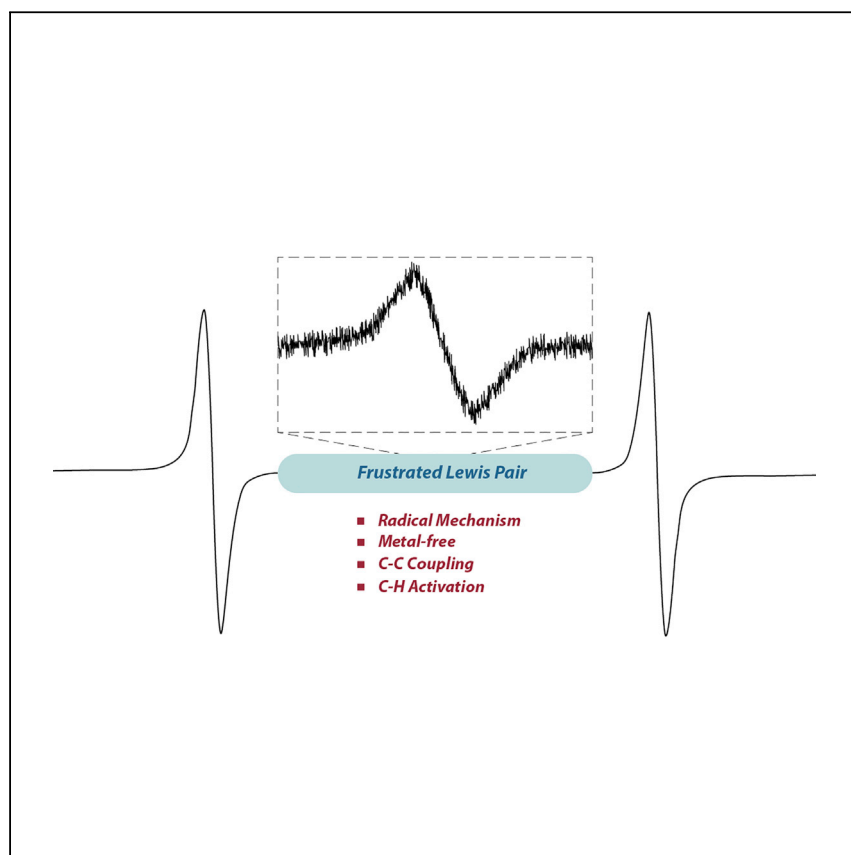


Article

Radical Reactivity of Frustrated Lewis Pairs with Diaryl Esters



Recently, specific combinations of Lewis acids and bases have been demonstrated to generate frustrated radical pairs (FRPs). Here, Soltani et al. exploit FRPs to afford a new avenue for metal-free C–H activation and C–C bond formation, providing a strong basis for further FRP single-electron transformations in organic synthesis.

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HIGHLIGHTS

Divergent reactivity facilitated by frustrated radical pairs (FRPs)

Radical generation from non-redox active esters

Detailed EPR and DFT analysis to elucidate FRP mechanisms

35 examples, with yields up to 89%

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Article

Radical Reactivity of Frustrated Lewis Pairs with Diaryl Esters

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SUMMARY

Advances in the chemistry of metal-free systems known as frustrated Lewis pairs (FLPs) has exposed new reactivity of the *p*-block elements, particularly in small-molecule activation and catalysis. Typically, the mode of activation by FLPs has been predicated on a heterolytic two-electron process, although recently, select FLPs have been shown to participate in single-electron processes. Here, we report the reaction of diaryl substituted esters with FLPs. This results in divergent pathways, one whereby the diaryl moiety is stabilized by the Lewis basic phosphine, and the alternative pathway, wherein a single-electron transfer process occurs, generating the $[\text{Mes}_3\text{P}]^{+\bullet}/[\text{C}(\text{H})\text{Ar}_2]^{-\bullet}$ radical ion pair. The latter species undergoes a homocoupling reaction to yield tetraphenylethane derivatives. In the presence of olefins, this reactivity can be harnessed through an sp^2 - sp^3 C–C heterocoupling reaction to generate α,β -substituted olefins. Notably, this work showcases an FLP approach to metal-free radical C–H bond activation with subsequent C–C bond formation, which also displays complementary reactivity to other approaches.

INTRODUCTION

A revolutionary paradigm shift occurred in 2006 with the first report of a non-metal system $4\text{-(Mes}_2\text{P)C}_6\text{F}_4\text{(B(C}_6\text{F}_5)_2)_2$, which could reversibly activate dihydrogen.¹ This unusual reactivity was brought about by the presence of sterically demanding groups at both boron and phosphorus, which precluded adduct formation. Thus, the concept of frustrated Lewis pairs (FLPs) was born. Advances in the chemistry of FLPs over the last decade has exposed new reactivity concepts and resulted in broad applications, particularly in small-molecule activation and catalysis.² However, the mode of activation by FLPs has been almost exclusively predicated on a heterolytic two-electron process (Scheme 1). Computational studies have been crucial in developing a mechanistic understanding of how this activation takes place.^{3–7} The utilization of two-electron processes has dominated FLP chemistry and has become synonymous with the general mechanistic overview since its inception, with only a few studies that probed their potential as reagents in single-electron processes (Scheme 1).^{8–11} In contrast, Stephan and colleagues¹² have recently shown by Electron Paramagnetic Resonance (EPR) and UV-visible spectroscopy that select FLPs participate in single-electron processes. These authors demonstrated both heterolytic and homolytic pathways for Sn–H activation by the FLPs $\text{P}^t\text{Bu}_3/\text{E}(\text{C}_6\text{F}_5)_3$ and $\text{PMes}_3/\text{E}(\text{C}_6\text{F}_5)_3$ ($\text{E} = \text{B, Al}$), respectively. Subsequently, this concept demonstrated that the single-electron process can be used in the homolytic cleavage of O–O bonds.^{13,14} The access to divergent mechanisms for FLPs suggests that new reaction pathways could be exploited in organic synthesis. To this end, this

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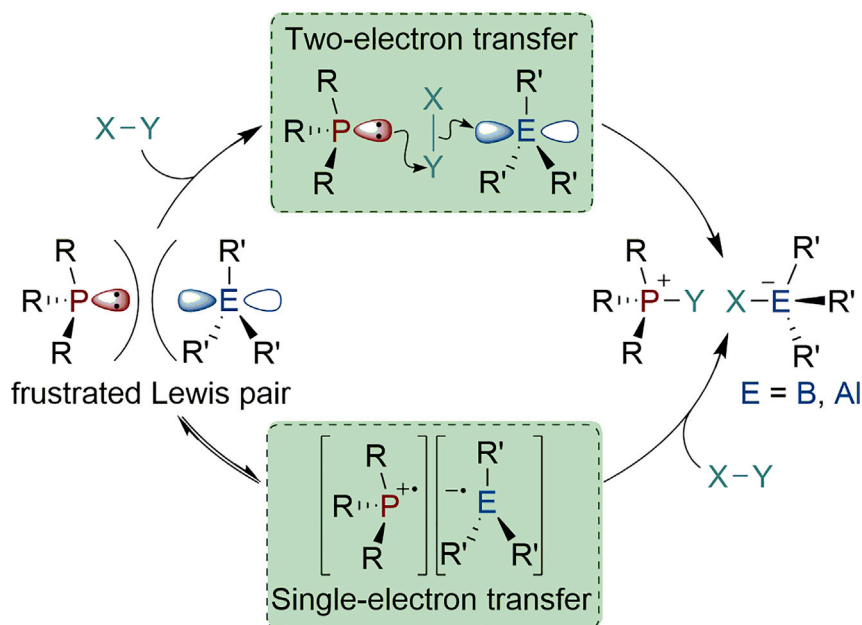
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Scheme 1. FLP Activation of Small Molecules

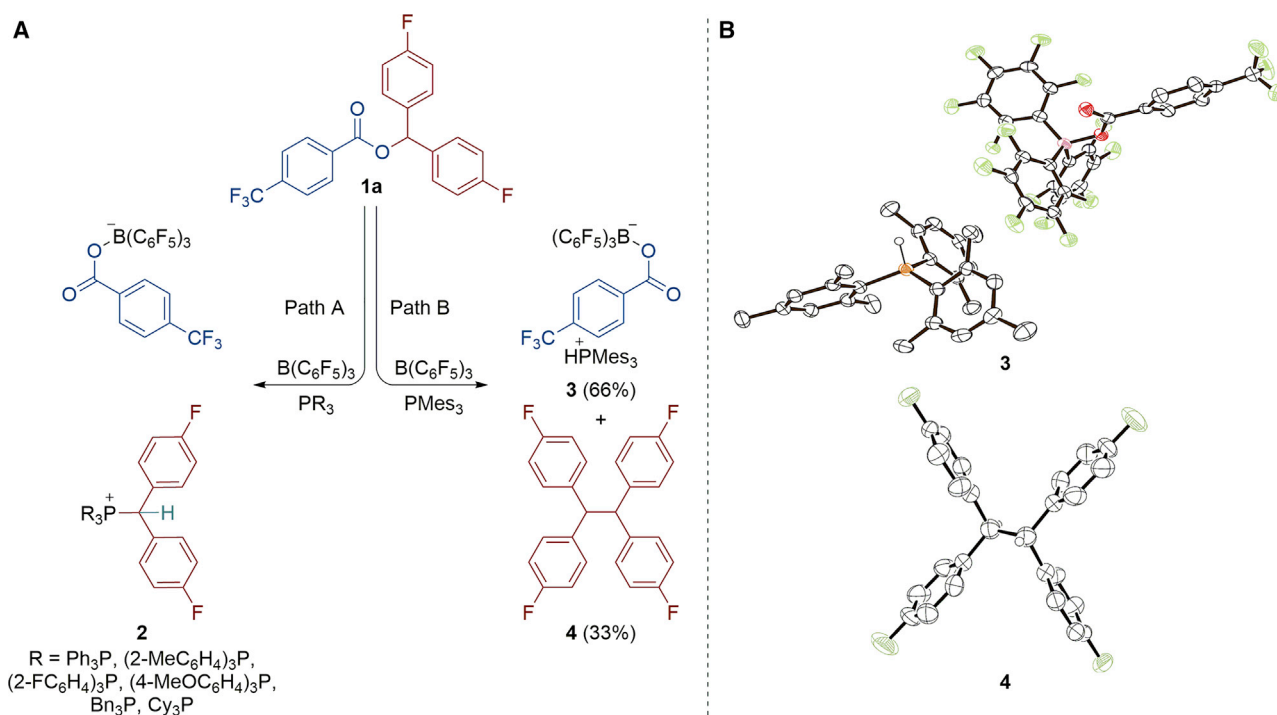
Proposed contradistinct FLP reaction pathways in the activation of X-Y bonds via two- and single-electron processes.

work shows how the divergent reactivity of readily available diaryl esters can be steered toward radically different pathways by judicious choice of the phosphine base used. This reaction pathway affords a new avenue for metal-free C-H activation and C-C bond formation, providing access to a range of α,β -substituted alkenes.

RESULTS

Reactivity Studies

To begin this study, a fluoro-substituted benzhydryl ester derivative **1a** was prepared (Scheme 2). Reactions of **1a** with the Lewis acid B(C₆F₅)₃ in combination with various Lewis basic phosphines (Ph₃P, (2-MeC₆H₄)₃P, (2-FC₆H₄)₃P, (4-MeOC₆H₄)₃P, Bn₃P, or Cy₃P) were explored. *In situ* NMR spectroscopy showed unusual C(sp³)-O bond cleavage in **1a** accompanied by the rapid and clean conversion to the corresponding phosphonium-borate **2** (Scheme 2). In all of the cases, this was identified by the observation of an ylidic CH resonance in the ¹H and ³¹P NMR spectra, with ²J_{PH} = 16–18 Hz (Scheme 2, path A; Table S1). While this reaction pathway was true for several borane-phosphine pairs, when PMes₃ was tested, a distinctly different reaction pathway was observed. In this instance, upon addition of the B(C₆F₅)₃/PMes₃ FLP to **1a** in CDCl₃, a bright purple solution was observed (λ_{max} = 571 nm), suggestive of the radical cation [PMes₃]^{·+}.^{12,15} Over the course of 12 h at ambient temperature, or 4 h at 70°C, this purple coloration slowly gave way to a clear orange solution, which was associated with a new doublet resonance in the ³¹P NMR spectrum (δ = 27.5 ppm, ¹J_{PH} = 492 Hz), suggesting the presence of a P-H bond in the resulting product. Slow evaporation of the solvent yielded a mixture of colorless crystals suitable for single-crystal X-ray diffraction. These studies unambiguously identified 2 different components from the reaction mixture, namely the phosphonium-borate **3** (66% yield), in addition to the homocoupled benzhydryl **4** (33% yield) (Scheme 2; Figures S122–S123; Tables S2–S3). The identification of products **3** and **4**, as well as the observation of a purple-colored solution, suggests that this reaction proceeds via a single-electron radical mechanism.



Scheme 2. Outline of the Divergent Reactivity of Frustrated Lewis Pairs

(A) Divergent reactivity depending on the phosphine used.

(B) Solid-state structure of 3 and 4. C, black; O, red; B, coral; F, green; P, orange. Thermal ellipsoids drawn at 50% probability. Non-essential H atoms omitted for clarity.

EPR Studies

EPR spectroscopy (see Figures S126–S130; Table S6) on a solution of the reaction mixture of 1a and the $B(C_6F_5)_3/PMes_3$ FLP showed a doublet signal in the room temperature EPR spectrum (Figure 1A). The measured g_{iso} value of 2.0072 and isotropic ^{31}P hyperfine coupling constant of 670 MHz (238.5 G) are comparable with those reported previously for $[PMes_3]^{+\bullet}$.¹² The corresponding anisotropic spectrum recorded of a frozen solution of the reaction mixture yielded an axial spectrum from which the principal values of the g and ^{31}P A-tensors could be determined (Figure 1A). Analysis of the s -orbital and p -orbital occupation of $[PMes_3]^{+\bullet}$ gave a calculated total spin density at P of 71% (5% s -character, 66% p -character).^{15,16} The quasi-reversible single-electron oxidation of bulky tri-aryl phosphines, induced via electrochemical and chemical routes, has previously been reported in detail by Boéré et al.,¹⁶ who report that the oxidation potential is intricately linked to the size of the aryl substituent and coordination geometry around the central phosphorus. The radical cations generated by bulk electrolysis were observed to be stable for at least 2 h, which ensures their availability for participation in subsequent radical reactions and is therefore of direct relevance to our studies herein. In addition to the phosphorus doublet, a much weaker signal could be observed in the anisotropic spectrum centered at $g = 2.006$ ($B = 336$ mT). The signal intensity of this species could be increased relative to the $[PMes_3]^{+\bullet}$ in the isotropic spectrum upon heating the sample to 70°C *in situ*. In an attempt to better resolve this species, a 9H-fluorenyl ester 1b was synthesized.¹⁷ Upon reaction with $B(C_6F_5)_3/PMes_3$, formation of the $[PMes_3]^{+\bullet}$ doublet was clearly observed in the isotropic EPR spectrum, in addition to a small contribution from a second radical species, which displayed some evidence of hyperfine coupling (Figure 1B). The origin of this second species

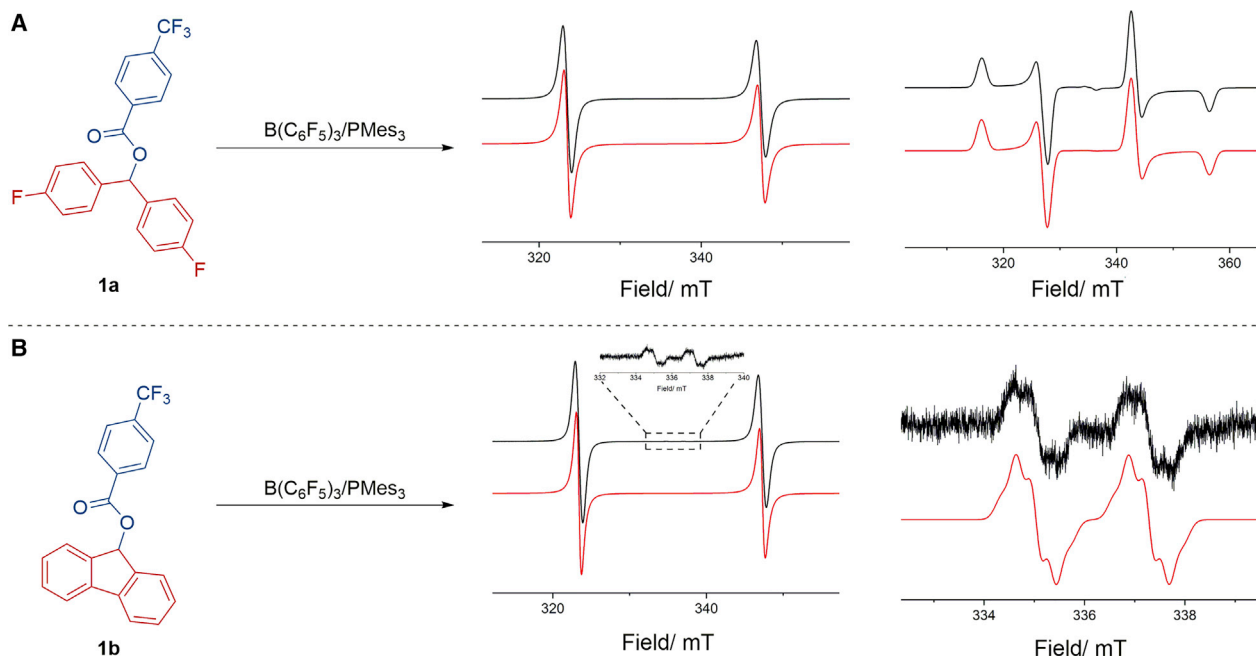


Figure 1. EPR Studies

(A) CW X-band EPR spectra of **1a** and B(C₆F₅)₃/PMes₃ FLP recorded at T = 298 K and 140 K, respectively.

(B) CW X-band EPR spectrum of **1b** and (C₆F₅)₃/PMes₃ FLP recorded at T = 298 K, and expansion of signal attributed to the persistent fluorenyl radical. Corresponding simulations are shown in red.

was attributed to a persistent fluorenyl-based radical, formed upon FLP-mediated cleavage of the C(sp³)-O bond in **1b**. The low concentration of radicals leads to poor resolution of the spectrum (Figure 1B) and precludes the accurate determination of the hyperfine coupling. Nonetheless, a simulation is consistent with the presence of 1 large proton coupling ($a_{\text{iso}} \approx 63$ MHz) arising from the central 9-H proton and 2 smaller couplings arising from the 2 equivalent 3-H ($a_{\text{iso}} \approx 9$ MHz) and 6-H protons ($a_{\text{iso}} \approx 7$ MHz) on the aryl rings. These are of similar relative magnitude to those reported previously for the 9-fluorenyl radical.¹⁸

DFT Studies

Density functional theory (DFT) calculations (Tables S7–S17) using the PW6B95-D3 functional^{19,20} and def2-tzvp basis set were also performed to examine the differing pathways A and B in Scheme 2A, in which PPh₃ was used as a comparator to PMes₃. For path B, the reaction to yield products **3** and **4** for PMes₃ was 2.1 kcal/mol more favorable than the hypothetical reaction with PPh₃. Formation of the [PMes₃]⁺⁺ moiety was determined to be 15.6 kcal/mol more favorable than the [PPh₃]⁺⁺ species, and similarly, formation of [HPMes₃]⁺ is favored over [HPPH₃]⁺ by 12.0 kcal/mol, suggesting that formation of the radical is decisive to follow reaction path B.²¹ Moreover, for path A, the hypothetical PMes₃ phosphonium-borate product is disfavored with respect to the experimentally realized PPh₃ phosphonium product **2** by 27.9 kcal/mol, explaining the divergent reaction mechanisms observed.

Substrate Scope

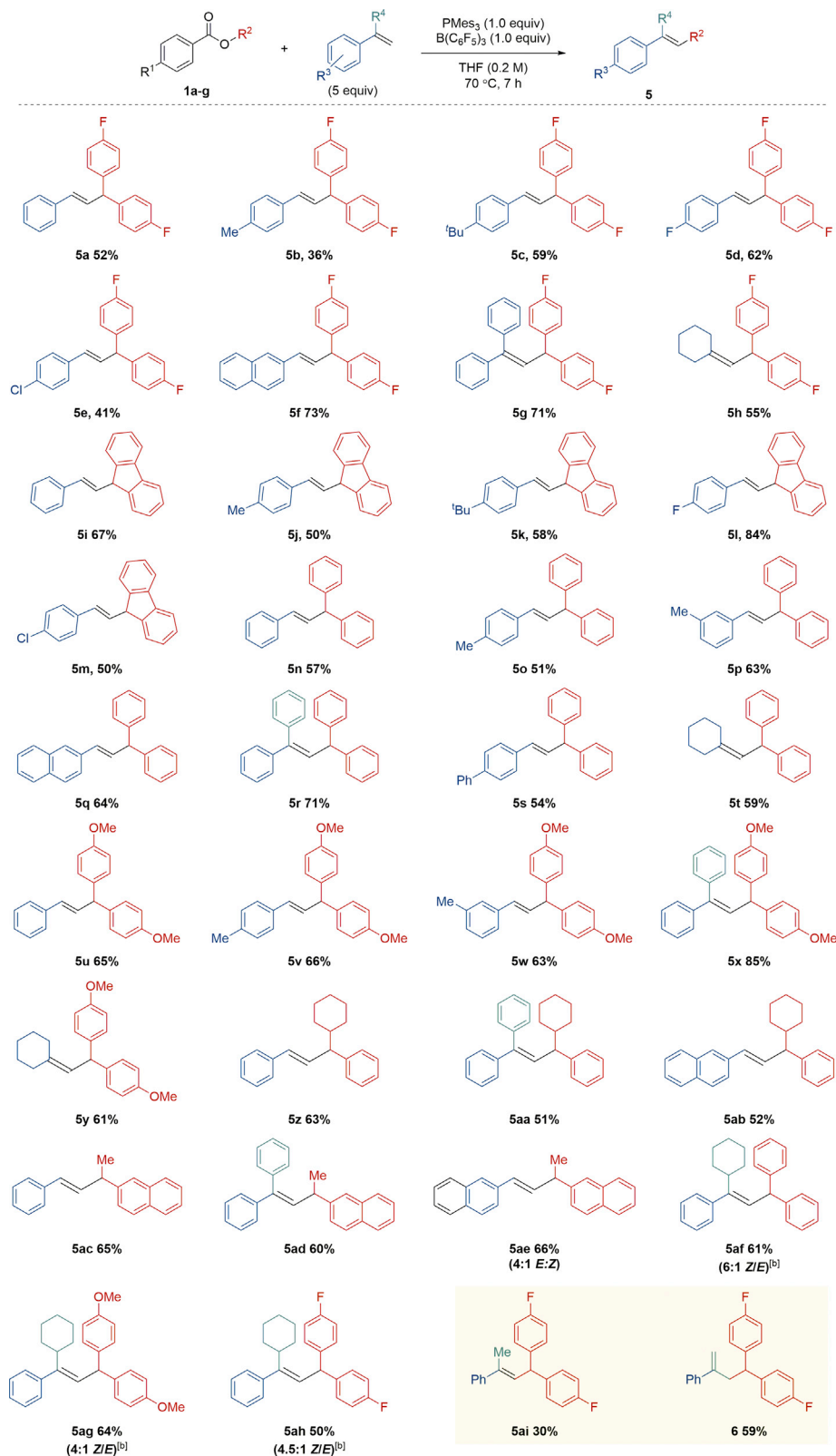
As the [PMes₃]⁺⁺ radical is ultimately quenched by a hydrogen source, through C–H bond activation generating [HPMes₃]⁺, subsequent reactions were conducted to probe the origin of this quenching agent in the reaction between **1b**, PMes₃, and B(C₆F₅)₃ (see Figure S121). Under anhydrous conditions in C₆D₆ or CDCl₃, a doublet

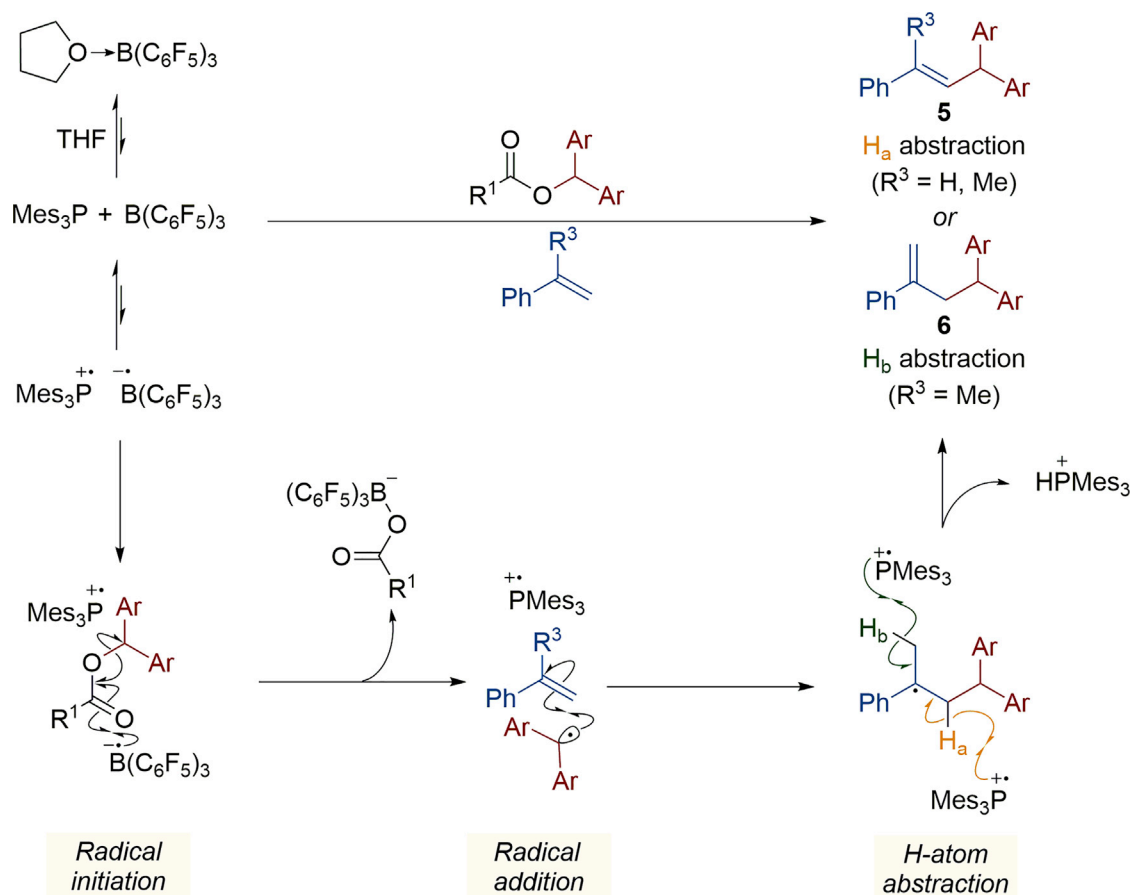
was observed in the ^1H and ^{31}P spectra due to $^1J_{\text{P-H}}$ coupling, suggesting that the substrate must be the hydrogen source. Toluene- d_8 acted as a better ^2H source, showing a triplet:doublet ratio of 4:1 in the ^{31}P NMR spectrum due to $^1J_{\text{P-D}}$ and $^1J_{\text{H-D}}$ coupling, respectively. Addition of one equivalent of water or D_2O also showed the incorporation of ^1H or ^2H , respectively.

Radical reactions have become increasingly important in organic synthesis and are commonly used as key steps in the construction of pharmaceutically relevant compounds and natural products.^{22–24} An interesting possibility would be to use frustrated radical pairs in further synthetic reactions. To this end, the reaction of **1a** with the FLP was performed in the presence of styrene.²⁵ This led to the β -functionalization of the olefin to yield the *E*-isomer of the heterocoupled product **5a** (Scheme 3). Optimization of the reaction conditions revealed that an excess of styrene is necessary to ensure maximal yields, as using one equivalent limited the product yield (11% versus 52% using one equivalent or excess, respectively, for **5a**). In addition, the reaction of **1b** with 4-fluorostyrene in various solvents revealed that chloro- or bromo-benzene, dichloromethane, and chloroform result in similar yields ($\sim 40\%$), whereas acetonitrile shuts down reactivity altogether. Conversely, tetrahydrofuran (THF) afforded the best recovered yield of 85% for **5x** (Scheme 3). In THF, the observed purple coloration is much fainter, indicating a lower concentration of $[\text{PMes}_3]^+$ due to coordination of THF to the borane, thus metering the equilibrium between the THF- $\text{B}(\text{C}_6\text{F}_5)_3$ adduct and the radical formation step between $\text{B}(\text{C}_6\text{F}_5)_3$ and PMes_3 . While this has a marginally deleterious effect in terms of reaction times when compared to CDCl_3 (7 h versus 3 h, respectively), a concomitant increase in yield and purity is observed.

Having evaluated the reaction conditions, a range of commercially available styrenes were reacted with easily prepared esters (**1a–1g**) to afford the corresponding di- and tri-substituted olefins (**5a–5ai**) in moderate to good yields (36%–85% yield; Scheme 3; Figures S1–S120 and S124–S125; Tables S4–S5). The reaction was amenable to styrenes bearing weakly electron-donating and electron-withdrawing substituents. Substitution on the ester moiety was tolerated, allowing the introduction of both electron-deficient (**5a–5h**) and electron-rich (**5u–5y**) functionalities. The 9*H*-fluorenyl moiety could also be introduced (**5i–5m**). The reaction was not limited to esters that generate the more stable benzhydryl radicals $[\text{HCAr}_2]^\cdot$, with unsymmetrical esters bearing either cyclohexyl or methyl groups also being tolerated, delivering the desired products in good yields (**5z–5ae**). However, it was observed that a combination of electron-rich esters and electron-deficient styrenes leads to the formation of a complex mixture of products. These results indicate that a more stabilized radical translates into better yields due to longer lifetimes.¹⁸

In addition to monosubstituted styrenes and symmetrical 1,1-disubstituted olefins, unsymmetrical 1,1'-disubstituted olefins could also be used. Styrenes bearing an α -cyclohexyl moiety furnished the desired trisubstituted olefin products in moderate to good yields, with *Z*:*E* ratios up to 6:1. α -Methyl-styrene was also used to probe this FLP-mediated radical coupling further (Scheme 3). The *E*-isomer of the C–C heterocoupled product **5ai** was formed in 30% yield. However, another product was evident in solution, which was determined to be the result of hydrogen abstraction at the methyl group, yielding the *exo*-vinyl product **6** as the major product (59% yield) (see also Figures S131 and S132). Other metal-free approaches toward analogous products involve the formation of the *endo*-olefin product; hence, it is noted that our conditions offer a complementary approach to the formation of the more





Scheme 4. Reaction Mechanism

Postulated mechanism of the C–H activation and C–C bond-forming reaction.

challenging *exo*-olefin product.²⁶ The reactions with olefins were predominantly limited to those bearing an aryl substituent, and with the exception of the formation of **5h** and **5t**, other alkyl-substituted olefins such as cyclohexene gave slow and unselective reactions.

Proposed Mechanism

Considering the observed reactivity, as well as the EPR spectroscopic data (*vide supra*), it is speculated that the reaction proceeds in the manner outlined in [Scheme 4](#) (although alternative mechanisms could operate. For example, in the final step, in which single-electron oxidation of the radical formed after addition to the olefin by $[\text{P}(\text{Mes})_3]^{++}$ generates a benzyl cation and subsequent deprotonation by the phosphine generates the product). The reactivity to generate **5** or **6** may be rationalized when scrutinizing the steric demand about which the hydrogen atom is abstracted ([Scheme 4](#)), whereby the more exposed methyl hydrogen is abstracted by $[\text{P}(\text{Mes})_3]^{++}$. DFT calculations ([Tables S18–S24](#); [Figure S133](#)) using the PW6B95-D3 functional^{19,20} and the def2-tzvp basis set confirmed this

Scheme 3. Substrate Scope

C–H activation and C–C coupling using the $\text{P}(\text{Mes})_3/\text{B}(\text{C}_6\text{F}_5)_3$ FLP.

^aReactions performed on a 0.2-mmol scale.

^bZ:E ratio was determined by 2D-NMR spectroscopy.

assertion. Compound **6** was found to be fractionally more stable than **5ai** by 0.8 kcal/mol, although this difference is smaller than kT under the reaction conditions, suggesting marginal selectivity. However, when the pathways toward **5ai** and **6** were compared, the barrier for formation of **6** was found to be 3.4 kcal/mol, while for **5ai** the barrier was determined to be 4.5 kcal/mol. The higher barrier for **5ai** can be attributed to molecular deformations to provide access to hydrogen at the β -position and the greater availability of the methyl hydrogen to the phosphorus center, thus explaining the larger yield of **6**.

In conclusion, we have shown that the $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$ FLP reacts with diaryl substituted esters via a single-electron transfer pathway, as observed using EPR spectroscopy. This reactivity can be used as a powerful metal-free tool for C–H activation and C–C bond formation. The synthesized olefins show high stereoisomeric purity, yielding solely the *E*-isomer when styrene precursors are used. This work provides a strong basis for further FLP-mediated single-electron reactions, a topic that is vastly underrepresented in the field of main group and FLP chemistry.

EXPERIMENTAL PROCEDURES

General

Full experimental methods are provided in [Methods S1](#).

DATA AND CODE AVAILABILITY

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under accession numbers CCDC: 1862560–1862561, 1915381, and 1915382. These data can be obtained free of charge from the CCDC at http://www.ccdc.cam.ac.uk/data_request/cif. Information about the data that underpin the results presented in this article, including how to access them, can be found in the Cardiff University data catalog at <https://doi.org/10.17035/d.2020.0091287984>. All other data are available from the lead contact upon reasonable request.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.xcrp.2020.100016>.

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AUTHOR CONTRIBUTIONS

Y.S. initiated the project and designed the initial experiments. A.D. developed the synthetic scope of the reactions. A.D., T.A.G., Y.S., K.S., V.Y.V., and D.W. performed the synthetic studies. D.M.C.O. and L.C.W. carried out the single-crystal X-ray diffraction studies. E.R. performed the EPR experiments. B.S. performed the DFT calculations. R.L.M., A.D., Y.S., and D.W. designed the experiments. L.C.W., D.W., and R.L.M. wrote the manuscript. All of the authors analyzed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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