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N,*N*-Addition of Frustrated Lewis Pairs to Nitric Oxide: An Easy Entry to a Unique Family of Aminoxyl Radicals

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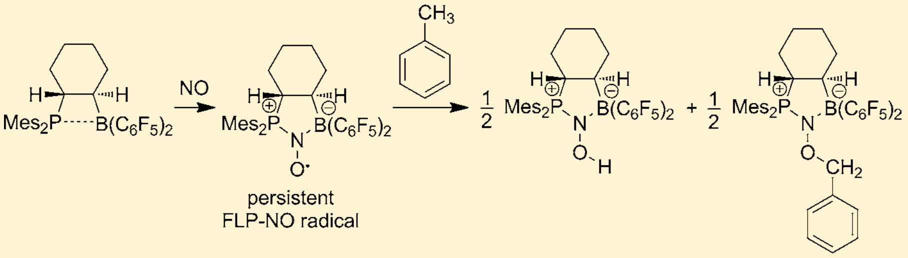
Ⓢ *Supporting Information*



ABSTRACT: The intramolecular cyclohexylene-bridged P/B frustrated Lewis pair [$Mes_2P—C_6H_{10}—B(C_6F_5)_2$] **1b** reacts rapidly with NO to give the persistent FLP-NO aminoxyl radical **2b** formed by P/B addition to the nitrogen atom of NO. This species was fully characterized by X-ray diffraction, EPR and UV/vis spectroscopies, C,H,N elemental analysis, and DFT calculations. The reactive oxygen-centered radical **2b** undergoes a H-atom abstraction (HAA) reaction with 1,4-cyclohexadiene to give the diamagnetic FLP-NOH product **3b**. FLP-NO **2b** reacts with toluene at 70 °C in an HAA/radical capture sequence to give a 1:1 mixture of FLP-NOH **3b** and FLP-NO—CH_2Ph **4b**, both characterized by X-ray diffraction. Structurally related FLPs [$Mes_2P—CHR^1—CHR^2—B(C_6F_5)_2$] **1c**, **1d**, and **1e** react analogously with NO to give the respective persistent FLP-NO radicals **2c**, **2d**, and **2e**, respectively, which show similar HAA and O-functionalization reactions. The FLP-NO—CHMePh **6b** derived from 1-bromoethylbenzene undergoes NO—C bond cleavage at 120 °C with an activation energy of E_a = 35(2) kcal/mol. Species **6b** induces the controlled nitroxide-mediated radical polymerization (NMP) of styrene at 130 °C to give polystyrene with a polydispersity index of 1.3. The FLP-NO systems represent a new family of aminoxyl radicals that are easily available by *N*,*N*-cycloaddition of C_2-bridged intramolecular P/B frustrated Lewis pairs to nitric oxide.

■ INTRODUCTION

The number of examples of sterically encumbered, persistent aminoxyl radicals (or nitroxyl radicals or nitroxides, as they are sometimes synonymously called) is steadily increasing, and they are utilized for diverse applications.[1,2] They have long been used as essential reagents for controlling free-radical polymerization processes (nitroxide-mediated polymerization, NMP).[3] This leads to marked changes in the properties of the obtained polymers principally because of a dramatic reduction of their polydispersities.[4] Frustrated Lewis pair (FLP) chemistry is a significant emerging field in the chemical sciences.[5] It is characterized by the modification of pairs of Lewis acids and Lewis bases such that they become coexistent in solution,[6] usually achieved by introducing appropriate steric bulk.[7] Frustrated Lewis pairs can have their active Lewis acid/Lewis base components react separately (i.e., conventionally) with added substrates, but they typically have the potential to undergo cooperative reactions,[5,8] which distinguishes them from classical Lewis-acid- or Lewis-base-catalyzed reactions. The cooperative FLP reactions are then more favorable than the sum of their three (or more) hypothetical bilateral reaction parts (i.e., better than additive). It seems that cooperative FLP behavior often becomes favored by (or may even require) weak interactions between the bulky Lewis acid/Lewis base components. Reactive FLPs[5,8] have been used extensively in small-molecule activation or binding.

Many FLP examples have been shown to react in sometimes unique ways with dihydrogen,[6,9−11] organic carbonyl compounds,[12] alkenes,[13] alkynes,[14] conjugated π-systems,[15] and even CO_2[16] or N_2O.[17] We recently combined the seemingly unrelated fields of N-oxyl radicals and frustrated Lewis pair

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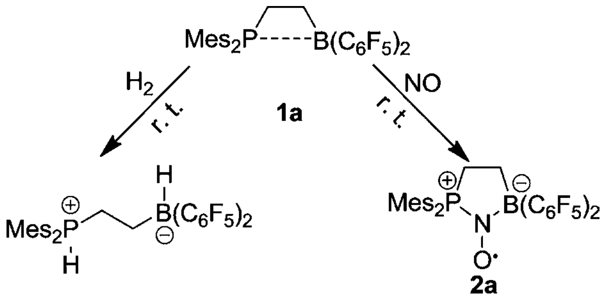
chemistry through capture of NO by an FLP. The intramolecular ethylene-bridged frustrated Lewis pair **1a**, one of the most active hydrogen-activating FLPs,[18] cleanly reacts with nitric oxide. The phosphorus Lewis base and the boron Lewis acid components of FLP **1a** add to the nitrogen atom of NO to give the new heterocyclic "FLP-NO" N-oxyl radical **2a** (Scheme 1).[19] The new persistent aminoxyl radical **2a** was isolated as a pale blue/turquoise solid in good yield and characterized by a number of physical methods, including X-ray diffraction and electron paramagnetic resonance (EPR) spectroscopy. Somewhat surprisingly, it is significantly more reactive than the prototypical TEMPO radical[20] in H-atom abstraction (HAA)/O-functionalization[21] reactions. Reaction with suitable organic hydrocarbon substrates R—H (cyclohexene, ethylbenzene) gives 1:1 mixtures of FLP-NOH **3a** and FLP-NO-R at room temperature. We have now substantially extended these initial findings by employing a variety of related intramolecular phosphorus/boron (P/B) FLPs for the capture of nitric oxide, which has led to a series of novel examples of this new family of FLP-NO radicals. In this report, we illustrate their syntheses, structures, and chemical reactivities, which include HAA and O-functionalization pathways along with their use in NMP. We also discuss their electronic structures, which rationalize the O-centered reactivity of NO upon capture by these FLPs.

Scheme 1



■ RESULTS AND DISCUSSION

Formation and Characterization of the New FLP-NO Radicals. Dimesitylcyclohexenylphosphane undergoes clean hydroboration with Pier's borane [$HB(C_6F_5)_2$][22] to yield the intramolecular P/B frustrated Lewis pair **1b**, which is a powerful H_2-activating system (Scheme 2).[23] It is also potent toward the capture of NO. Stirring the in situ prepared frustrated Lewis pair **1b** in pentane under a NO atmosphere (2 bar) at ambient temperature resulted in precipitation of the FLP-NO adduct **2b** as a pale turquoise solid in 81% yield. Single crystals obtained by diffusion of pentane into a dichloromethane solution of **2b** allowed X-ray crystal structure analysis, which confirmed the formation of the new five-membered heterocycle by *N*,*N*-addition of the P/B Lewis pair to NO.[24] The resulting bicyclic framework is trans-fused at the bridgehead carbon atoms C1 and C2, which is a consequence of the hydroboration route[25] to its precursor **1b** (see above and Scheme 2). Inside the five-membered core of **2b**, we find characteristic bond lengths of P1—N1 = 1.719(2) Å and B1—N1 = 1.597(3) Å, along with a P1—N1—B1 angle of 115.9(1)°.[26] The coordination geometry at the nitrogen atom N1 is trigonal planar (sum of bond angles at N1 = 359.9°). The N1—O1 bond is still relatively short at 1.296(2) Å, which indicates a substantial degree of N—O multiple-bond character, but it is, of course, much longer than the nitric oxide N—O distance of 1.151 Å.[27] The N1—O1 distance of 1.296(2) Å in **2b** compares well with the N—O bond lengths in **2a** (see Scheme 1 and Table 1) and in TEMPO [1.284(8) Å][28] or *t*-Bu_2N—O [gas-phase value = 1.28(2) Å][29] (see Scheme 3).

Scheme 2

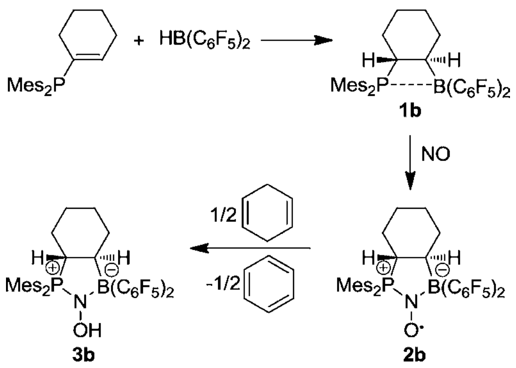
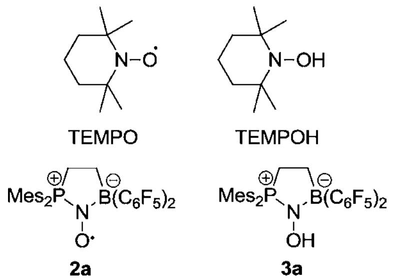


Table 1. Selected Structural Data for FLP-NO Radicals 2 and Corresponding Diamagnetic FLP-NOH Compounds 3[a,b]

compound	N—O	N—P	N—B	P—N—B	angle sum at N
2a[19]	1.296(2)	1.713(1)	1.592(2)	114.3(1)	360.0[19]
3a[19]	1.422(2)	1.632(2)	1.561(3)	114.3(1)	359.8[19]
2b	1.296(2)	1.719(2)	1.597(3)	115.9(1)	359.9
3b	1.430(3)	1.631(2)	1.559(4)	119.9(2)	360.0
2c	1.304(2)	1.707(2)	1.581(2)	116.2(1)	360.1
3c	1.430(3)	1.631(2)	1.564(4)	119.6(2)	359.8
2d	1.325(3)	1.686(3)	1.589(5)	116.1(2)	359.9
3e	1.432(3)	1.624(3)	1.576(4)	118.7(2)	359.9

[a] For the structural formulas, see Schemes 2–4 and Figure 1. [b] Bond lengths in angstroms, angles in degrees.

Scheme 3



Compound **2b** exhibits a multiline EPR spectrum at room temperature in fluorobenzene solution that results from coupling of the unpaired electron to ^{14}N, ^{31}P, and $^{11/10}B$ nuclei (see Table 2 and Figure 2). Simulation of the signal centered at $g = 2.0084$ gives $A(^{14}N) = 20.4$ MHz, $A(^{31}P) = 50.5$ MHz, and $A(^{11}B) = 8.9$ MHz (coupling to ^{10}B neglected). Although these hyperfine couplings are closely related to those found for **2a** (Table 2),[19] $A(^{14}N)$ in these P/B FLP-NO species is significantly lower than found in the related aminoxyl radicals TEMPO[30] and *t*-Bu_2NO[31] (43.5 and 43.3 MHz, respectively, in toluene).

FLP-NO radical **2b** features a UV/vis spectrum characterized by a long-wavelength absorption at $\lambda_{max} = 708$ nm (5.0 M^{-1}

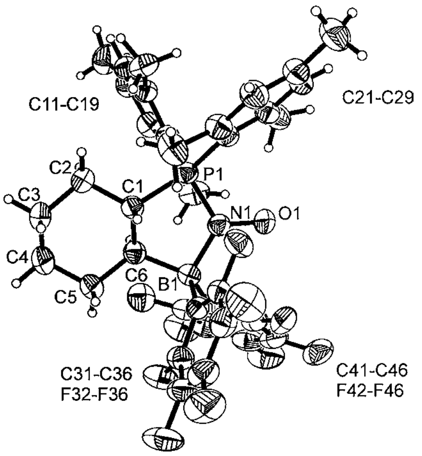


Figure 1. Molecular structure of compound **2b**.

Table 2. Spectroscopic Parameters of FLP-NO Radicals 2 in Fluorobenzene Solution at Room Temperature[a]

	EPR[b,c]				UV/vis[d]
compound	g	$A(^{14}N)$	$A(^{31}P)$	$A(^{11}B)$	λ (ε)
2a[19]	2.0089	18.5 [16.7]	48.5 [46.9]	9.1 [10]	705 (6.7)
2b	2.0084	20.4 [17.4]	50.5 [46.7]	8.9 [10.1]	708 (5.0)
2c	2.0085	19.5 [16.9]	50.5 [47.7]	9.0 [10.1]	712 (4.2)
2d	2.0081	19.5 [17]	50.5 [46.4]	9.1 [10.1]	708 (6.1)
2e	2.0083	20.7 [18.2]	51.0 [47.4]	9.0 [9.5]	754 (9.1)

[a]For structures, see Schemes 2–4 and Figure 1. [b]EPR parameters obtained by simulation. [c]A in megahertz, ^{10}B contribution neglected, DFT-calculated values in brackets. [d]λ in nanometers, ε in M^{-1} cm^{-1}.

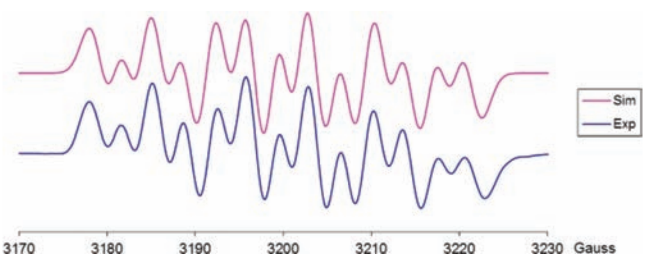


Figure 2. X-band EPR spectrum and simulation for **2b** (fluorobenzene, room temperature).

cm^{-1}). Similarly to **2a**, it features vibronic coupling with an average spacing of 1097(24) cm^{-1} (see Figure 3). Because the NO stretch in analogue **2a** appears at 1474 cm^{-1} [$\nu(^{15}NO)$ = 1457 cm^{-1}], a value consistent with some N—O multiple-bond character, this lower energy vibration corresponds to the electronic excited state of **2b** expected to have a reduced N—O bond order. For instance, **2a** exhibits a vibronic coupling of 1109(11) cm^{-1} in its optical spectrum, whereas **3a** features a N—O single bond with a N—O stretch at 1110 cm^{-1} [$\nu(^{15}NO)$ = 1082 cm^{-1}].[19]

The structural and electronic features of FLP-NO radical **2b** were manifested by DFT calculations (see Table 3). Calculated Mulliken spin-density populations indicate that the FLP-NO radical is slightly more oxygen-centered as compared to TEMPO, with the unpaired electron density strongly biased toward oxygen (O, 0.54 e^-; N, 0.33 e^-; see Scheme 3 and Table 3).[19] Computed isotropic hyperfine couplings nicely support the experimental results (Table 2; see the Supporting Information for further details).

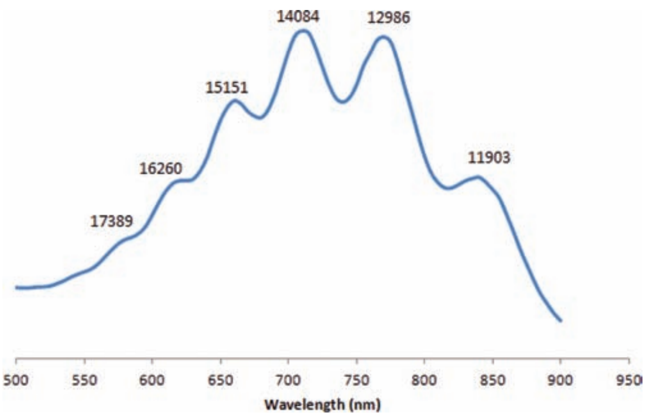


Figure 3. Vibrational fine structure present in the optical spectrum of **2b** (fluorobenzene, room temperature). Numbers that appear as labels indicate the peak positions in cm^{-1}.

Table 3. Calculated Mulliken Spin-Density Populations of FLP-NO Radicals 2 and Calculated Bond Dissociation Enthalpies (Δ*H*) of Corresponding FLP-NOH Compounds 3[a]

	2		3
compound	$N^{\bullet b}$	$O^{\bullet b}$	ΔH(O—H) (kcal mol^{-1})
a	0.33	0.54	75.8
b	0.33	0.54	74.8
c	0.32	0.54	76.0
d	0.33	0.54	75.5
e	0.34	0.54	73.9
TEMPO	0.44	0.50	65.0

[a]All values taken from the TPSS-D3/def2-TZVP calculations. [b]Mulliken spin-density populations (electrons).

Consistent with its O-centered radical character, **2b** readily undergoes a hydrogen-atom abstraction (HAA) reaction with C—H bonds of modest strength such as 1,4-cyclohexadiene [C—H bond dissociation energy (BDE) ≈ 76 kcal/mol].[39] Addition of this H-atom donor to **2b** readily resulted in the formation of the diamagnetic FLP-NOH compound **3b** (see Scheme 2). It shows typical borate (δ ^{11}B = −4.6) and phosphonium (δ ^{31}P = +48.9) heteronuclear NMR resonances and a ^1H NMR —OH signal at 4.36 (1H, d, $^3J_{PH}$ = 10 Hz). The X-ray crystal structure analysis (see Figure 4 and Table 1)

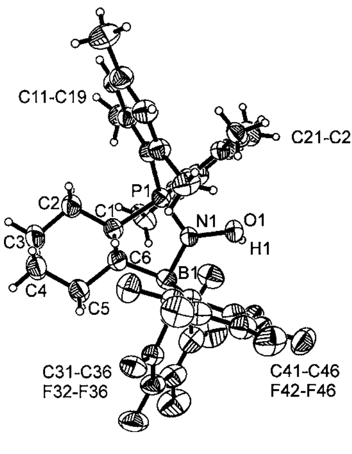
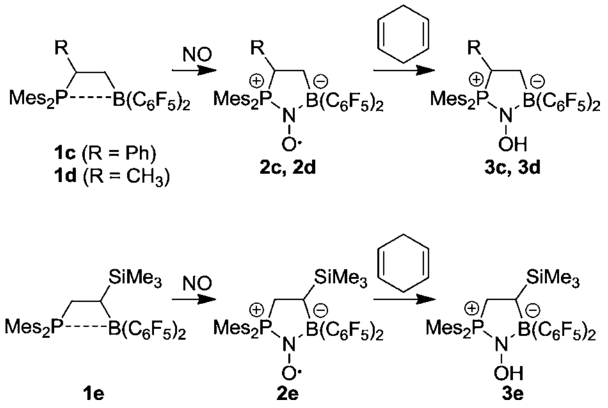


Figure 4. Molecular structure of FLP-NOH compound **3b**.

reveals the N—OH unit. Its N1—O1 bond is much longer [1.430(3) Å] than that in the FLP-NO radical [**2b**, 1.296(3) Å] from which it was derived. The nitrogen coordination of **3b** in the crystal is again trigonal-planar, but here the P1—N1 bond [1.631(2) Å] is markedly shorter than that in **2b** [1.719(2) Å] and even the B1—N1 bond in the [N]—OH compound **3b** is slightly shorter [1.559(4) Å] than the B—N bond in the radical **2b** [1.597(3) Å].

NO capture by C_2-bridged P/B FLPs appears general. FLPs **1c** and **1d**,[18] which have each a single aryl (**1c**) or alkyl (**1d**) substituent attached at the C_2 bridge, cleanly react with NO to give the respective FLP-NO radicals (**2c**, **2d**), isolated as turquoise solids in good yields (**2c**, 69%; **2d**, 63%) (Scheme 4).

Scheme 4



The closely related FLP **1e**, which bears a —$SiMe_3$ substituent at the bridging carbon atom adjacent to boron, also reacts readily to form the respective FLP-NO radical **2e**, which was isolated in 67% yield (Scheme 4).These new FLP-NO species **2c**–**2e** are similar in electronic structure to **2a** and **2b**, as judged by their EPR spectra as well as supporting DFT calculations (for further details, see Tables 2 and 3 and the Supporting Information). The X-ray structure of **2d** shows the typical twist-like conformation[40] of the central five-membered heterocycle featuring the planar tricoordinate coordination environment at the central nitrogen atom and the nonplanar arrangement of the —$CH(CH_3)$—CH_2— unit at the "backside" of the molecule bridging the Mes_2P and $B(C_6F_5)_2$ units. The bonding parameters in **2d** around nitrogen are similar to those found for the other FLP-NO radicals (see Table 1): The N1—O1 bond is quite short [1.325(3) Å]. The X-ray structure of phenyl-substituted FLP-NO radical **2c** exhibits similar metrical parameters (for details, see Table 1 and the Supporting Information).

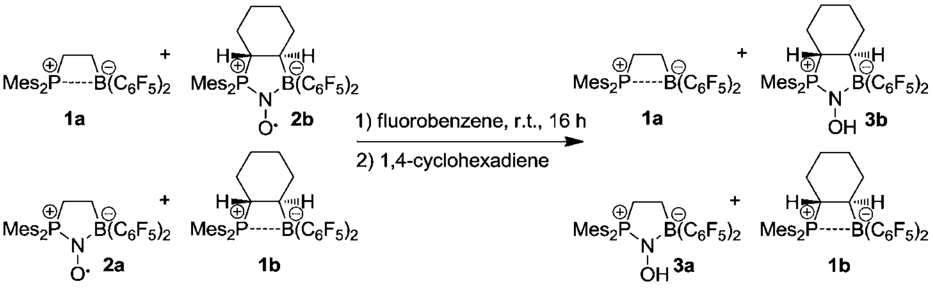
All of the FLP-NO radicals **2c**–**2e** readily undergo HAA reactions with 1,4-cyclohexadiene at room temperature to form the respective FLP-NOH compounds in good yields (see Scheme 4; **3c**, 63%; **3d**, 57%; **3e**, 62%). The diamagnetic products **3c**–**3e** were characterized by NMR spectroscopy. As a typical example, the methyl-substituted system **3d** shows heteronuclear NMR resonances at $\delta = -6.3$ (^{11}B) and $\delta = +52.4$ (^{31}P). It features ^{19}F NMR signals of a pair of diastereotopic —C_6F_5 groups at boron and a pair of diastereotopic mesityl substituents at phosphorus (for details, see the Experimental Section and the Supporting Information). In addition, the [P]—$CH(CH_3)$—CH_2[B] bridge of compound **3d** gives ^1H NMR signals at $\delta = 3.39$ (1H), $\delta = 1.17$ (3H, dd, $^3J_{PH} = 19.2$ Hz, $^3J_{HH} = 6.8$ Hz, CH_3), and $\delta = 1.78/1.62$ (CH_2).

We also characterized the diamagnetic FLP-NOH compounds **3c** and **3e** by X-ray diffraction. The molecular structure of compound **3e** features the typical elongated N—O bond [1.432(3) Å] found in FLP-NOH species **3a** and **3b**, as well as a nonplanar [P]—CH_2—$CH(SiMe_3)$[B] bridging unit (for structural details of the compounds **3c** and **3e**, see Table 1 and the Supporting Information). The [N]O—H bond dissociation energies of FLP-NOH compounds **3a**–**3e** were also calculated by DFT to provide a measure of the relative radical stabilization energies of the corresponding FLP-NO radicals **2a**–**2e**.

For this purpose, structural optimizations were performed at the TPSS[32] level using the large Gaussian-AO basis set def2-TZVP[33] and the resolution of identity (RI) approximation,[34,35] followed by single-point calculations at the high B2PLYP level.[36] Both methods were enhanced with the recently developed D3 dispersion correction.[37,38] Together with thermodynamic corrections, this yielded the enthalpy values given in Table 3, which have an estimated accuracy of 1–2 kcal/mol (compare the Supporting Information for further details). The obtained values (see Table 3) show that the FLP-NO radicals are slightly less thermodynamically stabilized than the TEMPO reference (see Scheme 3): For example, the O—H bond dissociation enthalpy (at 298 K) for **2b** is 74.8 kcal/mol, whereas it is only 65.0 kcal/mol in TEMPO-H. We rationalize the higher [N]O—H dissociation energies in FLP-NOH species **3a**–**3e** in terms of the higher Mulliken spin-density populations at O of about 0.54 e^- for **2a**–**2e** compared to 0.50 e^- for TEMPO. These effects render the FLP-NO radicals prepared in this study quite reactive toward H-atom abstraction (HAA) reactions.

Robust FLP-NO Linkage. We see no evidence of exchange of NO between different FLPs. For instance, stirring FLP-NO species **2b** with FLP **1a** for 16 h at room temperature in fluorobenzene, followed by quenching of any FLP-NO species present with 1,4-cyclohexadiene, resulted in the exclusive

Scheme 5

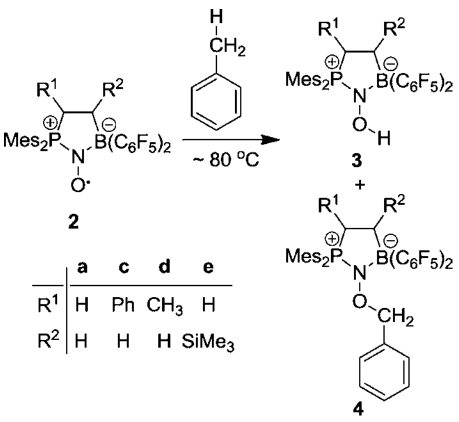


formation of FLP-NOH species **3b** (Scheme 5). Similarly, allowing FLP-NO species **2a** to stand in the presence of FLP **1b** and then quenching with 1,4-cyclohexadiene provided only FLP-NOH species **3a**. These findings are consistent with initial calculations that capture of NO is thermodynamically strongly favored [$\Delta E = -24.6$ kcal/mol and $\Delta G(298) = -11.9$ kcal/mol for **1a**][19] and irreversible under the typical conditions employed.

FLP-NO O-Centered C—H Functionalization Reactivity. FLP-NO radicals **2** functionalize relatively strong C—H bonds in substrates R—H by an HAA/radical capture sequence to initially form FLP-NOH **3**, followed by capture of $R^\bullet$ by another equivalent of FLP-NO radical **2** to give FLP-NOR.

In reactions of **2a** and **2c**–**2e** with neat toluene (C—H BDE ≈ 90 kcal/mol)[39] at 80 °C for ca. 1 h, clean HAA at the benzylic position took place to form the respective FLP-NOH compounds **3a** and **3c**–**3e**, along with the FLP-NO—CH_2Ph products **4a** and **4c**–**4e**. Compounds **3** and **4c**–**4e** were separated by column chromatography, and each compound was isolated in good yield from these experiments (typically about 40%; maximum yield = 50% because 2 equiv of **2** are required) (Scheme 6). Compounds **3a**/**4a** have not been separated as yet (present in a ratio of 1:0.8 as determined by ^{31}P NMR spectroscopy of the crude reaction mixture).

Scheme 6



	a	c	d	e
R¹	H	Ph	CH₃	H
R²	H	H	H	SiMe₃

The reaction of phenyl-substituted FLP-NO **2c** with toluene serves as an illustrative example. After FLP-NO **2c** was allowed to react in neat toluene at 80 °C for 1 h, workup and chromatographic separation gave FLP-NOH product **3c** (42%) and FLP-NO—CH_2Ph product **4c** (40%) in good isolated yields. Compound **4c** was characterized by C,H,N elemental analysis and by spectroscopy. It features a ^{31}P NMR resonance at $\delta = +50.5$ and a ^{11}B NMR signal at $\delta = -6.1$. It shows the typical sets of ^{19}F NMR signals of a pair of diastereotopic —C_6F_5 substituents at boron and the $^{1}H/^{13}C$ NMR signals of a diastereotopic pair of mesityl substituents at phosphorus, and we monitored the ABX ^{1}H NMR spin system of the [P]—CHPh—CH_2—[B] bridge at $\delta = 4.68$, 2.53, and 1.66. The products **4a**, **4d**, and **4e** show similar spectroscopic features (for details, see the Experimental Section and the Supporting Information). The X-ray structure of compound **4d** clearly reveals attachment of the benzyl group at the [N]O oxygen (see Figure 5). The central five-membered heterocyclic framework features the typical twist-like conformation with the staggered —$CH(CH_3)$—CH_2— bridge connecting the planar P—N—B unit at the front side of the molecule. Both the P1—N1 and N1—B1 bonds are rather short (see Table 4 and Figure 5). In compound **4d**, the coordination geometry at nitrogen deviates only marginally from trigonal-planar. Compound **4a** shows a very similar structure in the solid state (for details, including a view of the molecular structure, see the Supporting Information).

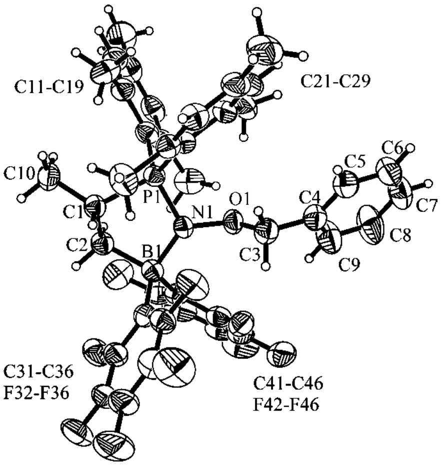


Figure 5. Molecular structure of FLP-NO-benzyl compound **4d**.

We also reacted the bicyclic FLP-NO radical **2b** with toluene. H-abstraction took place at only 70 °C in toluene solution (2 h) to give a near-quantitative yield of products **3b** and **4b** (see Scheme 7). The ^{1}H NMR spectrum of chiral compound **4b** shows the AB spin system of the benzylic O—CH_2 group at $\delta = 4.95/3.77$ ($^{2}J_{HH} = 9.6$ Hz) and a ^{13}C NMR resonance at $\delta = 76.2$. Compound **4b** shows the heteronuclear NMR resonances of its core five-membered ring at $\delta = +48.7$ (^{31}P) and -4.5 (^{11}B) and the signals of the diastereotopic pair of C_6F_5 rings at boron, as well as the mesityl substituents at phosphorus. The X-ray crystal structure analysis of **4b** features the central heterobicyclic core with a trans-fusion between the six- and five-membered ring systems (see Figure 6). The benzyl group is oriented away from the heterocyclic ring system [dihedral angle N1—O1—C50—C51 = (I) 177.0°, (II) 177.3°].

Reaction of FLP-NO radical **2b** with excess cyclohexene in benzene gave the H-abstraction product FLP-NOH **3b** in 41% yield, along with the formal allylic substitution product FLP-NO(2-cyclohexenyl) **5b** (see Scheme 8). The latter could have been formed by addition of the FLP-NO radical to the cyclohexene double bond, followed by intermolecular H-abstraction or, because FLP-NO (**2b**) is a rather reactive oxygen-centered radical, by direct allylic H-abstraction followed by radical recombination.[41] From the currently available experimental data, we cannot distinguish between these two mechanistic possibilities. Of interest is the generation of an additional chiral center that results in the formation of a pair of diastereoisomers (**5bA** and **5bB**) observed in a close-to-equimolar ratio (combined yield of 40%). The **5bA** and **5bB** diastereoisomers were separated by column chromatography and separately crystallized to allow the determination of their relative configuration by X-ray crystal structure analysis. In solution, compounds **5bA** and **5bB** show similar, yet distinct, NMR spectra. Each compound features the $^{1}H/^{13}C$ NMR signals of the cyclohexylene bridge and the O-bonded cyclohexenyl substituent.

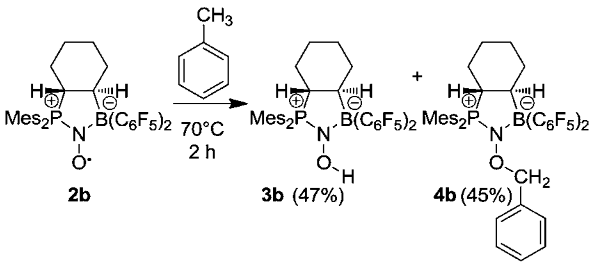
Each exhibits the signals of the pairs of diastereotopic mesityl substituents at phosphorus and C_6F_5 groups at boron.

Table 4. Selected Structural Data of FLP-NOR Compounds 4, 5, and 6bA[a,b]

compound	N—O	O—C	P—N	B—N	P—N—B	N—O—C	angle sum at N
4a	1.431(5)	1.476(6)	1.638(4)	1.580(7)	116.4(3)	111.2(4)	357.1
4b (molecule A)	1.436(2)	1.453(3)	1.647(2)	1.581(3)	118.0(1)	110.5(2)	358.4
4b (molecule B)	1.439(2)	1.454(3)	1.645(2)	1.583(3)	117.9(1)	110.6(2)	358.1
4d	1.432(2)	1.433(3)	1.646(2)	1.581(3)	116.9(1)	114.8(2)	355.5
5bA	1.440(3)	1.469(4)	1.656(3)	1.593(4)	116.1(2)	113.9(2)	354.4
5bB (molecule A)	1.436(3)	1.459(4)	1.646(2)	1.587(4)	117.1(2)	114.6(2)	357.1
5bB (molecule B)	1.440(3)	1.464(4)	1.651(2)	1.590(4)	116.3(2)	113.1(2)	356.6
6bA	1.424(4)	1.466(4)	1.664(3)	1.612(5)	115.2(2)	116.1(3)	353.6

[a] For the structural formulas, see Schemes 6–9 and Figure 5. [b] Bond lengths in angstroms, angles in degrees.

Scheme 7



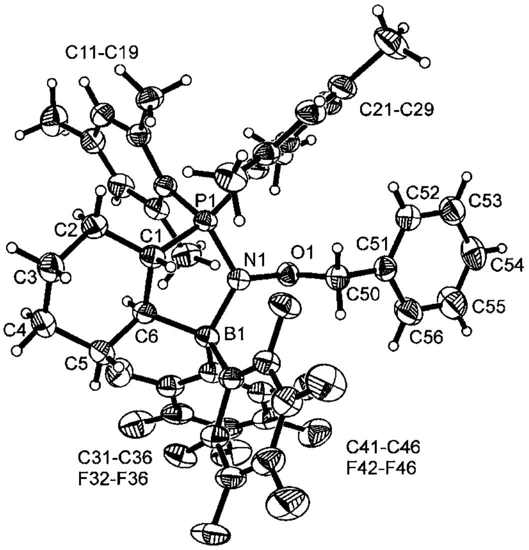


Figure 6. View of the molecular structure of one of the two independent molecules of **4b**.

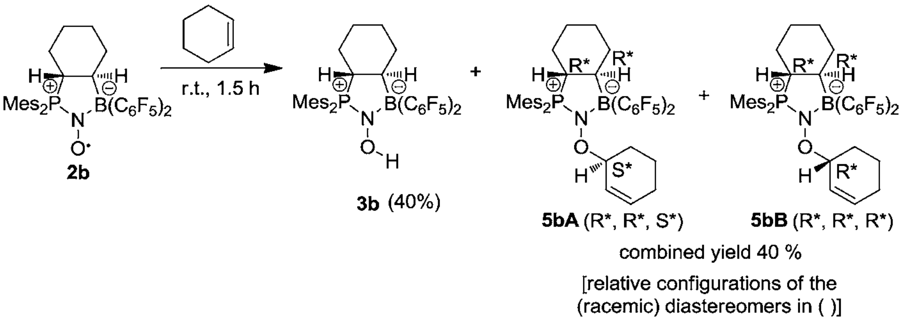
Compound **5bA** shows the heteronuclear NMR features of the five-membered core at $\delta = -4.1$ (^{11}B) and $\delta = +50.8$ (^{31}P), whereas the diastereoisomer **5bB** shows the respective NMR resonances at $\delta = -4.1$ (^{11}B) and $\delta = +51.2$ (^{31}P) (for further details, see the Experimental Section and the Supporting Information).

In the crystal, compound **5bA** shows the typical heterobicyclo[4.3.0]nonane-derived structural core with a trans-fusion between the six- and five-membered rings. The N—B and N—P bond lengths are in the typical range (see Table 4). The N—O bond is much longer than was found in the corresponding radical, and the [N]O oxygen atom has the 2-cyclohexenyl group bonded to it. Attachment of the [N]O moiety to an allylic position of the cyclohexene substituent creates a new chiral center at the carbon.

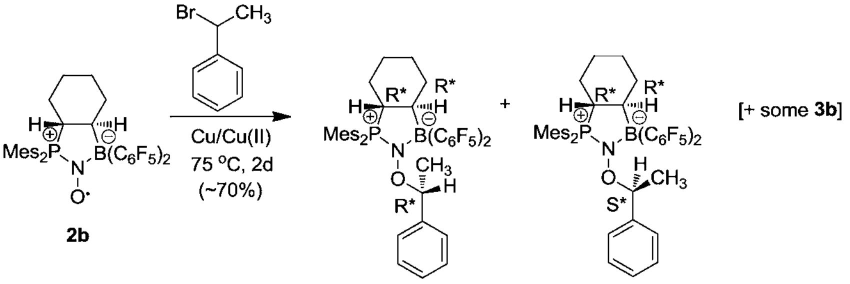
The *trans*-FLP-NO framework features two chiral centers at its bridgehead carbon atoms of defined relative configuration. Overall the (racemic) product **5bA** can, according to its X-ray crystal structure analysis, be assigned the relative configuration of *R**,*R**,*S**-**5bA**. Compound **5bB** contains two crystallographically independent molecules in the unit cell (see Table 4).

FLP-NO-Mediated Free-Radical Polymerization of Styrene. Given the robust nature of the FLP-NO moiety, it was tempting to examine the possibility of controlling radical polymerization processes of alkenes by these novel types of aminoxyl radicals derived from the capture of NO by frustrated Lewis pairs. We initiated a preliminary study involving styrene polymerization for which we would need a diamagnetic benzylic FLP-NO—CH(R)Ph-type precursor with a sufficiently low O—C bond dissociation energy. Because the rigid nature of the cyclohexenyl P/B backbone could help ensure stability at high temperatures, we chose the ethylbenzene derivative **6b** to serve as an initiator (see Scheme 9 and Figure 7). In principle, we could have prepared **6b** by direct reaction of **2b** with ethylbenzene, but this would have resulted in a loss of 50% of the FLP-NO starting material due to the "unproductive" formation of the stoichiometric FLP-NOH byproduct **3b** (see

Scheme 8



Scheme 9



2b

6bA
relative configurations (R*,R*,R*)

6bB
(R*,R*,S*)

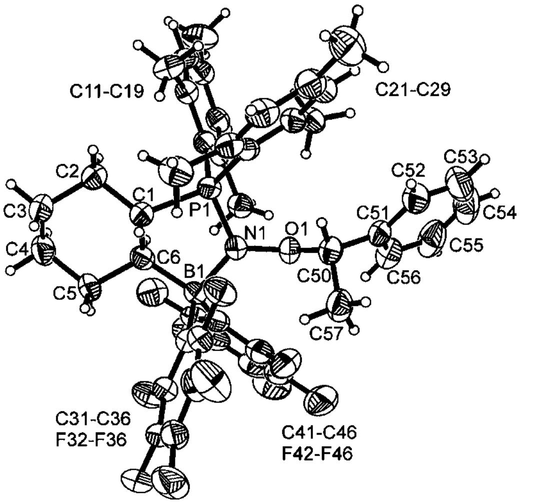
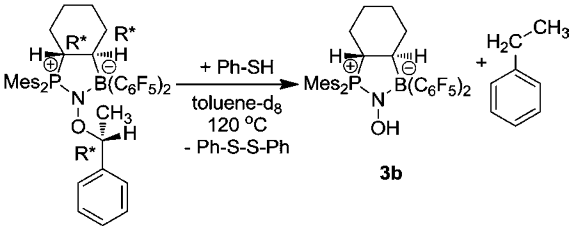


Figure 7. Molecular structure of the diastereoisomer *R**,*R**,*R**-**6bA**.

above). Therefore, we chose to prepare **6b** by a copper-mediated redox route in analogy with the respective organic alkoxy amine systems.[42] We treated the FLP-NO radical **2b** with (racemic) 1-bromoethylbenzene, Cu powder, and Cu(II) triflate in the presence of 4,4′-di-*tert*-butyl-2,2′-bipyridine (75 °C, 2 days). Workup gave a total yield of **6b** of 73%. The new product was admixed with some FLP-NOH (**3b**) contamination. Chromatography then gave the samples of the pure **6bA** (*R**,*R**,*R**) and **6bB** (*R**,*R**,*S**) diastereoisomers. The **6bA** compound showed characteristic NMR features at δ = −3.2 (^{11}B), δ = +50.3 (^{31}P), and δ = 4.38 (^{1}H, 1H, q, $^{3}J_{HH}$ = 6.4 Hz, PhCH), whereas the **6bB** diastereoisomer featured the analogous NMR signals at δ = −4.0 (^{11}B), δ = +51.9 (^{31}P), and δ = 5.15 (^{1}H, 1H, q, $^{3}J_{HH}$ = 6.6 Hz, PhCH). The X-ray structure of compound **6bA** features the typical heterobicyclic framework with a trans-junction between the rings and the 1-phenylethyl substituent bonded to the FLP-NO oxygen atom (see Table 4 and Figure 7). The relative configuration of this diastereoisomer is *R**,*R**,*R**-**6bA**.

Planning to use compound **6bA** to initiate the radical polymerization of styrene,[3] we first determined the activation barrier of the thermally induced homolytic [N]O—CHMePh oxygen−carbon bond cleavage.[2c,43] Compound **6bA** and 10 equiv of thiophenol were dissolved in deuterated toluene and sealed in an NMR tube under Ar. At 120 °C, we monitored the conversion of compound **6bA** to compound **3b** by ^{1}H NMR spectroscopy, observing an increase in the intensity of the [N]O—H signal and a decrease in the intensity of the benzylic H in compound **6bA**. This reaction takes place by homolytic cleavage of the [N]O—CHMePh oxygen−carbon bond, resulting in the formation of the FLP-NO **2b** and a benzylic radical. Each of these radicals quickly abstracts hydrogen atoms from thiophenol, giving ethylbenzene and FLP-NOH **3b** (see Scheme 10).

Scheme 10

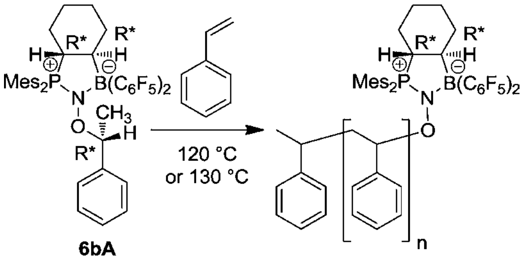


3b

6bA
(R*,R*,R*)

Kinetic data were plotted to determine the dissociation rate constant, k_d, of 1.7(5) × 10^{-4} s^{-1} at 120 °C. The activation energy (E_a) for the thermally induced homolytic [N]O—CHMePh oxygen−carbon cleavage in compound **6bA** was calculated using the Arrhenius equation. Assuming an Arrhenius *A* factor of 2.4 × 10^{14} s^{-1}, which is typical for C—O bond homolysis of styryl-derived alkoxyamines,[44] we found an E_a value of 34.9 kcal/mol. This value is significantly larger than E_a for the C—O bond homolysis of styryl-TEMPO, which lies at 31.8 kcal/mol.[44] This observation is in line with the generally higher reactivity of the FLP-NO-radicals compared to TEMPO, as reflected by their higher spin density at oxygen and their larger H—O bond dissociation energies in the corresponding hydroxylamines (see above). We then conducted nitroxide-mediated polymerizations of styrene with alkoxyamine **6bA** as the initiator/regulator (Scheme 11). Reactions were performed in sealed tubes in neat styrene at

Scheme 11. NMP of Styrene with Alkoxyamine 6bA as the Initiator/Regulator



6bA

Table 5. Autopolymerization of Neat Styrene and NMP of Styrene with 0.5% Initiator/Alkoxyamine 6bA: Variation of Temperature and Polymerization Time

entry	initiator (mol %)	time (h)	temp (°C)	conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,exp}$ (g/mol)	PDI
1	0.5	3	120	39	8200	35100	1.35
2	0.5	2	130	98	20000	34300	1.30
3[a]	0.5	3	120	36	8800	40500	1.35
4[a]	0.5	2	130	89	18100	29700	1.34
5	–	2	130	36	–	271700	1.61

[a] Free aminoxyl radical **2b** (0.025%) was added.

120 and 130 °C for 2−3 h under argon using 0.5 mol % **6bA**. Conversion to polystyrene was determined gravimetrically, and the molecular weight and polydispersity index (PDI) of the polymers were analyzed by size-exclusion chromatography (SEC) (Table 5). All polymers obtained showed well-defined molecular weights and PDIs below the theoretical limit of 1.5 that can be obtained for a noncontrolled radical polymerization. For instance, at 120 °C, we isolated polystyrene (PS) in a moderate yield (39%) with a number-average molecular weight (M_n) of 35100 g/mol and a PDI of 1.35 (entry 1). We noted that, at this temperature, a significant amount of alkoxyamine **6bA** remained unreacted. This is in agreement with the high activation energy measured for the C—O bond homolysis in **6bA**. Consequently, the experimentally determined M_n value was far larger than the theoretical calculated M_n value in this case. Therefore, we repeated polymerization at a higher temperature (130 °C) for a decreased reaction time of 2 h (entry 2). Pleasingly, under these conditions, polymerization occurred with high conversion (98% yield), giving PS with a M_n of 34300 g/mol and marginally narrower PDI (1.30). Unreacted alkoxyamine **6bA** was no longer identified (entry 2). Note that, at a polymerization temperature of 130 °C, styrene autopolymerization already contributes to a significant extent (entry 5). We decided to add free FLP-NO **2b** to control the growth of polymer chains started by the autoinitiation process (entries 3 and 4). As expected, in the presence of free aminoxyl radical, conversion slightly decreased. However, the PDI and M_n values were not significantly altered.

CONCLUSIONS

The use of *intramolecular* P/B FLPs to capture NO to form the unique family of versatile, nitroxide-like species **2** seems crucial. We showed previously that the intermolecular frustrated Lewis pair t-$Bu_3P/B(C_6F_5)_3$ disproportionates nitric oxide[19] to give a combination of the known t-$Bu_3P—O—B(C_6F_5)_3$ and known t-$Bu_3P—N{=}N—O—B(C_6F_5)_3$ addition product,[17] closely related to the NO reactivity of phosphanes in the absence of a Lewis acid.[45] By directly enabling the synergistic effects of the phosphane Lewis base and borane Lewis acid upon initial contact with NO in solution, our C_2-linked intramolecular FLPs (**1**) react differently with NO, delivering five-membered heterocycles reminiscent of nitroxides through *N,N*-cycloaddition of NO.

A combination of experimental and theoretical studies points to the considerable stability of the FLP-NO linkage that results in a family of readily isolable, turquoise species **2** that bear significant resemblance to organic aminoxyl radicals such as TEMPO. The new FLP-NO radicals **2** exhibit greater oxygen-centered HAA/O-atom functionalization chemistry as compared to the ubiquitous TEMPO radical, owing to significant polarization of the unpaired electron density toward the O atom in this family of FLP-NO species **2**. Thus, capture of NO by these readily prepared intramolecular frustrated Lewis pairs (**1**) results in a dramatic activation of NO toward HAA and C—H functionalization reactions. Whereas NO is typically a very poor partner in HAA reactions owing to the modest H—NO bond strength of 47 kcal/mol,[39] capture and activation of NO by the FLP provides a "spin-density Umpolung" toward the O-atom, dramatically enhancing its reactivity. The resulting FLP-NO radicals are highly valuable new members of the important family of aminoxyl radicals. Their easy and straightforward preparation from readily available FLPs through simple reaction with NO, their thermodynamic stability, and their persistence as sterically hindered oxygen-centered radicals will probably offer many new and interesting uses, especially because their structures can probably be specifically tailored to suit the needs of a particular application.

EXPERIMENTAL SECTION

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) in dry solvents under an atmosphere of argon. NMR spectra were recorded on a Varian Inova 500 spectrometer (^{19}F, 470 MHz; ^{11}B, 160 MHz; ^{31}P, 202 MHz) and on a Varian UnityPlus 600 spectrometer (^{19}F, 564 MHz; ^{11}B, 192 MHz; ^{31}P, 243 MHz). For ^{19}F NMR spectra, chemical shifts δ are given relative to $CFCl_3$ (external reference); for ^{11}B NMR spectra, chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference); and for ^{31}P NMR spectra, chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments were supported by additional two-dimensional NMR experiments. Elemental analyses were performed on an Elementar Vario El III instrument. IR spectra were recorded on a Varian 3100 FT-IR spectrometer (Excalibur Series). Melting points and decomposition points were obtained with a DSC 2010 differential scanning calorimeter (TA Instruments). High-resolution mass spectrometry (HRMS) was performed on a GTC Waters Micromass instrument (Manchester, U.K.). Size-exclusion chromatography (SEC) was carried out with degassed tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at room temperature on a system consisting of a Smartline Pump 1000 solvent delivery system (Knauer), a set of two PLgel 5 μm MIXED-C columns (300 × 7.5 mm, Polymer Laboratories), and a Knauer refractive index (RI) differential refractometer detector. Data were analyzed with PSS WinGPC Compact V.7.20 software (Polymer Standards Service) based on calibration curves built on polystyrene standards (Polymer Laboratories Polystyrene Medium MW Calibration Kit S-M-10 to determine the molecular weight of polystyrene) with peak molecular weights ranging from 1530 to 1319000 g/mol. For X-ray diffraction, data sets were collected with a Nonius KappaCCD diffractometer. The programs used were COLLECT (Nonius B.V., 1998) for data collection, Denzo-SMN[46] for data reduction, Denzo[47] for absorption correction, SHELXS-97[48] for structure solution, SHELXL-97[49] for structure refinement, and XP (BrukerAXS, 2000) for graphics. Thermals ellipsoids are shown with 50% probability, R values are given for observed reflections, and wR^2 values are given for all reflections.

General Procedure for Synthesis of FLP-NO Radicals 2. Bis(pentafluorophenyl)borane $[HB(C_6F_5)_2]$ (Pier's borane) and the corresponding alkenylphosphane were dissolved in equivalent amounts in *n*-pentane to produce a yellow solution of compound **1**. The solution was cooled to −78 °C, the cooling bath was removed, and NO gas was added to the flask containing the solution (1.5−2.0 bar, manometer pressure). The color of the solution changed to greenish, and a precipitate was formed within a few minutes; after some time, the color of the reaction mixture changed to brown. After the reaction mixture had been stirred for 45 min at room temperature, the gas pressure was released, and the solvent was removed by a filter canula. The residue was washed with *n*-pentane and dried under a vacuum to reveal a turquoise solid. Crystallization was carried out by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of **2** at −35 °C.

2b: Cyclohexenyldimesitylphosphane (643 mg, 1.83 mmol) and $HB(C_6F_5)_2$ (632 mg, 1.83 mmol) in *n*-pentane (50 mL) were stirred for 1 h at room temperature to produce **1b**. Reaction of **1b** with NO (2.0 bar, manometer pressure) gave **2b** (1.057 g, 81%, turquoise crystals). HRMS: calcd for $C_{36}H_{32}NOPBF_{10}Na$, 749.20471; found, 749.20420. X-ray crystal structure analysis of **2b**: formula $C_{36}H_{32}BF_{10}NOP\cdot{}^1/_2C_5H_{12}$, M = 762.48, colorless crystal, 0.13 × 0.10 × 0.07 mm, a = 8.6599(3) Å, b = 10.7452(8) Å, c = 21.1333(6) Å, α = 84.775(4)°, β = 82.784(2)°, γ = 86.802(5)°, V = 1940.86(17) Å^3, ρ_{calc} = 1.305 g cm^{-3}, μ = 1.326 mm^{-1}, empirical absorption correction ($0.846 \le T \le 0.913$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 20588 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 6626 independent (R_{int} = 0.050) and 5437 observed reflections [$I > 2\sigma(I)$], 502 refined parameters, R = 0.049, wR^2 = 0.133, max (min) residual electron density = 0.69 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2c: 1-Phenylethenyldimesitylphosphane (500 mg, 1.34 mmol) and $HB(C_6F_5)_2$ (465 mg, 1.34 mmol) in *n*-pentane were stirred for 30 min at room temperature to produce **1c**. Reaction of **1c** with NO (1.5 bar, manometer pressure) gave **2c** (687 mg, 69%, green crystals). HRMS: calcd for $C_{38}H_{30}NOPBF_{10}Na$, 771.18971; found, 771.18998. X-ray crystal structure analysis of **2c**: formula $C_{38}H_{30}BF_{10}NOP$, M = 748.41, colorless crystal, 0.42 × 0.25 × 0.17 mm, a = 11.6585(3) Å, b = 16.4256(5) Å, c = 18.7671(4) Å, β = 106.113(1)°, V = 3452.68(16) Å^3, ρ_{calc} = 1.440 g cm^{-3}, μ = 1.485 mm^{-1}, empirical absorption correction ($0.574 \le T \le 0.786$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 27234 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 5999 independent (R_{int} = 0.045) and 5419 observed reflections [$I > 2\sigma(I)$], 475 refined parameters, R = 0.043, wR^2 = 0.116, max (min) residual electron density = 0.29 (−0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2d: Propenyldimesitylphosphane (140 mg, 0.45 mmol) and $HB(C_6F_5)_2$ (156 mg, 0.45 mmol) in *n*-pentane (30 mL) were stirred at room temperature for 30 min to produce **1d**. Reaction of **1d** with NO (2.0 bar, manometer pressure) gave **2d** (205 mg, 63%, green crystals). HRMS: calcd for $C_{33}H_{28}NOPBF_{10}H$, 687.19147; found, 687.19091. X-ray crystal structure analysis of **2d**: formula $C_{33}H_{28}BF_{10}NOP$, M = 686.34, colorless crystal, 0.17 × 0.07 × 0.02 mm, a = 7.9245(5) Å, b = 10.6961(5) Å, c = 18.9336(19) Å, α = 79.222(4)°, β = 79.203(7)°, γ = 88.914(3)°, V = 1548.40(2) Å^3, ρ_{calc} = 1.472 g cm^{-3}, μ = 1.597 mm^{-1}, empirical absorption correction ($0.773 \le T \le 0.969$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 15934 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 5086 independent (R_{int} = 0.064) and 3488 observed reflections [$I > 2\sigma(I)$], 431 refined parameters, R = 0.054, wR^2 = 0.128, max (min) residual electron density = 0.22 (−0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2e: *E*-(2-Trimethylsilyl)ethenyldimesitylphosphane (500 mg, 1.36 mmol) and $HB(C_6F_5)_2$ (470 mg, 1.36 mmol) in toluene (25 mL) were heated to 80 °C for 30 min. The solvent was removed under a vacuum to produce **1e**, which was dissolved in *n*-pentane (30 mL). Reaction of **1e** with NO (1.5 bar, manometer pressure) gave **2e** (670 mg, 67%, turquoise crystals). HRMS: calcd for $C_{35}H_{34}NOPBF_{10}SiNa$, 767.19729; found, 767.19913. X-ray crystal structure analysis of **2e**: formula $C_{35}H_{34}BF_{10}NOPSi$, M = 744.50, colorless crystal, 0.15 × 0.09 × 0.03 mm, a = 10.5468(3) Å, b = 10.6122(3) Å, c = 17.4537(7) Å, α = 86.333(1)°, β = 85.007(1)°, γ = 63.541(2)°, V = 1741.55(10) Å^3, ρ_{calc} = 1.420 g cm^{-3}, μ = 0.197 mm^{-1}, empirical absorption correction ($0.971 \le T \le 0.994$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 8853 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 5962 independent (R_{int} = 0.043) and 4428 observed reflections [$I > 2\sigma(I)$], 460 refined parameters, R = 0.079, wR^2 = 0.170, max (min) residual electron density = 0.36 (−0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

[For more details on the paramagnetic FLP-NO radicals, see the Supporting Information.]

General Procedure for the Preparation of Compounds 3. Compound **2** was dissolved in benzene to produce a green solution. 1,4-Cyclohexadiene (about 10 equiv) was added to the solution, and the green color instantly disappeared. The solvent was removed under a vacuum, the obtained residue was dissolved in CH_2Cl_2, and slow diffusion of *n*-pentane into this solution at −35 °C gave compound **3** as a colorless crystalline solid.

3b: 1,4-Cyclohexadiene (0.20 mL, 2.11 mmol) and **2b** (151 mg, 0.20 mmol) in benzene gave a colorless solution that was crystallized to produce compound **3b** (103 mg, 68%). The obtained crystals were suitable for an X-ray crystal structure analysis. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.03 (d, $^4J_{PH}$ = 4.0 Hz, 1H, *m*-Mes^A), 6.94 (s, 1H, *m*-Mes^B), 6.86 (s, 1H, *m′*-Mes^A), 6.75 (d, $^4J_{PH}$ = 4.0 Hz, 1H, *m′*-Mes^B), 4.34 (t, J = 8.5 Hz, 1H, OH), 3.06 (qm, $^2J_{PH} \approx {}^3J_{HH} \approx {}^3J_{HH} \approx$ 12 Hz, 1H, 1-H), 2.65 (s, 3H, *o*-CH_3Mes^A), 2.49 (s, 3H, *o*-CH_3Mes^B), 2.33 (m, 1H, 5-H), 2.31 (s, 3H, *p*-CH_3Mes^A), 2.27 (s, 3H, *p*-CH_3Mes^B), 2.17 (dm, $^3J_{HH} \approx$ 12 Hz, 1H, 2-H), 2.00 (s, 3H, *o′*-CH_3Mes^A), 1.89 (br t, $J \approx$ 12 Hz, 1H, 6-H), 1.74 (s, 3H, *o′*-CH_3Mes^B), 1.69 (br m, 1H, 3-H), 1.62 (m, 1H, 4-H), 1.19 (m, 1H, 3-H′), 1.15 (m, 1H, 4-H′), 1.09 (m, 1H, 2-H′), 0.86 (m, 1H, 5-H′). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$,298 K): δ = 144.7 (d, $^2J_{PC}$ = 7.4 Hz, *o′*-Mes^A), 144.2 (d, $^2J_{PC}$ = 6.8 Hz, *o*-Mes^B), 143.1 (d, $^5J_{PC}$ = 2.8 Hz, *p*-Mes^A), 142.4 (d, $^5J_{PC}$ = 2.9 Hz, *p*-Mes^B), 140.4 (d, $^2J_{PC}$ = 12.5 Hz, *o*-Mes^A), 139.6 (d, $^2J_{PC}$ = 14.2 Hz, *o′*-Mes^B), 132.5 (d, $^3J_{PC}$ = 10.2 Hz, *m*-Mes^B), 131.9 (d, $^3J_{PC}$ = 12.3 Hz, *m*-Mes^A), 131.6 (d, $^3J_{PC}$ = 11.0 Hz, *m′*-Mes^A), 130.7 (d, $^3J_{PC}$ = 11.6 Hz, *m′*-Mes^B), 122.6 (d, $^1J_{PC}$ = 78.2 Hz, *i*-Mes^B), 121.9 (d, $^1J_{PC}$ = 86.9 Hz, *i*-Mes^A), 46.6 (d, $^1J_{PC}$ = 58.8 Hz, C-1), 35.6 (br, C-6), 30.1 (d, $^3J_{PC}$ = 12.2 Hz, C-5), 26.5 (C-2), 26.4 (br, C-4), 26.2 (d, $^3J_{PC}$ = 14.6 Hz, C-3), 24.3 (br, *o*-CH_3Mes^A), 24.0 (d, $^3J_{PC}$ = 3.9 Hz, *o′*-CH_3Mes^A), 23.4 (d, $^3J_{PC}$ = 3.9 Hz, *o′*-CH_3Mes^B), 21.02 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3Mes^A), 20.97 (d, $^5J_{PC}$ = 1.4 Hz, *p*-CH_3Mes^B), 20.6 (d, $^3J_{PC}$ = 4.5 Hz, *o*-CH_3Mes^B), (C_6F_5 not listed). ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, 298 K): δ = −4.6 ($\nu_{1/2} \approx$ 150 Hz). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 298 K): δ = 48.9 ($\nu_{1/2} \approx$ 20 Hz). ^{19}F NMR (564 MHz, $CDCl_3$, 273 K,): δ = −127.0 (m, 1F, *o*-$C_6F_5{}^A$), −128.7 (m, 1F, *o*-C_6F_5B), −134.0 (m, 1F, *o′*-$C_6F_5{}^B$), −145.5 (m, 1F, *o′*-$C_6F_5{}^A$), −159.6 (t, $^3J_{FF}$ = 43.4 Hz, 1F, *p*-$C_6F_5{}^B$), −159.7 (t, $^3J_{FF}$ = 43.6 Hz, 1F, *p*-$C_6F_5{}^A$), −163.5 (m, 1F, *m*-$C_6F_5{}^A$), −163.9 (m, 1F, *m*-$C_6F_5{}^B$), −164.7 (m, 1F, *m′*-$C_6F_5{}^A$), −165.0 (m, 1F, *m′*-$C_6F_5{}^B$). HRMS: calcd for $C_{36}H_{33}NOPBF_{10}H$, 728.23122; found, 728.23141. IR (KBr): υ'/cm^{-1} = 3522 (s, NO-H), 2936 (m), 1641 (s), 1605 (s), 1514 (m), 1382 (s), 1278 (m). X-ray crystal structure analysis of **3b**: formula $C_{36}H_{33}BF_{10}NOP\cdot C_5H_{12}$, M = 799.56, colorless crystal, 0.35 × 0.18 × 0.08 mm, a = 17.4646(2) Å, b = 10.6452(1) Å, c = 20.7316(2) Å, β = 91.147(1)°, V = 3853.53(7) Å^3, ρ_{calc} = 1.378 g cm^{-3}, μ = 1.359 mm^{-1}, empirical absorption correction ($0.648 \le T \le 0.899$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 41168 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 6761 independent (R_{int} = 0.069) and 5252 observed reflections [$I > 2\sigma(I)$], 507 refined parameters, R = 0.058, wR^2 = 0.167, max (min) residual electron density = 0.75 (−0.42) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

3c: 1,4-Cyclohexadiene (0.1 mL, 1.06 mmol) and compound **2c** (96 mg, 0.13 mmol) in benzene gave a colorless solution that was crystallized to give compound **3c** (61 mg, 63%). The obtained crystals were suitable for X-ray crystal structure analysis. ^{1}H NMR (500 MHz, CD_2Cl_2, 183 K) (selected resonances): δ = 7.29 (d, $^3J_{HH}$ = 7.4 Hz, 1H, *o*-Ph), 7.15 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *m*-Ph), 7.09 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph), 6.83 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *m′*-Ph), 6.11 (d, $^3J_{HH}$ = 7.4 Hz, 1H, *o′*-Ph), 4.79 (br m, 1H, NOH), 4.56 (br m, 1H, 1-H), 2.27 (m, 1H, 2-H), 1.81 (br dm, $^3J_{PH} \approx$ 44 Hz, 1H, 2-H′). ^{13}C{^{1}H} NMR (126 MHz,

CD_2Cl_2, 183 K) (selected resonances): $\delta = 137.2$ (*i*-Ph), 128.9 (d, $^{3}J_{PC} = 7.1$ Hz, *o*-Ph), 127.9 (*o*′-Ph), 127.4 (*m*′-Ph), 127.3 (*m*-Ph), 127.1 (*p*-Ph), 48.4 (d, $^{1}J_{PC} = 56.2$ Hz, C-1), 29.9 (br, C-2). $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 253 K): $\delta = -4.6$ ($\nu_{1/2} \approx 250$ Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 253 K): $\delta = 45.0$ ($\nu_{1/2} \approx 80$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 183 K): $\delta = -129.8$, -132.7 (each m, each 1F, *o*′-, *o*-$C_6F_5{}^{A}$), -132.5, -143.5 (each br, each 1F, *o*′-, *o*-$C_6F_5{}^{B}$), -159.6 (1F, *p*-$C_6F_5{}^{A}$), -160.5 (1F, *p*-$C_6F_5{}^{B}$), -163.9, -164.2 (each br, each 1F, *m*-, *m*′-$C_6F_5{}^{B}$), -164.3, -164.7 (each br, each 1F, *m*-, *m*′-$C_6F_5{}^{A}$). Elemental analysis: calcd for $C_{38}H_{31}NOPBF_{10}$, C, 59.53; H, 4.44; N, 1.93; found, C, 60.19; H, 4.98; N, 1.69. IR (KBr): $\upsilon'/cm^{-1} = 3545$ (s, NO-H), 1642 (s), 1605 (s), 1513 (s), 1458 (s), 1277 (s), 1101 (s). X-ray crystal structure analysis of **3c**: formula $C_{38}H_{31}BF_{10}NOP$, $M = 749.42$, colorless crystal, 0.33 × 0.22 × 0.02 mm, $a = 10.8277(2)$ Å, $b = 11.4950(3)$ Å, $c = 14.8377(3)$ Å, $\alpha = 87.546(1)°$, $\beta = 73.836(1)°$, $\gamma = 82.013(2)°$, $V = 1756.54(7)$ Å^3, $\rho_{calc} = 1.417$ g cm^{-3}, $\mu = 1.459$ mm^{-1}, empirical absorption correction ($0.644 \le T \le 0.971$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 22323 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 5834 independent ($R_{int} = 0.066$) and 4380 observed reflections $[I > 2\sigma(I)]$, 476 refined parameters, $R = 0.052$, $wR^2 = 0.129$, max (min) residual electron density = 0.27 (−0.27) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

3d: 1,4-Cyclohexadiene (0.1 mL, 1.06 mmol) and compound **2d** (92 mg, 0.13 mmol) in benzene gave a colorless solution that was crystallized to give compound **3d** (92 mg, 57%). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) (selected resonances): $\delta = 4.73$ (t, $J = 7.3$ Hz, 1H, OH), 3.39 (m, 1H, H-1), 1.78 (m, 1H, H-2), 1.62 (ddd, $^{3}J_{PH} = 35.0$ Hz, $^{2}J_{HH} = 13.9$ Hz, $^{3}J_{HH} = 5.2$ Hz, 1H, H-2′), 1.17 (dd, $^{3}J_{PH} = 19.2$ Hz, $^{3}J_{HH} = 6.8$ Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) (selected resonances): $\delta = 38.9$ (d, $^{1}J_{PC} = 59.1$ Hz, C-1), 30.4 (br, C-2), 17.8 (d, $^{2}J_{PC} = 1.2$ Hz, CH_3). $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 298 K): $\delta = -6.3$ ($\nu_{1/2} \approx 110$ Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 298 K): $\delta = 52.4$ ($\nu_{1/2} \approx 40$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): $\delta = -131.3$ (m, 2F, *o*-$C_6F_5{}^{A}$), -138.1 (m, 2F, *o*-$C_6F_5{}^{B}$), -160.7 (t, $^{3}J_{FF} = 20.3$ Hz, 1F, *p*-$C_6F_5{}^{A}$), -161.5 (t, $^{3}J_{FF} = 20.2$ Hz, 1F, *p*-$C_6F_5{}^{B}$), -165.1 (m, 2F, *m*-$C_6F_5{}^{B}$), -165.7 (m, 2F, *m*-$C_6F_5{}^{A}$). HRMS: calcd for $C_{38}H_{31}NOPBF_{10}Na$, 772.19754; found, 772.19778. IR (KBr): $\upsilon'/cm^{-1} = 3537$ (s, NO-H), 1642 (s), 1605 (s), 1513 (s), 1460 (s), 1277 (s), 1104 (s).

3e: 1,4-Cyclohexadiene (0.1 mL, 1.06 mmol) and compound **2e** (97 mg, 0.13 mmol) in benzene gave a colorless solution that was crystallized to give compound **3e** (61 mg, 62%). The obtained crystals were suitable for X-ray crystal structure analysis. ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K) (selected resonances): $\delta = 4.45$ (d, $J = 7.5$ Hz, 1H, OH), 3.03 (m, 1H, H-1), 2.35 (m, 1H, 1-H′), 1.26 (m, 1H, 2-H), -0.27 [s, 9H, $Si(CH_3)_3$]. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 193 K) (selected resonances): $\delta = 31.9$ (d, $^{1}J_{PC} = 62.0$ Hz, C-1), 16.1 (br, C-2), -2.1 [$Si(CH_3)_3$]. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 193 K): $\delta = -5.2$ ($\nu_{1/2} \approx 1000$ Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 193 K): $\delta = 45.0$ ($\nu_{1/2} \approx 15$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 193 K): $\delta = -126.3$ (m, 1F, *o*-$C_6F_5{}^{A}$), -128.3 (m, 1F, *o*-$C_6F_5{}^{B}$), -128.9 (m, 1F, *o*′-$C_6F_5{}^{B}$), -146.9 (m, 1F, *o*′-$C_6F_5{}^{A}$), -160.0 (t, $^{3}J_{FF} = 21.4$ Hz, 1F, *p*-$C_6F_5{}^{B}$), -160.2 (t, $^{3}J_{FF} = 21.3$ Hz, 1F, *p*-$C_6F_5{}^{A}$), -163.9 (m, 1F, *m*-$C_6F_5{}^{A}$), -164.4 (m, 1F, *m*′-$C_6F_5{}^{A}$), -164.6 (m, 1F, *m*-$C_6F_5{}^{B}$), -164.9 (m, 1F, *m*′-$C_6F_5{}^{B}$). HRMS: calcd for $C_{35}H_{35}NOPBF_{10}SiH$, 746.22381; found, 746.22491. IR (KBr): $\upsilon'/cm^{-1} = 3526$ (s, NO-H), 2952 (br), 1644 (s), 1606 (s), 1515 (m), 1451 (s), 1249 (s), 1110 (m). X-ray crystal structure analysis of **3e**: formula $C_{35}H_{35}BF_{10}NOPSi$, $M = 745.51$, colorless crystal, 0.27 × 0.12 × 0.06 mm, $a = 9.4443(2)$ Å, $b = 10.7197(2)$ Å, $c = 19.2926(5)$ Å, $\alpha = 82.938(1)°$, $\beta = 86.248(1)°$, $\gamma = 82.508(1)°$, $V = 1919.39(7)$ Å^3, $\rho_{calc} = 1.290$ g cm^{-3}, $\mu = 0.179$ mm^{-1}, empirical absorption correction ($0.953 \le T \le 0.989$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 9146 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 6597 independent ($R_{int} = 0.035$) and 5357 observed reflections $[I > 2\sigma(I)]$, 461 refined parameters, $R = 0.066$, $wR^2 = 0.159$, max (min) residual electron density = 0.30 (−0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4a: Compound **2a** (40.0 mg, 0.059 mmol) was dissolved in toluene (5 mL). After the solution had been stirred at room temperature for 4 days, the solvent of the colorless solution was removed in vacuo to give a mixture of **3a** (56%) and **4a** (44%) (determined by ^{31}P NMR). Crystals of compound **4a** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the crude reaction mixture in CH_2Cl_2. HRMS: calcd for $C_{39}H_{33}BF_{10}NOP + Na^{+}$, 786.21253 g/mol; found, 786.21373 g/mol. ^{1}H NMR (500 MHz, $CDCl_3$, 228 K) (selected resonances): $\delta = 5.10$, 3.79 (each br, each 1H, $CH_2{}^{O}$), 3.15, 2.43 (each br, each 1H, $CH_2{}^{P}$), 1.85, 1.34 (each br, each 1H, $CH_2{}^{B}$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 228 K) (selected resonances): $\delta = 76.4$ (br, $CH_2{}^{O}$), 30.5 (d, $^{1}J_{PC} = 66.5$ Hz, $CH_2{}^{P}$), 19.7 (br, $CH_2{}^{B}$). $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 228 K): $\delta = -6.1$ ($\nu_{1/2} \approx 1200$ Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 228 K): $\delta = 46.4$ ($\nu_{1/2} \approx 10$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): $\delta = -131.8$ (br, 2F, *o*-C_6F_5), -160.4 (br, 1F, *p*-C_6F_5), -165.2 (br m, 2F, *m*-C_6F_5). X-ray crystal structure analysis of **4a**: formula $C_{39}H_{33}BF_{10}NOP$, $M = 763.44$, colorless crystal, 0.23 × 0.03 × 0.01 mm, $a = 10.9350(12)$ Å, $b = 12.8316(16)$ Å, $c = 16.1354(10)$ Å, $\alpha = 68.007(4)°$, $\beta = 89.889(5)°$, $\gamma = 73.784(11)°$, $V = 2002.3(4)$ Å^3, $\rho_{calc} = 1.266$ g cm^{-3}, $\mu = 1.289$ mm^{-1}, empirical absorption correction ($0.756 \le T \le 0.987$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 26288 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 6673 independent ($R_{int} = 0.092$) and 4090 observed reflections $[I > 2\sigma(I)]$, 484 refined parameters, $R = 0.090$, $wR^2 = 0.224$, max (min) residual electron density = 0.27 (−0.39) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Preparation of Compounds 4b–e. Compound **2** was dissolved in toluene (green solution) and heated to 70–80 °C for 1–2 h, which resulted in a light yellow solution. The solvent was removed in a vacuum, and the residue was dissolved in a minimum amount of CH_2Cl_2 and loaded onto a silica gel column. Chromatography (CH_2Cl_2/*n*-pentane = 1:5) gave first compound **4** followed by compound **3**.

4b: **2b** (80 mg, 0.11 mmol) in toluene (1.0 mL) at 70 °C for 2 h gave the compounds **3b** (38 mg, 47%) and **4b** (41 mg, 45%). Crystals of **4b** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution at −35 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) (selected resonances): $\delta = 7.21$ (m, 3H, *m*-, *p*-Ph), 6.98 (m, 2 H, *o*-Ph), 4.95 (dd, $^{2}J_{HH} = 9.6$ Hz, $^{4}J_{PH} = 3.5$ Hz, 1H, $PhCH_2$), 3.77 (br d, $^{2}J_{HH} = 9.6$ Hz, 1H, $PhCH_2$), 3.18 (q, $^{2}J_{PH} \approx {}^{3}J_{HH} \approx {}^{3}J_{HH} = 11.8$ Hz, 1H, 1-H), 2.32 (m, 1H, 2-H), 2.11 (br m, 1H, 5-H), 1.95 (br m, 1H, 6-H), 1.72 (br, 1H, 3-H), 1.57 (br, 1H, 4-H), 1.24 (m, 1H, 3-H′), 1.16 (m, 1H, 2-H′), 1.13 (m, 1H, 4-H′), 0.72 (m, 1H, H-5′). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) (selected resonances): $\delta = 136.9$ (br d, $^{4}J_{PC} = 1.3$ Hz, *i*-Ph), 128.5 (d, $^{5}J_{PC} = 2.1$ Hz, *o*-Ph), 128.3 (*m*-Ph), 128.0 (*p*-Ph), 76.2 (m, $PhCH_2$), 46.2 (d, $^{1}J_{PC} = 59.6$ Hz, C-1), 35.8 (br, C-6), 29.9 (br d, $^{3}J_{PC} = 12.0$ Hz, C-5), 27.3 (C-2), 26.7 (d, $^{3}J_{PC} = 14.7$ Hz, C-3), 26.5 (br, C-4). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): $\delta = -4.5$ ($\nu_{1/2} \approx 150$ Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 48.7$ ($\nu_{1/2} \approx 20$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): $\delta = -126.9$ (m, 1F, *o*-$C_6F_5{}^{A}$), -127.6 (m, 1F, *o*-$C_6F_5{}^{B}$), -133.4 (m, 1F, *o*′-$C_6F_5{}^{B}$), -134.1 (m, 1F, *o*′-$C_6F_5{}^{A}$), -160.9 (t, $^{3}J_{FF} = 20.4$ Hz, 1F, *p*-$C_6F_5{}^{A}$), -161.8 (t, $^{3}J_{FF} = 20.4$ Hz, 1F, *p*-$C_6F_5{}^{B}$), -165.6 (m, 1F, *m*-$C_6F_5{}^{B}$), -165.7 (m, 1F, *m*′-$C_6F_5{}^{B}$), -166.1 (m, 1F, *m*′-$C_6F_5{}^{A}$), -166.3 (m, 1F, *m*-$C_6F_5{}^{A}$). HRMS: calcd for $C_{43}H_{39}NOPBF_{10}NH_4$, 835.30409; found, 835.30573. X-ray crystal structure analysis of **4b**: formula $C_{43}H_{39}BF_{10}NOP$, $M = 817.53$, colorless crystal, 0.23 × 0.20 × 0.17 mm, $a = 9.5024(1)$ Å, $b = 19.8280(3)$ Å, $c = 21.6374(2)$ Å, $\alpha = 74.247(1)°$, $\beta = 81.653(1)°$, $\gamma = 78.048(1)°$, $V = 3821.44(8)$ Å^3, $\rho_{calc} = 1.421$ g cm^{-3}, $\mu = 0.157$ mm^{-1}, empirical absorption correction ($0.965 \le T \le 0.974$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 37560 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 17591 independent ($R_{int} = 0.046$) and 14151 observed reflections $[I > 2\sigma(I)]$, 1039 refined parameters, $R = 0.059$, $wR^2 = 0.160$, max (min) residual electron density = 0.37 (−0.36) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4c: **2c** (67 mg, 0.09 mmol) in toluene (1.0 mL) at 80 °C for 1 h gave compounds **3c** (28 mg, 42%) and **4c** (30 mg, 40%). ^{1}H NMR

(600 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 7.22 (m, 3H, *m*-, *p*-$PhCH_2$), 7.17 (m, 1H, *p*-Ph), 7.05 (br m, 2H, *m*-Ph), 6.95 (m, 2H, *o*-$PhCH_2$), 6.77 (br, 2H, *o*-Ph), 5.19 (d, $^{2}J_{HH}$ = 9.4 Hz, 1H, $PhCH_2$), 4.68 (td, $^{2}J_{PH} \approx {}^{3}J_{HH}$ = 14.8 Hz, $^{3}J_{HH}$ = 4.2 Hz, 1H, 1-H), 3.70 (d, $^{2}J_{HH}$ = 9.4 Hz, 1H, $PhCH_2$), 2.53 (td, $^{2}J_{HH} \approx {}^{3}J_{HH}$ = 14.0 Hz, $^{3}J_{PH}$ = 8.5 Hz, 1H, 2-H), 1.66 (ddd, $^{3}J_{PH}$ = 39.2 Hz, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 4.2 Hz, 1H, 2-H′). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 138.7 (*i*-Ph), 136.9 (*i*-$PhCH_2$), 129.5 (br, *o*-Ph), 128.6 (*o*-$PhCH_2$), 128.3 (*m*-$PhCH_2$), 128.2 (d, $^{4}J_{PC}$ = 2.0 Hz, *m*-Ph), 128.1 (*p*-$PhCH_2$), 128.0 (d, $^{5}J_{PC}$ = 2.8 Hz, *p*-Ph), 76.4 (m, $PhCH_2$), 49.8 (d, $^{1}J_{PC}$ = 56.2 Hz, C-1), 33.4 (br, C-2). $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 298 K): δ = −6.1 ($\nu_{1/2} \approx$ 200 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 298 K): δ = 50.5 ($\nu_{1/2} \approx$ 20 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 183 K): δ = −127.9, −132.03 (each m, each 1F, *o*-$C_6F_5^{A}$), −132.08, −134.8 (each m, each 1F, *o*-$C_6F_5^{B}$), −159.6 (t, $^{3}J_{FF}$ = 21.0 Hz, 1F, *p*-$C_6F_5^{A}$), −161.4 (t, $^{3}J_{FF}$ = 21.0 Hz, 1F, *p*-$C_6F_5^{B}$), −164.94, −165.5 (each m, each 1F, *m*-$C_6F_5^{A}$), −164.99 (m, 2F, *m*-$C_6F_5^{B}$). Elemental analysis. Calcd for $C_{45}H_{37}NOPBF_{10}$: C, 64.38; H, 4.44; N, 1.67, Found: C, 63.91; H, 4.25; N, 1.58.

4d: **2d** (100 mg, 0.14 mmol) in toluene (5.5 mL) at 80 °C for 90 min gave compounds **3d** (37 mg, 37%) and **4d** (39 mg, 34%). Crystals of **4d** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution at −35 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 300 K) (selected resonances): δ = 7.22 (m, 3H, *m*-, *p*-Ph), 6.97 (m, 2H, *o*-Ph), 5.14, 3.75 (each d, $^{2}J_{HH}$ = 9.7 Hz, each 1H, $PhCH_2$), 3.44 (m, 1H, 1-H), 1.89 (m, 1H, 2-H), 1.31 (ddd, $^{3}J_{PH}$ = 37.2 Hz, $^{2}J_{HH}$ = 14.1 Hz, $^{3}J_{HH}$ = 4.1 Hz, 1H, 2-H′), 1.22 (dd, $^{3}J_{PH}$ = 18.8 Hz, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 137.1 (*i*-Ph), 128.5 (*o*-Ph), 128.3 (*m*-Ph), 128.0 (*p*-Ph), 76.3 (m, $PhCH_2$), 38.5 (d, $^{1}J_{PC}$ = 59.7 Hz, C-1), 32.4 (br, C-2), 18.4 (d, $^{2}J_{PC}$ = 2.2 Hz, CH_3). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, 297 K): δ = 51.8 ($\nu_{1/2} \approx$ 20 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 183 K): δ = −128.1, −132.3 (each m, each 1F, *o*-$C_6F_5^{A}$), −132.4, −135.2 (each m, each 1F, *o*-$C_6F_5^{B}$), −159.8 (m, 1F, *p*-$C_6F_5^{A}$), −161.6 (m, 1F, *p*-$C_6F_5^{B}$), −164.9, −165.5 (each m, each 1F, *m*-$C_6F_5^{A}$), −165.1, −165.3 (each m, each 1F, *m*-$C_6F_5^{B}$). HRMS: calcd for $C_{40}H_{35}NOPBF_{10}NH_4$, 795.27279; found, 795.27519. X-ray crystal structure analysis of **4d**: formula $C_{40}H_{35}BF_{10}NOP$, M = 777.47, colorless crystal, 0.23 × 0.15 × 0.07 mm, a = 10.8645(7) Å, b = 12.6096(4) Å, c = 14.7239(7) Å, α = 79.426(2)°, β = 69.495(4)°, γ = 75.950(4)°, V = 1822.01(16) Å^{3}, ρ_{calc} = 1.417 g cm^{-3}, μ = 0.427 mm^{-1}, empirical absorption correction (0.735 ≤ T ≤ 0.907), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 21742 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6246 independent (R_{int} = 0.043) and 5321 observed reflections [$I > 2\sigma(I)$], 494 refined parameters, R = 0.046, wR^2 = 0.134, max (min) residual electron density = 0.23 (−0.29) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4e: **2e** (83 mg, 0.12 mmol) in toluene (1.0 mL) at 80 °C for 1 h gave compounds **3e** (34 mg, 34%) and **4e** (36 mg, 32%). ^{1}H NMR (600 MHz, CD_2Cl_2, 253 K) (selected resonances): δ = 7.23 (m, 3H, *m*-, *p*-Ph), 6.96 (m, 2H, *o*-Ph), 4.79, 3.78 (each dm, $^{2}J_{HH}$ = 8.7 Hz, each 1H, $PhCH_2$), 3.28 (m, 1H, 1-H), 2.41 (br m, 1H, 1-H′), 1.42 (br, 1H, 2-H), −0.33 [s, 9H, $Si(CH_3)_3$]. $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 253 K) (selected resonances): δ = 135.6 (*i*-Ph), 129.1 (*o*-Ph), 128.2 (*m*-, *p*-Ph), 76.6 (m, $PhCH_2$), 31.8 (d, $^{1}J_{PC}$ = 63.1 Hz, C-1), 17.0 (br, C-2), −2.4 [$Si(CH_3)_3$]. $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ = −4.7 ($\nu_{1/2} \approx$ 150 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ = 44.9 ($\nu_{1/2} \approx$ 50 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 253 K): δ = −126.1 (m, 1F, *o*′-$C_6F_5^{A}$), −126.3 (m, 1F, *o*-$C_6F_5^{B}$), −130.8 (m, 1F, *o*-$C_6F_5^{A}$), −132.7 (m, 1F, *o*′-$C_6F_5^{B}$), −160.6 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F, *p*-$C_6F_5^{A}$), −161.1 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-$C_6F_5^{B}$), −164.9 (m, 1F, *m*-$C_6F_5^{B}$), −165.1 (m, 1F, *m*′-$C_6F_5^{B}$), −165.7 (m, 1F, *m*-$C_6F_5^{A}$), −166.2 (m, 1F, *m*′-$C_6F_5^{A}$). HRMS: calcd for $C_{42}H_{41}NOPBF_{10}SiNa$, 858.25281; found, 858.25315.

Preparation of Compound 5. The aminoxyl radical **2b** (80.0 mg, 0.11 mmol) was dissolved in benzene (1.5 mL), and cyclohexene (0.5 mL, 5.0 mmol) was added. The green color of the reaction mixture disappeared on stirring at room temperature for 1.5 h. The volatiles were removed in a vacuum, and the colorless residue was dissolved in a minimum amount of CH_2Cl_2 and loaded onto a silica gel column. Column chromatography (CH_2Cl_2/*n*-pentane = 1:10) gave compound **5bA** (*R_F = 0.34, 16.0 mg), compound **5bB** (*R_F = 0.31, 16.0 mg), a mixture of compounds **5bA** and **5bB** (12.0 mg), and compound **3b** (*R_F = 33.0 mg). The combined yield for compound **5** was 40%, and the yield for compound **3b** was 41%.

5bA: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 5.02 (dt, $^{3}J_{HH}$ = 10.5 Hz, J = 3.5 Hz, =CH^{CH2}), 4.73 (dm, $^{3}J_{HH}$ = 10.5 Hz, 1H, =CH), 4.38 (br m, 1H, OCH), 3.11 (m, 1H, 1-H), 2.00 (br, 1H, 6-H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 129.8 (=CH^{CH2}), 126.4 (d, J = 10.7 Hz, =CH), 75.1 (dd, $^{3}J_{PC}$ = 13.0 Hz, J = 2.2 Hz, OCH), 45.3 (d, $^{1}J_{PC}$ = 60.9 Hz, C-1), 34.9 (br, C-6). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ = −4.1 ($\nu_{1/2} \approx$ 200 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ = 50.8 ($\nu_{1/2} \approx$ 20 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −126.5 (m, 1F, *o*-$C_6F_5^{A}$), −126.8 (m, 1F, *o*-$C_6F_5^{B}$), −133.1 (m, 1F, *o*′-$C_6F_5^{A}$), −135.3 (m, 1F, *o*′-$C_6F_5^{B}$), −160.8 (t, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^{A}$), −162.1 (t, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5^{B}$), −165.6 (m, 1F, *m*′-$C_6F_5^{B}$), −165.8 (m, 1F, *m*-$C_6F_5^{B}$), −166.1 (m, 1F, *m*′-$C_6F_5^{A}$), −166.5 (m, 1F, *m*-$C_6F_5^{A}$). Elemental analysis. Calcd for $C_{44}H_{41}NOPBF_{10}$: C, 62.47; H, 5.12, N, 1.73. Found: C, 62.22, H, 5.05, N, 1.62. X-ray crystal structure analysis of **5bA**: formula $C_{42}H_{41}BF_{10}NOP \cdot C_7H_8$, M = 899.67, colorless crystal, 0.40 × 0.10 × 0.03 mm, a = 11.0700(1) Å, b = 21.3258(3) Å, c = 18.9405(3) Å, β = 105.085(1)°, V = 4317.33(10) Å^{3}, ρ_{calc} = 1.384 g cm^{-3}, μ = 0.146 mm^{-1}, empirical absorption correction (0.944 ≤ T ≤ 0.996), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 12743 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 7454 independent (R_{int} = 0.030) and 6030 observed reflections [$I > 2\sigma(I)$], 573 refined parameters, R = 0.069, wR^2 = 0.194, max (min) residual electron density = 0.57 (−0.50) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

5bB: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 5.65 (dm, $^{3}J_{HH}$ = 10.2 Hz, 1H, =CH^{CH2}), 5.35 (dm, $^{3}J_{HH}$ = 10.2 Hz, 1H, =CH), 4.49 (br, 1H, OCH), 3.11 (m, 1H, 1-H), 2.03 (br, 1H, 6-H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 131.0 (=CH^{CH2}), 129.0 (=CH), 78.1 (br, OCH), 45.4 (d, $^{1}J_{PC}$ = 61.4 Hz, C-1), 34.5 (br, C-6). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ = −4.1 ($\nu_{1/2} \approx$ 150 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ = 51.2 ($\nu_{1/2} \approx$ 15 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −125.1 (m, 1F, *o*-$C_6F_5^{A}$), −126.6, −135.4 (each m, each 1F, *o*-$C_6F_5^{B}$), −132.9 (m, 1F, *o*′-$C_6F_5^{A}$), −160.6 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-$C_6F_5^{A}$), −162.0 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5^{B}$), −165.8 (m, 2F, *m*-$C_6F_5^{B}$), −166.0 (m, 1F, *m*′-$C_6F_5^{A}$), −166.3 (m, 1F, *m*-$C_6F_5^{A}$). HRMS: calcd for $C_{42}H_{41}NOPBF_{10}Na$, 830.27514; found, 830.27742. X-ray crystal structure analysis of **5bB**: formula $C_{42}H_{41}BF_{10}NOP$, M = 807.54, colorless crystal, 0.20 × 0.17 × 0.05 mm, a = 11.8794(2) Å, b = 16.4445(2) Å, c = 19.7784(3) Å, α = 97.514(1)°, β = 94.091(1)°, γ = 92.643(1)°, V = 3814.78(10) Å^{3}, ρ_{calc} = 1.406 g cm^{-3}, μ = 0.156 mm^{-1}, empirical absorption correction (0.969 ≤ T ≤ 0.992), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 18493 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 13109 independent (R_{int} = 0.033) and 10674 observed reflections [$I > 2\sigma(I)$], 1031 refined parameters, R = 0.064, wR^2 = 0.148, max (min) residual electron density = 0.39 (−0.31) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 6. Compound **2b** (109 mg, 0.150 mmol), Cu powder (10.0 mg, 0.167 mmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.0 mg, 0.004 mmol), and copper(II) trifluoromethanesulfonate (2.0 mg, 0.006 mmol) were suspended in benzene, and 1-bromoethylbenzene was added. The resulting greenish reaction mixture was degassed by freeze−pump−thaw cycles and heated to 75 °C under argon for 2 days. The rown liquid part of the reaction mixture was taken up by glass pipet and loaded as such onto a silica gel column. Column chromatography (CH_2Cl_2/*n*-pentane = 1:5) gave compound **6bA** (R_F = 0.48, 35 mg), compound **6bB** (R_F = 0.41, 38 mg), a mixture of compounds **6bA** and **6bB** (18 mg), and compound **3c** (R_F = 0.22, 18 mg). The total yield for compound **6** was 73%.

6bA: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 4.38 (q, $^{3}J_{HH}$ = 6.4 Hz, 1H, PhCH), 3.22 (m, 1H, H-1), 1.94 (m, 1H, 6-H), 1.22 (br, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 145.0 (*i*-Ph), 85.0 (PhCH), 45.5 (d, $^1J_{PC}$ = 61.4 Hz, C-1), 34.4 (br, C-6), 25.8 (m, CH_3). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): $\delta = -3.2$ ($\nu_{1/2} \approx 150$ Hz). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 298 K): $\delta = 50.3$ ($\nu_{1/2} \approx 15$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): $\delta = -121.0$, -134.2 (each m, each 1F, *o*-$C_6F_5^A$), -127.7, -132.6 (each m, each 1F, *o*-$C_6F_5^B$), -161.0 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^A$), -161.6 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^B$), -165.5, -165.7 (each br, each 1F, *m*-$C_6F_5^B$), -166.6 (m, 2F, *m*-$C_6F_5^A$). HRMS: calcd for $C_{44}H_{41}NOPBF_{10}K$, 870.24907; found, 870.24830. X-ray crystal structure analysis of **6bA**: formula $C_{44}H_{41}BF_{10}NOP$, M = 831.56, colorless crystal, 0.17 × 0.13 × 0.07 mm, a = 19.6305(5) Å, b = 11.3087(4) Å, c = 18.2740(5) Å, β = 105.963(2)°, V = 3900.30(2) Å^3, ρ_{calc} = 1.416 g cm^{-3}, μ = 0.155 mm^{-1}, empirical absorption correction ($0.974 \leq T \leq 0.989$), Z = 4, monoclinic, space group *Cc* (No. 9), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 14745 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 5737 independent (R_{int} = 0.045) and 5263 observed reflections [$I > 2\sigma(I)$], 530 refined parameters, R = 0.051, wR^2 = 0.108, max (min) residual electron density = 0.30 (-0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

6bB: ^1H NMR (600 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 5.15 (q, $^3J_{HH}$ = 6.6 Hz, 1H, PhCH), 3.18 (m, 1H, H-1), 2.08 (br m, 1H, 6-H), 0.60 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) (selected resonances): δ = 144.7 (d, $^4J_{PC}$ = 1.5 Hz, *i*-Ph), 80.6 (m, PhCH), 45.4 (d, $^1J_{PC}$ = 60.9 Hz, C-1), 34.8 (br, C-6), 22.4 (d, $^4J_{PC}$ = 7.9 Hz, CH_3). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2 298 K): $\delta = -4.0$ ($\nu_{1/2} \approx 200$ Hz). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2 298 K): $\delta = 51.9$ ($\nu_{1/2} \approx 15$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): $\delta = -122.8$, -133.4 (each m, each 1F, *o*-$C_6F_5^A$), -126.6, -135.4 (each m, each 1F, *o*-$C_6F_5^B$), -160.8 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-$C_6F_5^A$), -162.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-$C_6F_5^B$), -165.5, -165.8 (each m, each 1F, *m*-$C_6F_5^B$), -166.46, -166.50 (each m, each 1F, *m*-$C_6F_5^A$). Elemental analysis. Calcd for $C_{43}H_{39}NOPBF_{10}$: C, 63.17; H, 4.81, N, 1.58. Found: C, 62.64, H, 4.80, N, 1.58.

General Procedure for the Polymerization of Styrene. A heat-gun-dried Schlenk tube was charged with initiator **6bA** and styrene. The tube was subjected to three freeze−thaw cycles and then sealed. The polymerization was carried out under argon at 100−120 °C. After the reaction mixture had cooled to room temperature, the residue was dissolved in dichloromethane (0.5 mL). The polymer was precipitated three times by addition of a 2:1 mixture of pentane and dichloromethane (5 mL) to afford polystyrene as a white solid. Molecular weight and polydispersity index (PDI) were determined by size-exclusion chromatography; conversion was determined gravimetrically.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details, EPR spectra, UV/vis spectra, X-ray crystallographic details, ^1H NMR and ^{13}C NMR spectra, and two-dimensional NMR data of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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