al_2O_2 core. This stands in contrast to the corresponding reaction of $Cp^*_2Fe/B(C_6F_5)_3$ that yields **65** in which the O–O bond remains intact (Scheme 18). The corresponding reactions of $Cp^*_2Fe/E(C_6F_5)_3$ with elemental Te and S_8 afford a unique tricyclic Al_3Te_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^*_2Fe to $E(C_6F_5)_3$, suggesting that the generated $[^{\bullet}E(C_6F_5)_3]^-$ 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 $[^{\bullet}Al(C_6F_5)_3]^-$ that was followed by decomposition during thermolysis of a C_6D_5Br solution of $Al(C_6F_5)_3$ with Cp_2Fe at 100 °C for 3 days,[44] although the radical anion $[^{\bullet}Al(C_6F_5)_3]^-$ was not observed.

In a recent work, this concept of SET was extended to systems based on the transition-metal-based LA; $Zn(C_6F_5)_2$ (Scheme 20).[45] In this case, the combination of $Zn(C_6F_5)_2$ and $[(PhC(S)S)_2]$ gave a weak CLA, while the cleavage of the S–S bond of $[(PhC(S)S)_2]$ was achieved immediately upon mixing the substrate with $Zn(C_6F_5)_2$ and Cp^*_2Fe, leading to a salt $[Cp^*_2Fe][PhCS_2Zn(C_6F_5)_2]$ **76**. No SET reaction from Cp^*_2Fe to $Zn(C_6F_5)_2$ 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 $Cp'_2Fe/Al(C_6F_5)_3$ (Cp′ = Cp* or Cp) with N_2O (Scheme 21), affording salts $[Cp'_2Fe][(\mu\text{-}HO)(Al(C_6F_5)_3)_2]$ (Cp′ = Cp*, **77**; Cp, **79**).[46] 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 $[^{\bullet}OAl(C_6F_5)_3]^-$ 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 $Ph_3C^{\bullet}/Al(C_6F_5)_3$ with N_2O, wherein $[^{\bullet}OAl(C_6F_5)_3]^-$ was trapped by the excess $Ph_3C^{\bullet}$ to give the salt $[Ph_3C][Ph_3COAl(C_6F_5)_3]$ **81**.



Scheme 19 Reactivity of $Cp^*_2Fe/E(C_6F_5)_3$ toward small molecule substrates.

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/$Zn(C_6F_5)_2$ (Scheme 22).[45] Specifically, the phenanthrene-9,10-dione or pyrene-4,5-dione donor–acceptor adduct $[(C_{14}H_8O_2)Zn(C_6F_5)_2]$ **82** or $[(C_{16}H_8O_2)Zn(C_6F_5)_2]$ **83** was shown to feature low-lying LUMOs relative to those of the corresponding free diones. One-electron reduction of these

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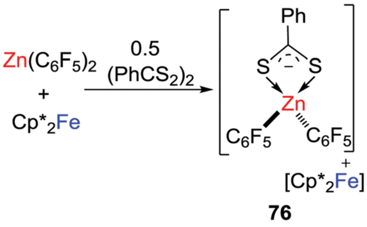
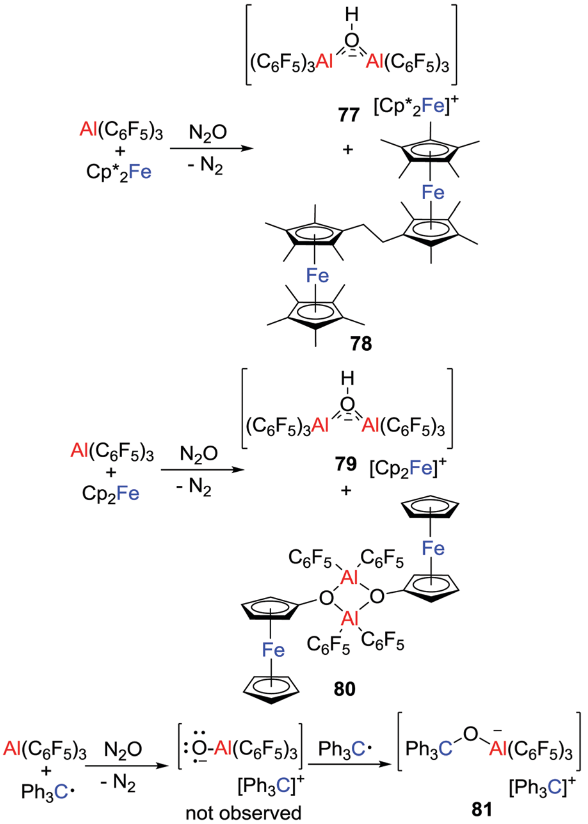
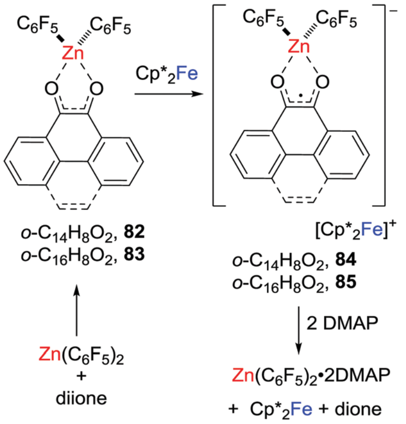


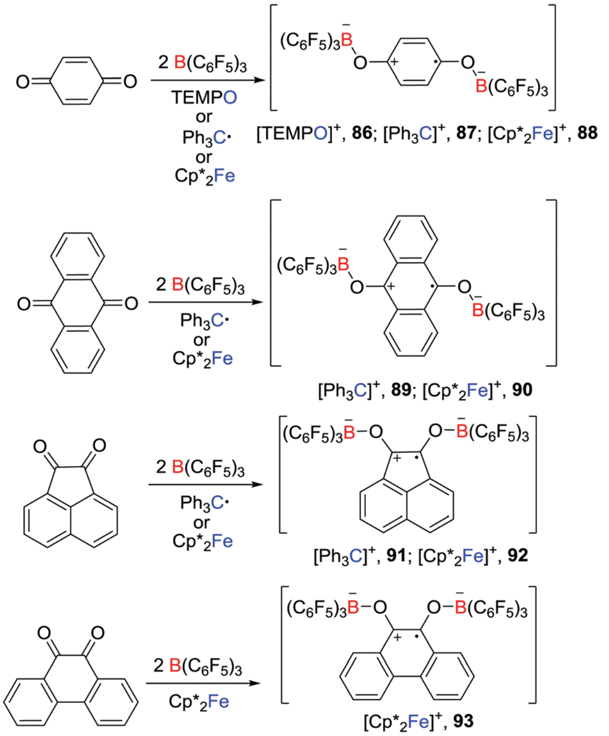
Scheme 20 Reaction of $Cp^*_2Fe/Zn(C_6F_5)_2$ with $[(PhC(S)S)_2]$.



Scheme 21 Reaction of $Cp'_2Fe/Al(C_6F_5)_3$ or $Ph_3C^\bullet/Al(C_6F_5)_3$ with N_2O.



Scheme 22 Synthesis and reactivity of zinc-containing radicals.



Scheme 23 Synthesis of semiquinone radical anions.

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 $[Zn(C_6F_5)_2(DMAP)_2]$ 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 $B(C_6F_5)_3$, *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 $B(C_6F_5)_3$, the corresponding reaction of the studied quinones with TEMPO, Gomberg dimer or Cp^*_2Fe did not react. The presence of $B(C_6F_5)_3$ 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 $[C_5H_6Me_4N{=}O][^\bullet O_2[B(C_6F_5)_3]_2]$ **94** and $[C_5H_6Me_4N{=}O][^\bullet O_2[B(p\text{-}C_6F_4H)_3]_2]$ **95** respectively. These species are analogous to the $[Cp^*_2Fe]^+$ salts reported by Agapie and Henthorn (Scheme 18) (*vide supra*).[42] Interestingly, the Gomberg dimer of the trityl radical reacted in a similar fashion to give the salt $[Ph_3C][^\bullet O_2[B(p\text{-}C_6F_4H)_3]_2]$ **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

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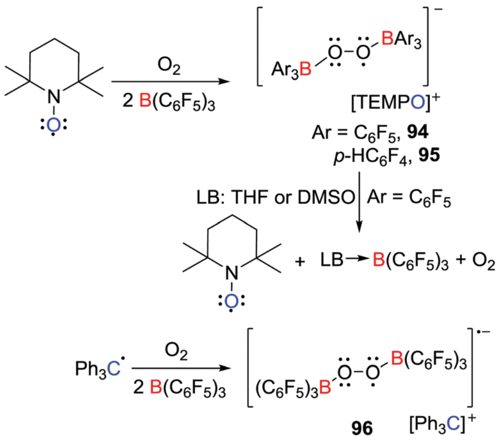

Scheme 24 Synthesis and reactivity of a bis(borane)superoxide radical anion.

anions. Interestingly, THF or DMSO reacted with **94** prompted the regeneration of TEMPO and O_2 and formation of (THF)$B(C_6F_5)_3$ or (DMSO)$B(C_6F_5)_3$, respectively. This observation indicates that displacement of $B(C_6F_5)_3$ 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 O_2.

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 serve to highlight the notion that donor–acceptor interactions are not be limited to classical dative two-electron adduct formation. Thus, while many combinations of Lewis acids and bases form either CLA and FLP combinations and react *via* a diamagnetic, two-electron pathway, judicious choice of donor–acceptor combinations can afford radical pathways, 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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