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Alkene Addition of Frustrated P/B and N/B Lewis Pairs at the [3]Ferrocenophane Framework

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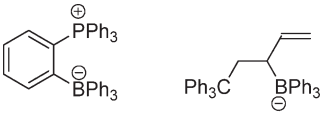
o-Vinyl/α-NRR′-substituted [3]ferrocenophane derivatives (R = R′ = Me (**8**), R = H, R′ = ^{t}Bu (**11**), R = R′ = H (**13**)) were prepared via a Wittig olefination route starting from the corresponding aldehyde. The NMe_2 group was further exchanged for $Pmes_2$ (**9**). The bulky α-substituents NH^tBu and $Pmes_2$ form frustrated Lewis pairs with $B(C_6F_5)_3$ that undergo cooperative intramolecular addition reactions to the adjacent alkene. In the case of **13** stable Lewis pair adduct (**14**) formation is observed instead. The corresponding α-dimesitylphosphino[3]ferrocenophanyl-substituted butadiene (**16**) and acrolein (**23**) derivatives were synthesized via multistep synthetic pathways. Upon treatment with $B(C_6F_5)_3$, intramolecular 1,4-addition of the frustrated Lewis pairs to the adjacent doubly unsaturated moieties takes place to yield the zwitterionic products **17** and **24**, respectively. The complexes **9**, **10**, **12**, **16**, **17**, **20**, **22**, and **23** were characterized by X-ray diffraction.

Introduction

Frustrated Lewis pairs add cooperatively to a variety of alkenes and alkynes. Early examples were discussed in 1959 by Wittig and Benz. They described the trapping reaction of in situ generated 1,2-didehydrobenzene by the PPh_3/BPh_3 Lewis pair[1] to yield the zwitterionic 1,2-addition product (**1**). Shortly thereafter, Tochtermann reported that the combined addition of trityl anion with BPh_3 to butadiene gave the addition product (**2**) at the expense of the usual anionic butadiene polymerization reaction.[2]

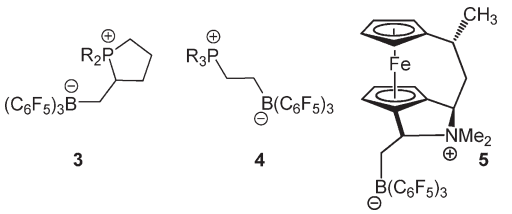
Decades later Stephan et al. demonstrated that $B(C_6F_5)_3$ added cooperatively to a bulky alkene-substituted phosphine to yield the intramolecular frustrated P/B Lewis pair addition product (**3**).[3] We demonstrated the cooperative nature of the concerted addition of the intramolecular Mes_2P-$(CH_2)_2B(C_6F_5)_2$ Lewis pair to norbornene.[3b] Intermolecular P/B addition to simple alkenes was also possible (**4**). We recently communicated the first example of an intramolecular frustrated N/B Lewis pair addition to a [3]ferrocenophane-bound vinyl group to yield the respective zwitterionic addition product (**5**).[4] Intramolecular N/B addition reactions at the related organic arene derivatives were reported consecutively.[5] The rigid [3]ferrocenophane framework has turned out to be very well suited to allow such cooperative Lewis pair addition reactions to alkenes take place. Therefore, we have extended our studies on the P/B and N/B frustrated pair addition reactions[6,7] to olefinic and conjugated dienyl moieties at the rigid [3]ferrocenophane framework. This gave some interesting new results.

Scheme 1



1 **2**

Scheme 2



3 **4** **5**

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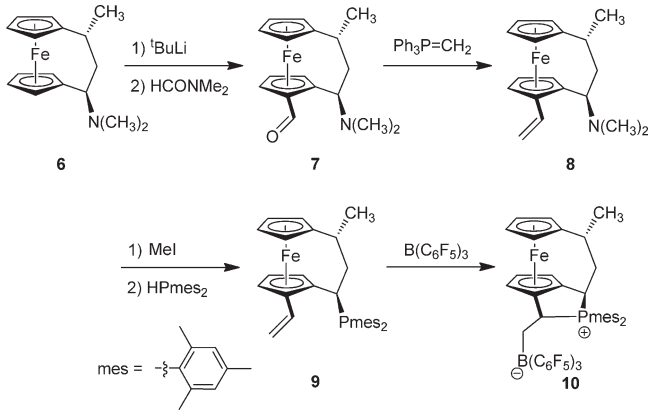
Scheme 3



Results and Discussion

The syntheses of the compounds used in this study started from the readily available α-dimethylamino[3]ferrocenophane system (**6**), which was easily prepared by an intramolecular Mannich reaction of 1,1′-diacetylferrocene followed by catalytic hydrogenation.[8−10] Formylation of **6** involving a directed *ortho*-lithiation step[11] then gave the α-dimethylamino[3]-ferrocenophane carbaldehyde (**7**). Subsequent Wittig olefination opened pathways to two series of alkenyl[3]ferrocenophane systems, bearing an *ortho*-vinyl or -butadienyl substituent at the "lower" ferrocene Cp ring. The vinyl derivative **8**[4] was prepared by reacting the previously reported aldehyde (**7**) with the Wittig reagent $Ph_3P{=}CH_2$. We used the system **8** as a synthetic "relay compound" to introduce various nucleophilic reagents at the α-position of the [3]ferrocenophane bridge.[12,13]

We first exchanged the α-dimethylamino group for P(mesityl)$_2$. For that purpose the $-NMe_2$ substituent was quaternized by treatment with methyl iodide to convert it into a good leaving group. Subsequent treatment with dimesitylphosphine ($HPmes_2$) in acetonitrile for 18 h at 75 °C eventually gave the α-Pmes$_2$-substituted [3]ferrocenophane **9** in 55% yield after chromatographic purification.

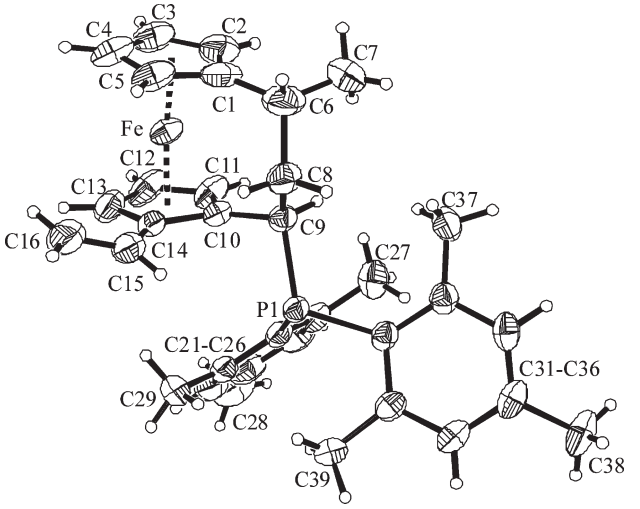


Figure 1. View of the [3]ferrocenophane derivative **9**.

Complex **9** features the typical ABX ^{1}H NMR spin system of the Cp-bound vinyl substituent (^{1}H: δ 7.31, 5.28, 5.05; ^{13}C: δ 136.6, 110.7). It features a total of seven ^{1}H NMR Cp signals of the ferrocene core and two sets of signals of the diastereotopic mesityl groups at phosphorus. Complex **9** shows a ^{31}P NMR signal at δ −9.2. Complex **9** was characterized by X-ray diffraction. Single crystals suitable for the crystal structure analysis were obtained by a slow evaporation of solvent from a solution of **9** in dichloromethane. The structure shows a typical [3]ferrocenophane core [Cp(centroid)−Fe−Cp(centroid) angle: 173.4°] with a folded saturated C_3 bridge. At this bridge the bulky dimesitylphosphino substituent is oriented in a pseudo-equatorial position at carbon atom C9, whereas the smaller C6-bound methyl group is oriented pseudo-axially (C9−P1: 1.884(2) Å, angle C10−C9−P1: 104.6(2)°, θ C6−C8−C9−P1: 171.6(2)°, C11−C10−C9−P1: 113.3(2)°). The vinyl substituent at C14 of the "lower" ferrocenophane Cp ring is oriented close to in-plane with the adjacent cyclopentadienyl ligand [C14−C15: 1.454(4) Å, C15−C16: 1.315(4) Å, angle C14−C15−C16: 125.8(3)°, θ C13−C14−C15−C16: −22.0(5)°]. The vinyl group is found conformationally rotated away from the bulky $-Pmes_2$ group (see Figure 1).

Treatment of **9** with one molar equivalent of the Lewis acid $B(C_6F_5)_3$ at room temperature resulted in rapid heterocyclic ring formation by cooperative 1,2-addition of the P/B pair to the vinyl substituent. Formation of the five-membered phosphole-type heterocycle was evident by the replacement of the typical vinylic ^{1}H NMR features by corresponding signals at δ 4.61, 2.22, and 1.40 (^{13}C: 49.7, $^1J_{PC}$ = 25.4 Hz). Complex **10** shows a ^{31}P signal at δ 81.4 (cf. **9**: δ −9.2) and a ^{11}B resonance at δ −13.4 (cf. $B(C_6F_5)_3$: δ 60). The ^{19}F NMR chemical shifts [δ −129.7 (o), −164.0 (p), −167.0 (m)] show the typical small Δδ (p,m) ≈ 3.0 of a four-coordinated borate system.[14] The structure of **10** was confirmed by an X-ray crystal structure analysis (for details see the Supporting Information). The addition of the phosphine to the vinylic C=C bond has formed a new chirality center, C15.

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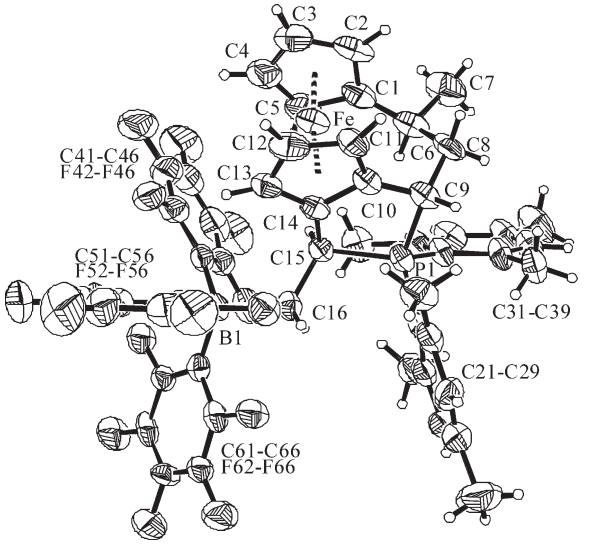
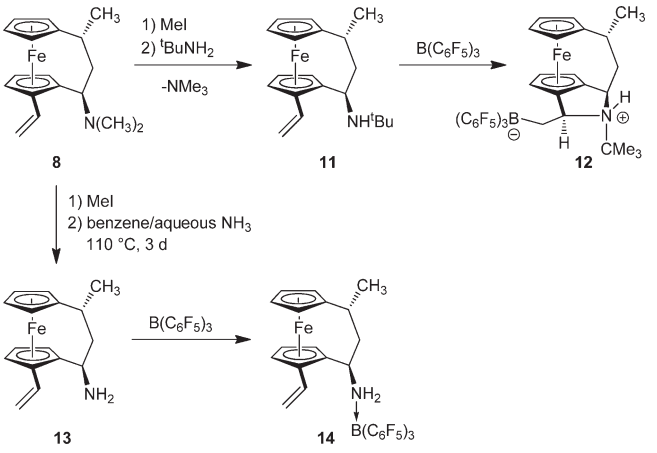


Figure 2. Molecular structure of the zwitterionic compound **10**.

Scheme 4



The reaction apparently has proceeded diastereoselectively to form the (6*R**,9*R**,*p*-*R**,15*R**)-**10** isomer. In this isomer the bulky $-CH_2$-$B(C_6F_5)_3^-$ substituent is oriented away from the metallocene core (see Figure 2).

We next exchanged the $-NMe_2$ *tert*-amino group of the "relay" starting material **8** for $-NH^tBu$. The secondary amine was isolated in ca. 95% yield after activation of **8** by quaternization with methyl iodide followed by exchange with *tert*-butylamine. The substitution reaction proceeded as usual under these conditions with overall retention of the configuration at C9. The amine **11** was then treated with $B(C_6F_5)_3$ at −32 °C in a layered two-phase system (dichloromethane/pentane) to give the amine/borane 1,2-addition product **12** (see Scheme 4). The pure zwitterionic heterocycle was crystallized at −32 °C and isolated as a crystalline solid in ca. 90% yield. The spectroscopic characterization of **12** was carried out at low temperature because the product was not stable at room temperature.

The heterocycle **12** shows a ^{11}B NMR signal at δ −14.4 and a typical borate set of ^{19}F NMR C_6F_5 resonances with a small $\Delta\delta$ (p,m) separation of ca. 5 ppm. Product **12** was characterized by X-ray diffraction (see Figure 3). It features the newly formed N1−C15 σ-bond (1.584(3) Å) and a pendant $-CH_2$-$B(C_6F_5)_3$ group at the annelated five-membered heterocycle (C16−B1: 1.675(4) Å, C15−C16: 1.521(4) Å, angle C15−C16−B1: 118.3(2)°, θ N1−C15−C16−B1: 157.1(2)°). The nitrogen atom N1 bears the bulky ^{t}Bu group oriented *trans* to the $-CH_2$-[B] substituent at the five-membered ring (bond lengths: N1−C15: 1.584(3) Å, N1−C9: 1.554(3) Å, N1−C17: 1.553(4) Å, angles C9−N1−C15: 110.3(2)°, C9−N1−C17: 113.0(2)°, C15−N1−C17 115.2(2)°).

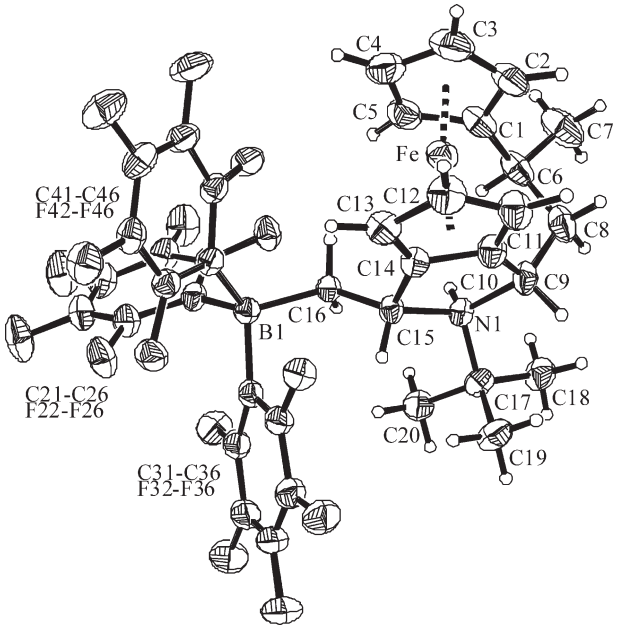


Figure 3. Molecular structure of complex **12**.

We reduced the steric bulk of the amine even further. Quaternization of the $-NMe_2$ group of **8** followed by treatment with NH_3 in a benzene/aqueous biphasic system at 110 °C[15] resulted in the formation of the $-NH_2$-substituted derivative **13** (95% isolated). In this case the primary amine proved to be not sufficiently bulky anymore to allow for the observation of typical frustrated Lewis pair chemistry. A stable adduct of **13** with $B(C_6F_5)_3$ was formed instead, which was isolated by crystallization from the reaction mixture in ca. 90% yield. The adduct **14** (see Scheme 4) shows a 1:1 intensity pair of broad $-NH_2$-[B] ^1H NMR signals at δ 5.75 and 4.68 (in contrast the starting material **13** exhibits only a single broad $-NH_2$ NMR resonance at δ 1.47). Complex **14** is characterized by a ^{11}B NMR signal at δ −7.6 and ^{19}F NMR features at δ −133.5 (o), −157.3 (p), and −163.8 (m) of the three symmetry equivalent C_6F_5 groups at boron. There is the typical ABX ^1H NMR pattern of the free ferrocenophane-bound vinyl substituent at δ 6.67, 5.50, and 5.30 (^{13}C: δ 131.3, 117.7).

We prepared the *ortho*-butadienyl-substituted α-dimethylamino[3]ferrocenophane system **15** by Wittig olefination of the aldehyde **7** (see Scheme 5).[16] For that purpose the aldehyde **7** was reacted with the ylide $Ph_3P{=}CH{-}CH{=}CH_2$, which was prepared in situ by treatment of allyltriphenylphosphonium bromide with *n*-butyllithium. Workup involving purification by column chromatography eventually furnished the product **15** in 21% yield. The product shows the typical NMR features of the *trans*-butadienyl substituent [^1H: δ 7.07, 6.70, 6.49, 5.18, 4.98; ^{13}C: δ 132.6, 129.0, 138.5, 114.7

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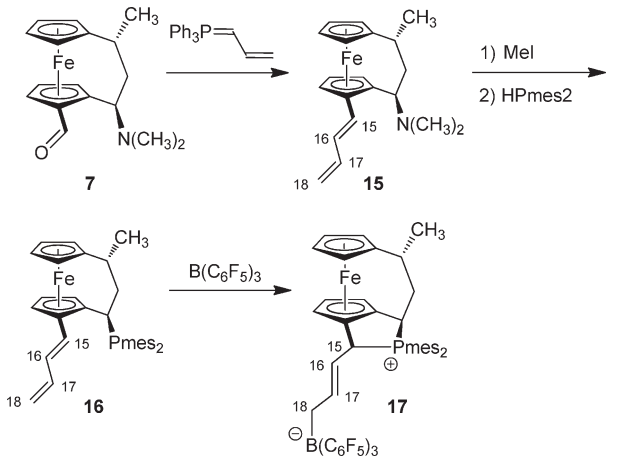
Scheme 5



(C15−C18)] and a large ^{1}H NMR singlet of the $-NMe_2$ group (δ 2.15).

Exchange of the $-NMe_2$ substituent at C9 of compound **15** for $-Pmes_2$ was achieved in the usual way by treatment with methyl iodide in acetonitrile followed by dimesitylphosphine to give **16** in 71% yield. Complex **16** was characterized by X-ray diffraction. It shows the butadienyl substituent attached at carbon C14 of the "lower" Cp ring. It contains the *trans*-configurated C15−C16 carbon−carbon double bond (1.330(3) Å). The butadienyl unit exhibits an *s-trans*-conformation at the central C(sp^2)−C(sp^2) single bond (C16−C17: 1.441(3) Å, C17−C18: 1.318(4) Å, θ C15−C16−C17−C18: 175.7(3)°). The butadienyl unit is oriented close to coplanar with the adjacent ferrocenophane Cp ring (θ C10−C14−C15−C16: −171.6(2)°), and it is rotated away from the bulky $-Pmes_2$ substituent at C9 (C9−P1: 1.884(2) Å). The bulky $-Pmes_2$ substituent is oriented pseudo-equatorially at the folded ferrocenophane C_3 bridge (θ C6−C8−C9−P1: 172.2(2)°, C14−C10−C9−P1: 68.7(2)°); it is in a *trans* arrangement to the $-CH_3$ substituent at the bridge carbon atom C6, which is found in a pseudo-axial orientation. The phosphorus atom P1 features a nonplanar three-coordinate geometry with a sum of C−P−C bond angles of 319.9°.

In solution complex **16** shows a ^{31}P NMR signal at δ −9.2. It shows the ^{1}H/^{13}C NMR resonances of a pair of diastereotopic mesityl groups at phosphorus and butadienyl resonances at δ 7.24 (15-H), 6.34 (16-H), 6.49 (17-H), and 5.17/5.04 (18-H^A/H^B) [^{13}C: δ 133.6 (C15), 127.3 (C16), 138.5 (C17), and 114.2 (C18)].

We then reacted complex **16** with one molar equivalent of $B(C_6F_5)_3$. Addition of the frustrated P/B Lewis pair comprised of the intramolecular phosphine and the external borane was facile. It gave the cyclic addition product **17** in ca. 90% yield after precipitation. Single crystals of **17** for the X-ray crystal structure analysis were grown from a dichloromethane solution at low temperature. It shows that the borane had added to the terminal butadienyl carbon atom C18 (B19−C18 1.644(10) Å), and the phosphine formed a bond to the former C(sp^2) center C15. The 1,4-addition of the frustrated Lewis pair has formed an annelated five-membered heterocycle involving the α-carbon atom of the bridge and the "lower" [3]ferrocenophane ring (P1−C15: 1.855(6) Å, C14−C15: 1.514(8) Å, C10−C14: 1.412(9) Å, C10−C9: 1.504(9) Å, C9−P1: 1.868(7) Å, angles C9−P1−C15: 96.5(3)°, P1−C15−C14: 100.0(4)°, θ C9−P1−C15−C14: 26.8(4)°). Phosphine addition to C15 has created a new chiral center. We observe

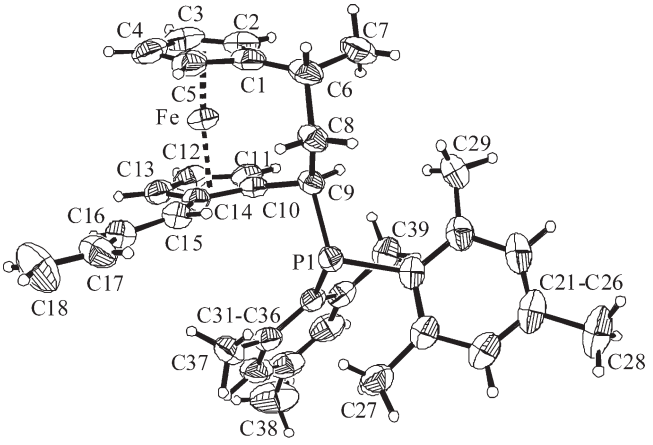


Figure 4. Molecular structure of the butadienyl-substituted dimesitylphosphino [3]ferrocenophane system **16**.

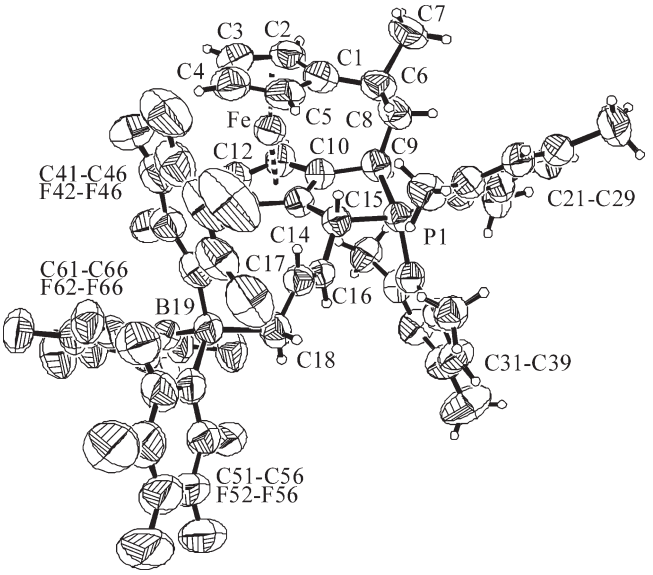
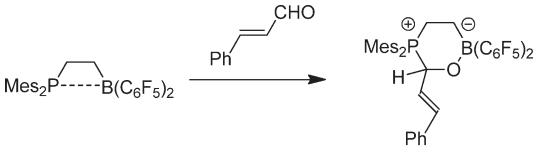


Figure 5. View of the zwitterionic P/B addition product **17**.

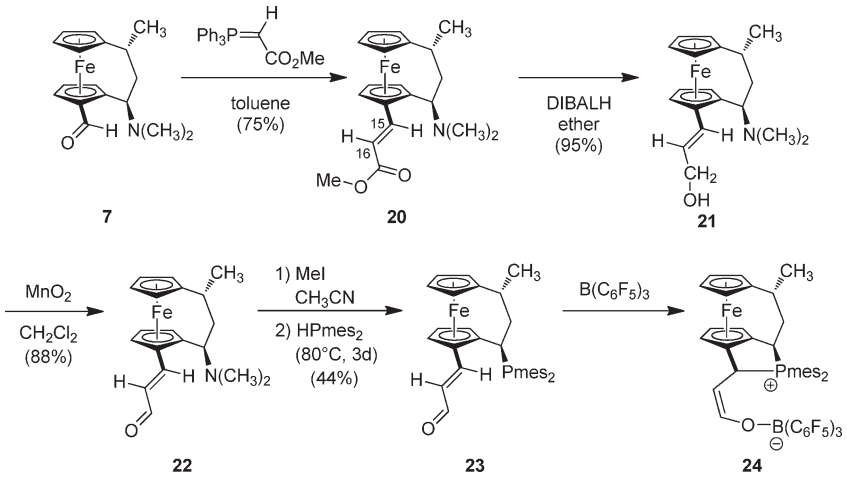
Scheme 6



only the formation of a single diastereomer of **17** that has the pendant side chain oriented away from the [3]ferrocenophane core (θ C10−C14−C15−C16: −146.9(6)°). The C_4 side chain contains a *trans*-1,2-disubstituted alkene in its center (C15−C16: 1.510(8) Å, C16−C17: 1.313(8) Å, C17−C18: 1.471(9) Å) (see Figure 5).

The zwitterionic P/B addition product features a ^{31}P NMR resonance at δ 74.5 and a ^{11}B NMR signal at δ −13.7 in solution. The C16−C17 carbon−carbon double bond of the C_4-[B] side chain shows ^{1}H NMR signals at δ 4.51 and 5.75 (^{13}C: δ 116.0 and 147.4), whereas the former butadiene terminus, which is now found bonded to boron, gives rise to ^{1}H NMR resonances at δ 2.41/1.61 (^{1}H).

Scheme 7



We had previously shown that the reactive intramolecular frustrated P/B Lewis pair **18**[7,17,18] selectively adds to the carbonyl functionality of *trans*-cinnamic aldehyde to form the six-membered ring product **19** featuring a *trans*-styryl side chain[3c] (see Scheme 6).

In view of the results presented above in this account it was tempting to speculate whether this typical reactivity of frustrated P/B Lewis pairs to α,β-unsaturated carbonyl compounds would be changed in a related intramolecular situation. We therefore prepared the α-dimesitylphosphino-substituted [3]ferrocenophane analogue of *trans*-cinnamic aldehyde to react it with $B(C_6F_5)_3$ (see Scheme 7).

Our synthesis of the α,β-unsaturated [3]ferrocenophane carbonyl derivatives started from the α-dimethylamino-[3]ferrocenophane carbaldehyde system **7**. Wittig olefination with the stabilized ylide $Ph_3P{=}CH{-}CO_2Me$ in toluene (reflux temperature, 12 h) gave the corresponding α,β-unsaturated ester **20**,[19] which was isolated in 75% yield after purification by column chromatography. Complex **20** was characterized by X-ray diffraction (single crystals were obtained from diethyl ether at −20 °C). The structure shows the attachment of a *trans*-$CH{=}CH{-}CO_2CH_3$ substituent at C14 of the "lower" ferrocenophane Cp ring (C14−C15: 1.457(3) Å, C15−C16: 1.321(3) Å, C16−C17: 1.469(3) Å). The carbonyl oxygen is oriented toward the side of the $-NMe_2$ substituent at the C_3−ferrocenophane bridge (C9−N1: 1.482(3) Å).

Compound **20** shows the typical ^{1}H NMR signals of the *trans*-substituted α,β-unsaturated ester group [δ 8.39/6.59, ^3J = 15.8 Hz; ^{13}C: δ 146.7, 116.9 (C15, C16)]. There is a sharp $-NMe_2$ ^{1}H NMR signal at δ 2.08 of 6H relative intensity.

The ester group in **20** was selectively reduced by treatment with the diisobutylaluminum hydride reagent in diethyl ether solution to give the corresponding allyl alcohol (95% isolated). It shows ^{1}H NMR features of the *trans* C(15)−C(16) carbon−carbon double bond at δ 6.97 and 6.10 with a $^3J_{HH}$ coupling constant of 15.8 Hz and two multiplets of the adjacent diastereotopic $-CH_2-$OH protons at δ 4.17 and δ 4.16.

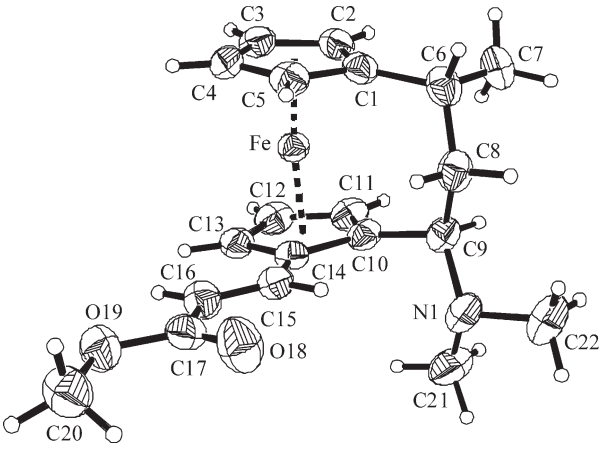


Figure 6. Molecular structure of complex **20**.

The alcohol **21** was subsequently oxidized to the α,β-unsaturated aldehyde by treatment with activated manganese dioxide in dichloromethane. The product **22** was isolated in 88% yield. It was characterized spectroscopically [^{1}H NMR: δ 9.63 ($-CHO$; ^{13}C: δ 192.3), 7.83, 6.66 ($^3J_{HH}$ = 16.0 Hz, C(15)=C(16)), 2.04 (s, 6H, 9-NMe_2)], by C, H, N elemental analysis, and by an X-ray crystal structure analysis (see Figure 7, left, single crystals from diethyl ether). The structure shows the 9-NMe_2 attached in a pseudo-equatorial position at the ferrocenophane C_3 bridge, *trans* to the pseudo-axially oriented 6-CH_3 substituent (C9−N1: 1.485(7) Å, C9−C8: 1.533(7) Å, C8−C6: 1.535(8) Å, C6−C7: 1.522(7) Å, θ C7−C6−C8−C9: −58.7(6)°, θ C6−C8−C9−N1: 171.1(4)°). The acrolein substituent at C14 is oriented in plane with the adjacent ferrocenophane Cp ring (θ C10−C14−C15−C16: −177.1(5)°, C14−C15−C16−C17: 178.1(5)°, C15−C16−C17−O1: 179.2(6)°). It features a *trans*-C=C double bond (C15−C16: 1.341(7) Å) and an *s-trans* configuration at their connecting C16−C17 σ-bond (C16−C17: 1.431(7) Å, C17−O1: 1.210(6) Å).

In the final step of the synthesis, the 9-NMe_2 substituent was replaced by the bulky $-Pmes_2$ group. This was achieved in the usual way by quaternization of the amine followed by treatment with the $HPmes_2$ nucleophile to give **23** in 44% yield after chromatographic workup. The $-Pmes_2$-substituted

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(19) For similar syntheses on ferrocene see: Debroy, P.; Nakar, D.; Roy, S. *Inorg. Chim. Acta* **2006**, 1215–1221.

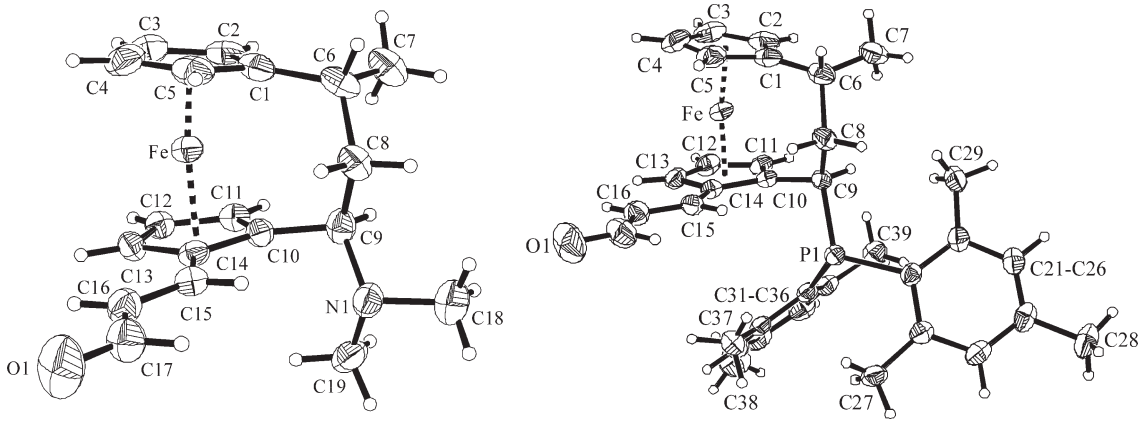
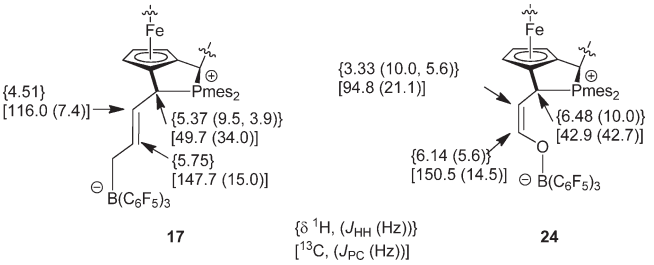


Figure 7. Comparison of the structures of the α,β-unsaturated [3]ferrocenophane derivatives **22** (−NMe_2, left) and **23** (−$Pmes_2$, right).

Scheme 8



α,β-unsaturated ferrocenophane carbaldehyde **23** was also characterized by X-ray diffraction. Its structure is very similar to that of its precursor **22** (see Figure 7). Complex **23** features the bulky −$Pmes_2$ substituent attached at C9 in a pseudo-equatorial position (C9−P1: 1.895(2) Å, angles C9−P1−C21: 113.4(1)°, C9−P1−C31: 101.8(1)°, C21−P1−C31: 104.9(1)°). The propenal-1-yl moiety attached at the ferrocene carbon atom C14 features a *trans*-C=C double bond (C15−C16: 1.334(3) Å) in conjugation with the carbaldehyde functionality (C17−O1: 1.201(3) Å, C17−C16: 1.438(3) Å, angles O1−C17−C16: 126.9(2)°, C17−C16−C15: 120.0(2)°, C16−C15−C14: 127.1(2)°, θ O1−C17−C16−C15: −179.8(2)°, θ C17−C16−C15−C14: −177.8(2)°, C16−C15−C14−C13: −2.0(3)°). In solution complex **23** features a $^1H/^{13}C$ NMR aldehyde resonance at δ 9.58/193.4. There are signals of a pair of diastereotopic mesityl groups at phosphorus (^{31}P: −6.6). The C15−C16 carbon−carbon double bond is *trans*-configurated (^1H NMR: δ 8.37/6.21, $^3J_{HH}$ = 15.5 Hz).

We then reacted the α-dimesitylphosphino[3]ferrocenophanyl-substituted acrolein **23** with $B(C_6F_5)_3$. Cooperative addition of the frustrated P/B Lewis pair occurred rapidly, and after slow crystallization (2 days) from the dichloromethane reaction mixture at −32 °C, we isolated product **24** in 95% yield.

Unfortunately we could not obtain single crystals of **24** suitable for an X-ray crystal structure analysis, but the product was amply characterized by C, H elemental analysis and spectroscopically to allow for a tentative structural assignement. We observe the typical $^1H/^{13}C$ NMR features of the [3]ferrocenophane framework and ^{31}P NMR (δ 73.8), ^{11}B NMR (δ −2.5), and ^{19}F NMR features (δ −133.8, −161.9, and −166.6) that indicate formation of a zwitterionic frustrated P/B Lewis pair addition product. The typical NMR signals of the −CH=CH-CHO substituents of the starting material **23** are no longer observed. They were replaced by a typical set of ^1H and ^{13}C NMR features that are very similar to those observed for the closely related butadienyl ferrocenophane-derived system **17** (see Scheme 8).

Therefore, we must assume that treatment of **23** with $B(C_6F_5)_3$ has resulted in 1,4-C/O addition of the P/B Lewis pair to the α,β-unsaturated aldehyde functional group in **23**. This led to the formation of an annelated five-membered P-heterocycle with a pendant −CH=CH-O-$B(C_6F_5)_3^-$ substituent at C15. According to the NOE data and a relatively small $^3J_{HH}$ coupling constant of 5.6 Hz,[20] it is most likely that this group in **24** now contains a *cis*-configured double bond.

Conclusions

P/B Lewis pairs can add to olefinic C=C double bonds. We had shown for the example of the addition of the intramolecular frustrated P/B Lewis pair **18** to norbornene that the observed *cis*-exo-2,3 addition reaction is probably concerted, although it has a very unsymmetrical transition state with the C−B bond formation preceding the formation of the C−P linkage.[3c,21,22] We had also shown that the Lewis pair **18** favors 1,4-addition to conjugated enynes or diynes to yield the respective zwitterionic cumulene derivatives.[6b] This study shows that P/B Lewis pair addition reactivity can be quite favorable if carried out with both the alkenyl group and the nucleophile being attached at the [3]ferrocenophane framework. Remarkably, even a secondary amino group can add cooperatively with the $B(C_6F_5)_3$ Lewis acid under these conditions, if the remaining alkyl substituent at nitrogen is bulky enough (here ^{t}Bu). The 1,2-P(or N)/B addition pattern breaks down when the Lewis base has become too small (here NH_2); then the usual formation of a stable Lewis pair takes over.

It is noteworthy that this general situation seems to be quite favorable for cooperative P/B 1,4-addition.[6c,23] We see this

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(21) (a) Stirling, A.; Hamza, A.; Rokob, T. A.; Papai, I. *Chem. Commun.* **2008**, 3148–3150. (b) Guo, Y.; Li, S. *Eur. J. Inorg. Chem.* **2008**, 2501–2505.

(22) For other theoretical frustrated Lewis pair studies see e.g.: (a) Rokob, T. A.; Hamza, A.; Stirling, A.; Papai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029–2036. (b) Rokob, T. A.; Hamza, A.; Papai, I. *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710. (c) Guo, Y.; He, X.; Li, Z.; Zou, Z. *Inorg. Chem.* **2010**, *49*, 3419–3423. (d) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem.* **2010**, *122*, 1444–1447. *Angew. Chem., Int. Ed.* **2010**, *49*, 1402−1405.

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happen here to the butadienyl group of the [3]ferrocenophane-derived substrate **16** to give the 1,4-P/B addition product **17**. In this special situation we have even observed the uncommon 1,4-frustrated P/B Lewis pair addition to the substituted [3]ferrocenophane-derived acrolein derivative **23** to readily take place, forming the respective zwitterions **24**. This indicates that quite complex addition and coupling patterns can be favored in frustrated Lewis pair addition chemistry under suitable reaction conditions.

Experimental Section

General Information. All reactions with air- and moisture-sensitive compounds were carried out under an argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The numbering scheme used for assignment of the NMR data is given in the Supporting Information. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. NMR: Bruker AC 200 P (^{1}H, 200 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz), Varian UNITY plus NMR spectrometers (^{1}H, 600 MHz; ^{13}C, 151 MHz). Assignments of the resonances are supported by 2D experiments. Melting points/decomposition temperature: DSC 2010 (TA-Instruments) apparatus. IR: Varian 3100 FT-IR (ExcaliburSeries) spectrometer. X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998) and APEX2 (BrukerAXS, 2006); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326) and APEX2 (BrukerAXS, 2006); absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426), Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), and SADABS (BrukerAXS, 2002); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122); graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids at the 50% probability level. *R*-values are given for observed, wR^2 values for all reflections.

Materials. The complexes **6**,[24] **7**,[11b] and **8**[4] and the reagents dimesitylphosphine[25] and tris(pentafluorophenyl)borane[26] were prepared according to modified literature procedures.

Preparation of Ferrocenophane 9. MeI (0.8 mL, 12.9 mmol) was added at rt to a solution of vinyl-ferrocenophane **8** (400 mg, 1.29 mmol) in CH_3CN (10 mL). The reaction was stirred for 2 h, then evaporated to dryness. The residue was redissolved in CH_3CN (10 mL), $HPMes_2$ (348.8 mg, 1.29 mmol) was added, and the solution was stirred at 75 °C for 18 h. After evaporation of the solvent, the residue was taken up in CH_2Cl_2 (5 mL) and the solution filtered over Celite. The pure compound (380 mg, 55% yield) was obtained after purification by column chromatography under argon (dry and degassed pentane, then pentane/EtOAc 5%). Single crystals were grown by evaporation of a CH_2Cl_2 solution. Anal. Calcd for $C_{34}H_{39}FeP$: C, 76.40; H, 7.35. Found: C, 76.34; H, 7.44. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 7.31 (ddd, J = 17.4 Hz, 10.8 Hz, 1.5 Hz, 1H, 15-H), 6.83 (d, $^4J_{PH}$ = 2.1 Hz, 2H, *m*-CH^{MesB}), 6.64 (d, $^4J_{PH}$ = 2.4 Hz, 2H, *m*-CH^{MesB}), 5.28 (dt, ^3J = 17.4 Hz, J = 1.6 Hz, 1H, 16-H^A), 5.05 (dd, ^3J = 10.8 Hz, ^2J = 1.6 Hz, 1H, 16-H^B), 4.39 (m, 1H, C_5H_3), 4.17 (m, 1H, C_5H_4), 3.98 (m, 1H, C_5H_4), 3.96 (m, 1H, C_5H_3), 3.93 (m, 1H, C_5H_3), 3.90 (m, 1H, 9-H), 3.88 (m, 1H, C_5H_4), 3.48 (m, 1H, C_5H_4), 2.64 (m, 1H, 6-H), 2.49 (s, 6H, *o*-CH$_3^{MesA}$), 2.42 (m, 1H, 8-H^A), 2.35 (s, 6H, *o*-CH$_3^{MesB}$), 2.23 (s, 3H, *p*-CH$_3^{MesA}$), 2.14 (m, 1H, 8-H^B), 2.12 (s, 3H, *p*-CH$_3^{MesB}$), 1.16 (d, ^3J = 7.2, 3H, 7-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_2$]-dichloromethane, 298 K): δ 143.4 (d, $^2J_{CP}$ = 15.7 Hz, *o*-C^{MesA}), 143.3 (d, $^2J_{CP}$ = 15.0 Hz, *o*-C^{MesB}), 138.3 (*p*-C^{MesA}), 137.7 (*p*-C^{MesB}), 136.6 (d, $^4J_{CP}$ = 14.5 Hz, C-15), 133.4 (d, $^1J_{CP}$ = 30.9 Hz, *i*-C^{MesA}), 132.1 (d, $^1J_{CP}$ = 27.9 Hz, *i*-C^{MesB}), 130.2 (d, $^3J_{CP}$ = 3.2 Hz, *m*-CH^{MesA}), 129.8 (d, $^3J_{CP}$ = 3.0 Hz, *m*-CH^{MesB}), 110.7 (C-16), 92.7 (C-1), 85.5 (d, $^2J_{CP}$ = 22.9 Hz, C-10), 81.7 (d, $^3J_{CP}$ = 2.4 Hz, C-14), 76.0 (C_5H_4), 73.7 (C_5H_3), 69.7 (C_5H_4), 68.0 (C_5H_4), 67.7 (C_5H_4), 67.6 (C_5H_3), 67.5 (C_5H_3), 46.0 (d, $^2J_{CP}$ = 26.3 Hz, C-8), 28.3 (d, $^1J_{CP}$ = 23.6 Hz, C-9), 26.6 (d, $^3J_{CP}$ = 10.6 Hz, C-6), 23.4 (d, $^3J_{CP}$ = 13.7 Hz, *o*-CH$_3^{MesB}$), 23.2 (d, $^3J_{CP}$ = 14.4 Hz, *o*-CH$_3^{MesA}$), 20.9 (*p*-CH$_3^{MesA}$), 20.7 (*p*-CH$_3^{MesB}$), 16.6 (C-7). ^{31}P{^{1}H} NMR (202 MHz, [D$_2$]-dichloromethane, 298 K): δ −9.2 ($\nu_{1/2} \approx 3$ Hz).

X-ray crystal structure analysis of 9: formula $C_{34}H_{39}FeP$, M = 534.47, yellow crystal, 0.50 × 0.20 × 0.10 mm, a = 16.3424(2) Å, b = 15.5018(2) Å, c = 21.9422(3) Å, V = 5558.76(12) Å^3, ρ_{calc} = 1.277 g cm^{-3}, μ = 0.621 mm^{-1}, empirical absorption correction (0.747 ≤ T ≤ 0.941), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 36 705 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.67 Å^{-1}, 6603 independent (R_{int} = 0.058) and 4728 observed reflections [$I \geq 2\sigma(I)$], 332 refined parameters, R = 0.048, wR^2 = 0.132, max. (min.) residual electron density 0.60 (−0.64) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 10. A solution of B(C$_6$F$_5$)$_3$ (55 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was added to a solution of compound **9** (53 mg, 0.10 mmol) in 1 mL of CH_2Cl_2. After 1 h of stirring at room temperature, the solution was cooled to −78 °C. A solid precipitated, which was collected by filtration, washed with pentane, and dried in vacuo to yield the product (70 mg, 0.07 mmol, 70%). Anal. Calcd for $C_{52}H_{39}BF_{15}FeP$: C 59.68, H 3.76. Found: C 59.45, H 3.83. ^{1}H NMR (600 MHz, [D$_8$]-tetrahydrofuran, 298 K): δ 7.23 (br, 1H, *m*-CH^{MesA}); 7.15 (br, 1H, *m*-CH^{MesB}); 7.11 (br, 1H, *m*-CH$^{MesA'}$); 6.98 (br, 1H, *m*-CH$^{MesB'}$); 4.61 (br d, ^3J = 14.2 Hz, 1H, 15-H); 4.55 (dt, ^3J = 13.3 Hz, 3.9 Hz, 1H, 9-H); 4.19 (m, 1H, C_5H_3); 4.14 (m, 1H, C_5H_4), 4.13 m, 1H, C_5H_3); 4.09 (m, 1H, C_5H_3); 4.08 (m, 1H, C_5H_4); 3.91 (m, 1H, C_5H_4); 2.88 (br s, 1H, C_5H_4); 2.59 (s, 3H, *o*-CH$_3^{MesA}$); 2.53 (s, 3H, *o*-CH$_3^{MesB}$); 2.44 (m, 1H, 8-H^A); 2.36 (s, 3H, *p*-CH$_3^{MesA}$); 2.32 (s, 3H, *p*-CH$_3^{MesB}$); 2.22 (m, 1H, 16-H^A); 2.04 (s, 3H, *o*-CH$_3^{MesA'}$); 1.83 (dm, ^2J=15.1 Hz, 1H, 8-H^B); 1.74 (s, 3H, *o*-CH$_3^{MesB'}$); 1.62 (m, 1H, 6-H); 1.40 (m, 1H, 16-H^B); 0.66 (d, ^3J = 6.6 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_8$]-tetrahydrofuran, 298 K): δ 149.0 (d, $^1J_{CF} \approx 244$ Hz, C_6F_5); 145.2 (d, $^4J_{CP}$ = 3.2 Hz, *p*-C^{MesA}); 144.6 (d, $^4J_{CP}$ = 2.5 Hz, *p*-C^{MesB}); 144.3 (d, $^2J_{CP}$ = 9.4 Hz, *o*-C$^{MesB'}$); 143.7 (d, $^2J_{CP}$ = 9.0 Hz, *o*-C^{MesB}); 143.0 (d, $^2J_{CP}$ = 11.5 Hz, *o*-C^{MesA}); 142.3 (d, $^2J_{CP}$ = 6.8 Hz, *o*-C$^{MesA'}$); n.o. (C_6F_5); 133.5 (d, $^3J_{CP}$ = 12.0 Hz, *m*-CH^{MesB}); 133.1 (d, $^3J_{CP}$ = 11.2 Hz, *m*-CH$^{MesB'}$); 133.0 (d, $^3J_{CP}$ = 11.2 Hz, *m*-CH^{MesA}); 132.6 (d, $^3J_{CP}$ = 9.4 Hz, *m*-CH$^{MesA'}$); 122.9 (d, $^1J_{CP}$ = 56.5 Hz, *i*-C^{MesA}); 119.5 (d, $^1J_{CP}$ = 66.0 Hz, *i*-C^{MesB}); 94.6 (d, $^2J_{CP}$ = 17.5 Hz, C-14); 93.6 (d, $^2J_{CP}$ = 16.6 Hz, C-10); 89.1 (C-1); 77.9 (C_5H_4); 71.8 (C_5H_3); 70.9 (C_5H_4), 69.8 (C_5H_4); 67.0 (C_5H_3); 65.9 (C_5H_4); 63.9 (d, J_{CP} = 11.3 Hz, C_5H_3); 49.7 (d, $^1J_{CP}$ = 25.4 Hz, C-15); 49.0 (C-8); 34.4 (d, $^1J_{CP}$ = 39.2 Hz, C-9); 28.9 (d, $^3J_{CP}$ = 3.5 Hz, C-6); 24.8 (d, $^3J_{CP}$ = 4.9 Hz, *o*-CH$_3^{MesB'}$); 24.4 (*o*-CH$_3^{MesA}$); 24.2 (*o*-CH$_3^{MesB}$); 22.9 (d, $^3J_{CP}$ = 4.0 Hz, *o*-CH$_3^{MesA'}$); 22.0 (C-7); 20.8 (*p*-CH$_3^{MesA}$); 20.7 (*p*-CH$_3^{MesB}$). ^{19}F NMR (282 MHz, [D$_8$]-tetrahydrofuran, 300 K): δ −129.7 (br, 2F, *o*-C_6F_5); −164.0 (br, 1F, *p*-C_6F_5); −167.0 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} (96 MHz, [D$_8$]-tetrahydrofuran, 300 K): δ −13.4 (s, $\nu_{1/2} \approx 70$ Hz). ^{31}P{^{1}H} (121 MHz, [D$_8$]-tetrahydrofuran, 300 K): δ 81.4 ($\nu_{1/2} \approx 55$ Hz).

X-ray crystal structure analysis of 10: formula $C_{52}H_{39}BF_{15}FeP \cdot CH_2Cl_2$, M = 1131.39, yellow crystal, 0.25 × 0.25 × 0.20 mm, a = 49.283(3) Å, b = 49.283(3) Å, c = 12.8460(5) Å, V = 27020(3) Å^3, ρ_{calc} = 1.252 g cm^{-3}, μ = 0.444 mm^{-1}, empirical absorption correction (0.897 ≤ T ≤ 0.916), Z = 18, trigonal,

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space group $R\bar{3}$ (No. 148), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 45 994 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 10 205 independent ($R_{int} = 0.084$) and 5506 observed reflections [$I \geq 2\sigma(I)$], 665 refined parameters, $R = 0.120$, $wR^2 = 0.345$, max. (min.) residual electron density 2.04 (−0.92) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms; during data collection the mosaicity of the investigated crystals increased; solvents in the voids could not be identified; SQUEEZE did not improve the result; the poor analysis was only done to prove the chemical composition.

Preparation of Amine 11. Vinyl ferrocenophane **8** (350 mg, 1.13 mmol) was dissolved in 5 mL of acetonitrile (5 mL), before methyl iodide (0.71 mL, 1.60 g, 11.3 mmol, 10 equiv) was added. The solution was stirred at room temperature for one hour, and all volatiles were removed in vacuo. K_2CO_3 (327.5 mg, 2.37 mmol, 2.1 equiv), acetonitrile (5 mL), and *tert*-butylamine (144 μL, 99.2 mg, 1.36 mmol, 1.2 equiv) were added to the remaining orange solid, and the reaction mixture heated to 80 °C for four days. Afterward it was evaporated to dryness, dichloromethane (5 mL) was added, and the suspension was filtered over Celite. After drying in vacuo a dark red oil was obtained (361 mg, 1.07 mmol, 95%). Anal Calcd for $C_{20}H_{27}FeN$: C: 71.22, H: 8.07, N: 4.15. Found: C: 70.90, H: 8.00, N: 4.58. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 6.94 (dd, ^3J = 17.9 Hz, 11.1 Hz, 1H, 15-H); 5.37 (dd, ^3J = 17.9 Hz, ^2J = 1.9 Hz, 1H, 16-H^A); 5.07 (dd, ^3J = 11.1 Hz, ^2J = 1.9 Hz, 1H, 16-H^B); 4.35 (m, 1H, 13-H); 4.14 (m, 1H, 4-H); 4.06 (m, 1H, 11-H); 4.04 (m, 2H, 12-H, 2-H); 3.86 (m, 1H, 3-H); 3.65 (m, 1H, 5-H); 3.61 (dd, ^3J = 11.7 Hz, 3.4 Hz, 1H, 9-H); 2.69 (m, 1H, 6-H); 2.60 (ddd, ^2J = 13.3 Hz, ^3J = 11.7 Hz, 3.8 Hz, 1H, 8-H^{ax}); 2.03 (dt, ^2J = 13.3 Hz, ^3J = 3.4 Hz, 1H, 8-H^{eq}); 1.51 (br, 1H, 17-H); 1.28 (d, ^3J = 7.4 Hz, 3H, 7-H); 1.02 (s, 9H, 19-H). ^{13}C{^{1}H} NMR (126 MHz, [D$_2$]-dichloromethane, 298 K): δ 135.6 (C-15); 111.9 (C-16); 94.2 (C-1); 86.4 (C-10); 82.2 (C-14); 74.7 (C-5); 71.9 (C-11); 69.3 (C-4); 68.1 (C-2); 67.6 (C-12); 67.3 (C-13,C-3); 52.5 (C-8); 52.0 (C-18); 45.7 (C-9); 29.9 (C-19); 28.1 (C-6); 17.1 (C-7).

Preparation of Complex 12. *rac-trans*-1′-Vinyl-2′,1″-[1-(*tert*-butylamino)butan-1,3-diyl]ferrocene (**11**) (20 mg, 0.059 mmol) and B(C$_6$F$_5$)$_3$ (30.2 mg, 0.059 mmol) were dissolved in dichloromethane (2 mL) and layered with pentane (5 mL). Upon storage at −32 °C, yellow crystals suitable for the X-ray structure analysis precipitated. These were isolated and dried in vacuo to yield the product (45 mg, 0.053 mmol, 90%). For the NMR spectroscopic analysis, the compound was placed in a NMR tube under argon and cooled to −78 °C. At this temperature the solvent was added and the sample placed in the precooled NMR spectrometer. Anal. Calcd for $C_{38}H_{27}BF_{15}FeN \cdot CH_2Cl_2$: C: 50.14, H: 3.13, N: 1.50. Found: C: 49.20, H: 3.40, N: 1.97. ^{1}H NMR (600 MHz, [D$_2$]-dichloromethane, 253 K): δ 4.80 (br, 1H, 17-H); 4.74 (m, 1H, C$_5$H$_4$); 4.32 (m, 1H, 9-H); 4.28 (m, 1H, C$_5$H$_4$); 4.18 (dm, ^3J = 12.2 Hz, 15-H); 4.14 (m, 2H, C$_5$H$_4$); 4.12 (m, 1H, C$_5$H$_3$); 3.99 (t, ^3J = 2.6 Hz, 1H, C$_5$H$_3$); 3.18 (br t, $^2J = {}^3J$ = 12.2 Hz, 1H, 16-H^A); 2.65 (m, 1H, C$_5$H$_3$); 2.40 (m, 1H, 6-H); 2.35 (m, 2H, 8-H); 1.84 (br, 1H, 16-H^B); 1.36 (d, ^3J = 6.4 Hz, 3H, 7-H); 1.12 (s, 9H, 19-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_2$]-dichloromethane, 253 K): δ 95.9 (C-14); 86.3 (C-1); 84.1 (C-10); 75.1 (C$_5$H$_4$); 72.1 (C$_5$H$_3$); 72.0 (C-15); 70.0 (C$_5$H$_4$); 69.8 (C$_5$H$_4$); 66.9 (C-18); 64.9 (C$_5$H$_4$); 62.7 (C$_5$H$_3$); 60.3 (C-9); 60.0 (C$_5$H$_3$); 49.0 (C-8); 31.7 (C-16)[1]; 25.9 (C-19); 25.3 (C-6); 21.8 (C-7); n.o. (C$_6$F$_5$) [[1]: from the ghsqc experiment]. ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 233 K): δ −14.4 ($\nu_{1/2} \approx 50$ Hz). ^{19}F NMR (470 MHz, [D$_2$]-dichloromethane, 233 K): δ −135.8 (br, 2F, *o*-C$_6$F$_5$); −160.6 (br, 1F, *p*-C$_6$F$_5$); −165.4 (br, 2F, *m*-C$_6$F$_5$).

X-ray crystal structure analysis of 12: formula $C_{38}H_{27}BF_{15}FeN \cdot CH_2Cl_2$, $M = 934.19$, yellow crystal, 0.27 × 0.15 × 0.12 mm, $a = 9.5446(1)$ Å, $b = 33.9450(5)$ Å, $c = 11.4541(2)$ Å, $\beta = 96.793(1)°$, $V = 3684.98(9)$ Å^3, $\rho_{calc} = 1.684$ g cm^{-3}, $\mu = 0.663$ mm^{-1}, empirical absorption correction ($0.841 \leq T \leq 0.925$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 33 851 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 8405 independent ($R_{int} = 0.051$) and 7005 observed reflections [$I \geq 2\sigma(I)$], 540 refined parameters, $R = 0.061$, $wR^2 = 0.173$, max. (min.) residual electron density 1.11 (−1.00) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Amine 13. Compound **8** (400 mg, 1.29 mmol) was dissolved in acetonitrile (5 mL) in a 100 mL Teflon screw-capped ampoule with the necessary safety precautions for reactions under pressure. After addition of MeI (0.81 mL, 1.84 g, 12.94 mmol), the solution was stirred at room temperature for one hour and all volatiles were removed in vacuo. Benzene (15 mL) and aqueous ammonia (8 mL) were added, and the resulting suspension was heated to 110 °C until the aqueous layer turned colorless (ca. 3 h). After cooling to room temperature, the ampoule was depressurized and dichloromethane (100 mL) was added. The organic phase was washed with brine, dried over $MgSO_4$, and evaporated to dryness to yield an orange oil (345 mg, 1.23 mmol, 95%). Anal. Calcd for $C_{16}H_{19}FeN$: C: 68.35, H: 6.81, N: 4.98. Found: C: 68.06, H: 6.63, N: 4.42. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 6.98 (dd, ^3J = 17.5 Hz, 10.8 Hz, 1H, 15-H); 5.37 (dd, ^3J = 17.5 Hz, ^2J = 1.8 Hz, 1H, 16-H^A); 5.07 (dd, ^3J = 10.8 Hz, ^2J = 1.8 Hz, 1H, 16-H^B); 4.36 (m, 1H, 13-H); 4.15 (m, 1H, 4-H); 4.06 (m, 1H, 11-H); 4.04 (m, 1H, 12-H); 4.03 (m, 1H, 2-H); 3.89 (m, 1H, 3-H); 3.79 (dd, ^3J = 11.3 Hz, 3.5 Hz, 1H, 9-H); 3.69 (m, 1H, 5-H); 2.69 (m, 1H, 6-H); 2.56 (ddd, ^2J = 13.8 Hz, ^3J = 11.3 Hz, 3.8 Hz, 1H, 8-H^{ax}); 2.08 (ddd, ^2J = 13.8 Hz, ^3J = 4.5 Hz, 3.5 Hz, 1H, 8-H^{eq}); 1.47 (br s, 2H, 17-H); 1.24 (d, ^3J = 7.3 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (126 MHz, [D$_2$]-dichloromethane, 298 K): δ 135.3 (C-15); 112.2 (C-16); 94.3 (C-1); 85.8 (C-10); 82.4 (C-14); 74.7 (C-5); 71.8 (C-11); 69.3 (C-4); 67.9 (C-2); 67.8 (C-12); 67.43 (C-3); 67.39 (C-13); 52.1 (C-8); 45.3 (C-9); 27.5 (C-6); 17.6 (C-7).

Preparation of Compound 14. Compound **13** (20 mg, 0.071 mmol) and B(C$_6$F$_5$)$_3$ (36.4 mg, 0.071 mmol) were dissolved in dichloromethane (2 mL). Upon addition of pentane (5 mL) and storing the reaction mixture at −32 °C for 2 days, a yellow precipitate was formed. This was isolated by filtration and dried in vacuo to yield the adduct (46 mg, 0.063 mmol, 89%). Anal. Calcd for $C_{34}H_{19}BF_{15}FeN$: C: 51.94, H: 2.41, N: 1.77. Found: C: 50.96, H: 2.45, N: 2.05. ^{1}H NMR (500 MHz, [D$_2$]-dichloromethane, 298 K): δ 6.67 (dd, ^3J = 16.2 Hz, 10.5 Hz, 1H, 15-H); 5.75 (br, 1H, 17-H^A); 5.50 (dd, ^3J = 16.2 Hz, ^2J = 1.4 Hz, 1H, 16-H^A); 5.30 (dd, ^3J = 10.5 Hz, ^2J = 1.4 Hz, 1H, 16-H^B); 4.68 (m, 1H, 17-H^B); 4.35 (m, 1H, 13-H); 4.20 (m, 1H, 4-H); 4.08 (m, 1H, 2-H); 3.97 (m, 1H, 12-H); 3.91 (m, 1H, 3-H); 3.87 (m, 1H, 9-H); 3.81 (m, 1H, 5-H); 3.68 (m, 1H, 11-H); 2.92 (m, 1H, 8-H^{ax}); 2.87 (m, 1H, 6-H); 2.41 (dt, ^2J = 12.5 Hz, ^3J = 3.3 Hz, 1H, 8-H^{eq}); 1.16 (d, ^3J = 7.1 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (126 MHz, [D$_2$]-dichloromethane, 298 K): δ 148.4 (dm, $^1J_{CF} \approx 240$ Hz, C$_6$F$_5$); 140.5 (dm, $^1J_{CF} \approx 252$ Hz, C$_6$F$_5$); 137.5 (dm, $^1J_{CF} \approx 252$ Hz, C$_6$F$_5$); 131.3 (C-15); 117.7 (C-16); 116.1 (*i*-C$_6$F$_5$); 92.7 (C-1); 82.9 (C-14); 77.1 (C-10) 73.7 (C-5); 71.3 (C-11); 71.0 (C-4); 69.4 (C-2); 68.9 (C-12); 68.6 (C-13); 68.5 (C-3); 53.1 (C-9); 49.8 (C-8); 28.1 (C-6); 15.6 (C-7). ^{19}F NMR (470 MHz, [D$_2$]-dichloromethane, 298 K): δ −133.5 (m, 2F, *o*-C$_6$F$_5$); −157.3 (m, 1F, *p*-C$_6$F$_5$); −163.8 (m, 2F, *m*-C$_6$F$_5$). ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 298 K): δ −7.6 (s, $\nu_{1/2} \approx 160$ Hz).

Preparation of Complex 15. A solution of allyltriphenylphosphonium bromide (10.6 g, 27.7 mmol, 2.15 equiv) in THF (100 mL) was treated with *n*-BuLi (1.6 M in cyclohexane, 13.0 mL, 20.8 mmol, 1.63 equiv) at −78 °C. After stirring at low temperature for 10 min, the red suspension was added to a solution of ferrocenophane carbaldehyde derivative **7** (4.00 g, 12.8 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature overnight, and the solvent removed in vacuo. The crude product was purified by column chromatography at silica gel using methanol as eluent to yield a red oil (0.88 g, 2.63 mmol, 21%). Anal. Calcd for $C_{20}H_{25}FeN$: C: 71.65, H: 7.52, N: 4.18. Found: C: 71.40, H: 7.45, N: 3.78. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 7.07 (d, ^3J = 15.7 Hz, 1H, 15-H); 6.70

(ddt, ^3J = 16.7 Hz, 15.7 Hz, ^4J = 0.9 Hz, 1H, 16-H); 6.49 (ddd, ^3J = 16.7 Hz, 10.9 Hz, 10.2 Hz, 1H, 17-H); 5.18 (dm, ^3J = 16.7 Hz, 1H, 18-H^A); 4.98 (dm, ^3J = 10.9 Hz, 1H, 18-H^B); 4.41 (m, 1H, 13-H); 4.18 (m, 1H, 4-H); 4.05 (m, 1H, 12-H); 3.87 (m, 1H, 2-H); 3.84 (m, 1H, 3-H); 3.83 (m, 1H, 11-H); 3.68 (m, 1H, 5-H); 2.58 (m, 1H, 9-H); 2.57 (m, 1H, 6-H); 2.40 (ddd, ^2J = 13.2 Hz, ^3J = 10.7 Hz, 3.3 Hz, 1H, 8-H^{ax}); 2.15 (m, 7H, 8-H^{eq}, 19-H); 1.05 (d, ^3J = 7.5 Hz, 3H, 7-H). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 138.5 (C-17); 132.6 (C-15); 129.0 (C-16); 114.7 (C-18); 93.7 (C-1); 84.2 (C-10); 81.6 (C-14); 74.8 (C-5); 72.6 (C-11); 69.8 (C-4); 68.17 (C-12); 68.16 (C-13); 68.0 (C-2); 67.7 (C-3); 60.9 (C-9); 45.9 (C-8); 45.6 (C-19); 27.7 (C-6); 17.3 (C-7).

Preparation of Complex 16. Methyl iodide (0.74 mL, 1.69 g, 11.9 mmol, 10 equiv) was added to a solution of ferrocene compound **15** (400 mg, 1.19 mmol) in CH_3CN (5 mL). After stirring at room temperature for one hour, all volatiles were removed under reduced pressure and the resulting orange solid was suspended in acetonitrile (5 mL). Dimesitylphosphine (323 mg, 1.19 mmol) was added, and the reaction mixture was heated to 80 °C for 3 days and evaporated to dryness. The crude product was dissolved in dichloromethane (2 mL) and placed on a predried silica column under argon. It was first washed with dry pentane (200 mL) and further eluted with a 30:1 mixture of pentane and ethyl acetate. The intended compound was isolated as an orange powder (473 mg, 0.84 mmol, 71%). Anal. Calcd for $C_{36}H_{41}FeP$: C: 77.14, H: 7.37. Found: C: 76.80, H: 7.44. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ 7.24 (d, ^3J = 15.3 Hz, 1H, 15-H); 6.85 (d, ^4J = 2.4 Hz, 2H, *m*-CH^{MesA}); 6.64 (d, ^4J = 2.2 Hz, 2H, *m*-CH^{MesB}); 6.49 (dt, ^3J = 17.1 Hz, 10.4 Hz, 1H, 17-H); 6.34 (dd, ^3J = 15.3 Hz, 10.4 Hz, 1H, 16-H); 5.17 (dm, ^3J = 17.1 Hz, 1H, 18-H^A); 5.04 (dm, ^3J = 10.4 Hz, 1H, 18-H^B); 4.40 (m, 1H, C_5H_3); 4.21 (m, 1H, 4-H); 4.01 (m, 2H, C_5H_3); 3.98 (m, 1H, 2-H); 3.95 (m, 1H, 9-H); 3.88 (m, 1H, 3-H); 3.55 (m, 1H, 5-H); 2.64 (m, 1H, 6-H); 2.51 (s, 6H, *o*-CH_3^{MesA}); 2.44 (m, 1H, 8-H^A); 2.36 (s, 6H, *o*-CH_3^{MesB}); 2.25 (s, 3H, *p*-CH_3^{MesA}), 2.13 (s, 3H, *p*-CH_3^{MesB}); 2.12 (m, 1H, 8-H^B); 1.17 (d, ^3J = 7.1 Hz, 3H, 7-H). $^{13}C\{^1H\}$ NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ 143.5 (d, $^2J_{CP}$ = 14.1 Hz, *o*-C^{MesA}); 143.2 (d, $^2J_{CP}$ = 14.7 Hz, *o*-C^{MesB}); 138.5 (C-17); 138.4 (*p*-C^{MesA}); 137.7 (*p*-C^{MesB}); 133.6 (d, J_{CP} = 14.6 Hz, C-15); 133.1 (d, $^1J_{CP}$ = 21.9 Hz, *i*-C^{MesA}); 132.2 (d, $^1J_{CP}$ = 27.9 Hz, *i*-C^{MesB}); 130.2 (d, $^3J_{CP}$ = 3.3 Hz, *m*-CH^{MesA}); 129.8 (d, $^3J_{CP}$ = 3.3 Hz, *m*-CH^{MesB}); 127.3 (C-16); 114.2 (C-18); 92.8 (C-1); 85.9 (C-10); 80.8 (C-14); 75.2 (C-3); 73.9 (d, $^3J_{CP}$ = 3.3 Hz, C_5H_3); 69.8 (C-4); 68.1 (C-2); 67.9 (C_5H_3); 67.7 (C-5); 67.4 (C_5H_3); 46.2 (d, $^2J_{CP}$ = 26.6 Hz, C-8); 28.0 (d, $^1J_{CP}$ = 27.2 Hz, C-9); 26.4 (d, $^3J_{CP}$ = 9.2 Hz, C-6); 23.4 (d, $^3J_{CP}$ = 13.7 Hz, *o*-CH_3^{MesB}); 23.2 (d, $^3J_{CP}$ = 14.3 Hz, *o*-CH_3^{MesA}); 20.8 (*p*-CH_3^{MesA}); 20.6 (*p*-CH_3^{MesB}); 16.5 (C-7). $^{31}P\{^1H\}$ NMR (243 MHz, [D_2]-dichloromethane, 298 K): δ −9.2 ($\nu_{1/2} \approx$ 3 Hz).

X-ray crystal structure analysis of 16: formula $C_{36}H_{41}FeP$, M = 560.51, yellow crystal, 0.30 × 0.25 × 0.05 mm, a = 15.6074(4) Å, b = 15.1336(4) Å, c = 12.8467(3) Å, β = 97.130(1)°, V = 3010.88(13) Å^3, ρ_{calc} = 1.237 g cm^{-3}, μ = 0.577 mm^{-1}, empirical absorption correction (0.846 ≤ T ≤ 0.972), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 29 435 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.68 Å^{-1}, 7856 independent (R_{int} = 0.031) and 5747 observed reflections [$I \geq 2\sigma(I)$], 350 refined parameters, R = 0.046, wR^2 = 0.143, max. (min.) residual electron density 0.89 (−0.43) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 17. A solution of compound **16** (40.0 mg, 0.071 mmol) and $B(C_6F_5)_3$ (36.4 mg, 0.071 mmol) in dichloromethane (2 mL) was layered with pentane (5 mL) and stored at −32 °C for 2 days. During this time a red powder precipitated, which was collected by filtration and dried in vacuo to yield the product (70.2 mg, 0.065 mmol, 92%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated dichloromethane solution at −32 °C. Anal. Calcd for $C_{54}H_{41}BF_{15}FeP$: C: 60.47, H: 3.85. Found: C: 60.56, H: 3.54. ^1H NMR (600 MHz, [D_2]-dichloromethane, 298 K): δ (500 MHz, [D_2]-dichloromethane, 298 K): δ 7.16 (br d, ^4J = 4.6 Hz, 1H, *m*-CH^{MesA}); 7.02 (m, 1H, *m*-$CH^{MesA'}$); 6.96 (d, ^4J = 3.7 Hz, 1H, *m*-CH^{MesB}); 6.87 (m, 1H, *m*-$CH^{MesB'}$); 5.75 (m, 1H, 17-H); 5.37 (dd, ^3J = 9.5 Hz, ^4J = 3.9 Hz, 1H, 15-H); 4.51 (m 1H, 16-H); 4.41 (m, 1H, 4-H); 4.33 (dt, J = 13.3 Hz, 4.1 Hz, 1H, 9-H); 4.26 (m, 1H, C_5H_3); 4.22 (m, 1H, C_5H_3); 4.13 (m, 1H, 2-H); 4.03 (m, 1H, 3-H); 3.81 (m, 1H, C_5H_3); 3.55 (m, 1H, 5-H); 2.79 (s, 3H, *o*-CH_3^{MesA}); 2.42 (m, 1H, 8-H^A); 2.41 (m, 1H, 18-H^A); 2.39 (s, 3H, *o*-CH_3^{MesB}); 2.37 (s, 3H, *p*-CH_3^{MesA}); 2.28 (s, 3H, *p*-CH_3^{MesB}); 2.01 (s, 3H, *o*-$CH_3^{MesA'}$); 1.83 (m, 2H, 6-H, 8-H^B); 1.75 (s, 3H, *o*-$CH_3^{MesB'}$); 1.61 (m, 1H, 18-H^B); 0.80 (d, ^3J = 6.6 Hz, 3H, 7-H). $^{13}C\{^1H\}$ NMR (126 MHz, [D_2]-dichloromethane, 298 K): δ 148.5 (dm, $^1J_{CF} \approx$ 238 Hz, C_6F_5); 147.4 (d, $^3J_{CP}$ = 15.0 Hz, C-17); 145.5 (d, $^4J_{CP}$ = 3.2 Hz, *p*-C^{MesA}); 145.3 (d, $^4J_{CP}$ = 3.2 Hz, *p*-C^{MesB}); 144.5 (d, $^2J_{CP}$ = 9.1 Hz, *o*-$C^{MesB'}$); 142.6 (d, $^2J_{CP}$ = 10.1 Hz, *o*-C^{MesA}); 142.1 (d, $^2J_{CP}$ = 9.3 Hz, *o*-C^{MesB}); 141.4 (d, $^2J_{CP}$ = 7.5 Hz, *o*-$C^{MesA'}$); 138.1 (dm, $^1J_{CF} \approx$ 247 Hz, C_6F_5); 136.7 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5); 133.3 (d, $^3J_{CP}$ = 12.2 Hz, *m*-CH^{MesB}); 133.2 (d, $^3J_{CP}$ = 11.8 Hz, *m*-CH^{MesA}); 133.1 (d, $^3J_{CP}$ = 11.1 Hz, *m*-$CH^{MesB'}$); 132.5 (d, $^3J_{CP}$ = 10.1 Hz, *m*-$CH^{MesA'}$); 126.6 (br, *i*-C_6F_5); 119.8 (d, $^1J_{CP}$ = 58.7 Hz, *i*-C^{MesA}); 116.0 (d, $^2J_{CP}$ = 7.4, C-16); 115.8 (d, $^1J_{CP}$ = 67.1 Hz, *i*-C^{MesB}); 93.0 (d, $^2J_{CP}$ = 18.2 Hz, C-10 or C-14); 90.7 (d, $^2J_{CP}$ = 14.1 Hz, C-10 or C-14); 89.2 (C-1); 78.0 (C-5); 72.3 (C_5H_3); 72.0 (C-4); 69.9 (C-3); 66.1 (d, J_{CP} = 8.5 Hz, C_5H_3); 66.0 (C-2); 64.4 (d, J_{CP} = 10.4 Hz, C_5H_3); 49.7 (d, $^1J_{CP}$ = 34.0 Hz, C-15); 47.8 (C-8); 34.7 (d, $^1J_{CP}$ = 42.0 Hz, C-9); 28.7 (d, $^3J_{CP}$ = 4.0 Hz, C-6); 28.5 (br, C-18); 25.5 (d, $^3J_{CP}$ = 2.2 Hz, *o*-CH_3^{MesA}); 24.0 (d, $^3J_{CP}$ = 4.9 Hz, *o*-$CH_3^{MesB'}$); 23.9 (d, $^3J_{CP}$ = 1.7 Hz, *o*-CH_3^{MesB}); 22.5 (d, $^3J_{CP}$ = 5.4 Hz, *o*-$CH_3^{MesA'}$); 21.8 (br, C-7); 21.2 (d, $^5J_{CP}$ = 1.4 Hz, *p*-CH_3^{MesA}); 21.0 (d, $^5J_{CP}$ = 1.6 Hz, *p*-CH_3^{MesB}). ^{19}F NMR (564 MHz, [D_2]-dichloromethane, 298 K): δ −132.4 (m, 2F, *o*-C_6F_5); −164.3 (m, 1F, *m*-C_6F_5); −167.2 (m, 2F, *p*-C_6F_5). $^{11}B\{^1H\}$ NMR (160 MHz, [D_2]-dichloromethane, 298 K): δ −13.7 ($\nu_{1/2} \approx$ 55 Hz). $^{31}P\{^1H\}$ NMR ([D_2]-dichloromethane, 243 MHz, 298 K): δ 74.5 ($\nu_{1/2} \approx$ 40 Hz).

X-ray crystal structure analysis of 17: formula $C_{54}H_{41}BF_{15}FeP$, M = 1072.50, yellow crystal, 0.30 × 0.03 × 0.03 mm, a = 21.7628(3) Å, b = 28.5866(6) Å, c = 19.1647(4) Å, β = 109.200(2)°, V = 11259.6(4) Å^3, ρ_{calc} = 1.265 g cm^{-3}, μ = 0.378 mm^{-1}, empirical absorption correction (0.895 ≤ T ≤ 0.989), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 13 347 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.54 Å^{-1}, 7239 independent (R_{int} = 0.052) and 5006 observed reflections [$I \geq 2\sigma(I)$], 656 refined parameters, R = 0.089, wR^2 = 0.237, max. (min.) residual electron density 0.28 (−0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms; due to the crystal form and quality, the analysis has limited accuracy; futhermore the structure contains big voids with unidentified solvent molecules; therefore the SQUEEZE procedure was used.

Preparation of Complex 20. A solution of *rac-trans*-1′-formyl-2′,1″-[1-(dimethylamino)butane-1,3-diyl]ferrocene (**7**, 4.50 g, 14.5 mmol) and [(methoxycarbonyl)methylene]triphenylphosphorane (5.80 g, 17.3 mmol, 1.20 equiv) in dry toluene (300 mL) was heated to reflux for 12 h. After removal of the solvent the residue was dissolved in dichloromethane (50 mL) and extracted with water (3 × 40 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography at silica gel using methanol as eluent yielded the product as a red solid (3.97 g, 10.8 mmol, 75%). Anal. Calcd for $C_{20}H_{25}FeNO_2$: C: 65.41, H: 6.86, N: 3.82. Found: C: 65.40, H: 6.82, N: 3.67. Crystals suitable for X-ray diffraction were grown from a concentrated solution in diethyl ether at −20 °C. ^1H NMR (600 MHz, [D_6]-benzene, 298 K): δ 8.39 (d, ^3J = 15.8 Hz, 1H, 15-H); 6.59 (d, ^3J = 15.8 Hz, 1H, 16-H); 4.29 (m, 1H, C_5H_3); 4.05 (m, 1H, C_5H_4); 4.03 (m, 1H, C_5H_3); 3.84 (m, 1H, C_5H_3); 3.75 (m, 3H, C_5H_4); 3.47 (s, 3H, 18-H); 2.54 (dd, ^3J = 12.4 Hz, 2.1 Hz, 1H, 9-H); 2.44 (m, 1H, 6-H); 2.31 (ddd, ^2J = 14.5 Hz, ^3J = 12.4 Hz, 3.4 Hz, 1H, 8-H^{ax}); 2.08 (s, 6H, 19-H); 2.05 (m, 1H, 8-H^{eq}); 0.96 (d, ^3J = 7.4 Hz, 3H, 7-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, [D_6]-benzene, 298 K): δ 167.5 (C-17); 146.7

(C-15); 116.9 (C-16); 94.0 (C-1); 86.2 (C-10); 78.0 (C-14); 74.0 (C_5H_3); 73.9 (C_5H_4); 70.1 (C_5H_3); 70.1 (C_5H_4); 69.7 (C_5H_3); 68.5 (C_5H_4); 68.4 (C_5H_4); 60.6 (C-9); 50.9 (C-18); 46.0 (C-8); 45.4 (br, C-19); 27.4 (C-6); 17.3 (C-7).

X-ray crystal structure analysis of 20: formula $C_{20}H_{25}FeNO_2$, M = 367.26, red-orange crystal, 0.35 × 0.10 × 0.07 mm, a = 14.9835(4) Å, b = 8.5481(1) Å, c = 14.0395(2) Å, β = 101.730(1)°, V = 1760.63(6) Å^3, ρ_{calc} = 1.386 g cm^{-3}, μ = 0.868 mm^{-1}, empirical absorption correction (0.751 ≤ T ≤ 0.942), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 11 794 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.66 Å^{-1}, 4165 independent (R_{int} = 0.053) and 3052 observed reflections [$I \geq 2\sigma(I)$], 221 refined parameters, R = 0.037, wR^2 = 0.095, max. (min.) residual electron density 0.34 (−0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 21. Compound **20** (4.00 g, 10.9 mmol) was dissolved in diethyl ether (100 mL) and cooled to 0 °C. At this temperature DIBALH (1.1 M in diethyl ether, 20.0 mL, 33 mmol, 3 equiv) was added, and the solution stirred for 20 min. Water (50 mL) was added carefully, and the reaction mixture stirred for another 20 min. After filtering of all solids, the phases were separated, the organic layer was washed with 50 water (50 mL) twice and dried over $MgSO_4$, and the solvents were evaporated to dryness. The product could be obtained as a yellow powder (3.51 g, 10.3 mmol, 95%). Anal. Calcd for $C_{19}H_{25}FeNO$: C: 67.27, H: 7.43, N: 4.13. Found: C: 67.13, H: 7.32, N: 3.86. ^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ 6.97 (dm, ^3J = 15.8 Hz, 1H, 15-H); 6.10 (dt, ^3J = 15.8 Hz, 5.2 Hz, 1H, 16-H); 4.37 (m, 1H, 13-H); 4.21 (m, 1H, C_5H_4); 4.17, 4.16 (each ddd, ^2J = 14.3 Hz, ^3J = 5.2 Hz, ^4J = 1.7 Hz, each 1H, 17-H); 4.02 (t, ^3J = 2.5 Hz, 1H, 12-H); 3.91 (m, 1H, C_5H_4); 3.88 (m, 1H, C_5H_4); 3.80 (m, 1H, C_5H_4); 3.78 (m, 1H, 11-H); 2.62 (m, 1H, 6-H); 2.55 (m, 1H, 9-H); 2.52 (m, 1H, 8-H^A); 2.14 (m, 1H, 8-H^B); 2.13 (s, 6H, 18-H); 1.05 (d, ^3J = 7.2 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 129.0 (C-16); 127.5 (C-15); 93.6 (C-1); 83.0 (C-10); 82.3 (C-14); 74.5 (C_5H_4); 72.4 (C-11); 70.0 (C_5H_4); 68.2 (C_5H_4); 68.1 (C-13); 67.8 (C-12); 67.6 (C_5H_4); 63.6 (C-17); 61.3 (C-9); 45.7 (C-18); 45.5 (C-8); 27.9 (C-6); 17.1 (C-7); n.o. (OH).

Preparation of Complex 22. Active manganese dioxide (8.00 g, 92.0 mmol, 12.5 equiv) was added to a solution of compound **21** (2.50 g, 7.37 mmol) in dichloromethane (100 mL), and the resulting suspension was stirred for 12 h at ambient temperature. After filtration over Celite and evaporation of the solvent, the aldehyde was isolated as red powder (2.19 g, 6.48 mmol, 88%). Single crystals suitable for X-ray diffraction were grown by evaporation from a saturated ethereal solution. Anal. Calcd for $C_{19}H_{23}FeNO$: C: 67.67, H: 6.87, N: 4.15. Found: C: 67.17, H: 6.72, N: 3.86. ^{1}H NMR (600 MHz, [D$_6$]-benzene, 298 K): δ 9.63 (d, ^3J = 7.9 Hz, 1H, 17-H); 7.83 (d, ^3J = 16.0 Hz, 1H, 15-H); 6.66 (dd, ^3J = 16.0 Hz, 7.9 Hz, 1H, 16-H); 4.23 (m, 1H, C_5H_3); 4.05 (m, 1H, C_5H_3); 4.03 (m, 1H, C_5H_4); 3.85 (m, 1H, C_5H_3); 3.72 (m, 2H, C_5H_4); 3.55 (m, 1H, C_5H_4); 2.51 (dd, ^3J = 11.4 Hz, 3.7 Hz, 1H, 9-H); 2.44 (m, 1H, 6-H); 2.09 (m, 1H, 8-H^A); 2.04 (s, 6H, 18-H); 2.03 (m, 1H, 8-H^B); 0.96 (d, ^3J = 7.3 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_6$]-benzene, 298 K): δ 192.3 (C-17); 154.8 (C-15); 128.7 (C-16); 93.9 (C-1); 86.7 (C-10); 77.1 (C-14); 74.4 (C_5H_4); 74.3 (C_5H_3); 70.4 (C_5H_3); 70.2 (C_5H_3); 70.1 (C_5H_4); 68.8 (C_5H_4); 68.4 (C_5H_4); 60.4 (C-9); 46.3 (C-8); 45.4 (C-18); 27.3 (C-6); 17.3 (C-7).

X-ray crystal structure analysis of 22: formula $C_{19}H_{23}FeNO$, M = 337.23, red crystal, 0.40 × 0.15 × 0.10 mm, a = 9.8624(2) Å, b = 14.0863(3) Å, c = 11.9550(3) Å, β = 102.213(1)°, V = 1623.26(6) Å^3, ρ_{calc} = 1.380 g cm^{-3}, μ = 0.930 mm^{-1}, empirical absorption correction (0.707 ≤ T ≤ 0.913), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 11 166 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.62 Å^{-1}, 3268 independent (R_{int} = 0.089) and 1989 observed reflections [$I \geq 2\sigma(I)$], 202 refined parameters, R = 0.048, wR^2 = 0.179, max. (min.) residual electron density 0.84 (−0.60) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 23. A solution of amine **22** (400 mg, 1.19 mmol) in acetonitrile (5 mL) was treated with methyl iodide (0.74 mL, 1.69 g, 11.9 mmol, 10 equiv) and stirred for one hour at ambient temperature. After removal of all volatiles, dry acetonitrile (5 mL) and dimesitylphosphine (321 mg, 1.19 mmol) were added, and the reaction mixture was heated to 80 °C for 3 days. The solvent was removed in vacuo, and the crude product was purified by column chromatography at silica under argon using a 50:1 mixture of pentane and ethylacetate as eluent. The product was isolated as a red powder (290 mg, 0.52 mmol, 44%). Crystals suitable for X-ray diffraction analysis were grown by evaporation of an ethereal solution at room temperature. Anal. Calcd for $C_{35}H_{39}FeOP$: C: 74.73, H: 6.99. Found: C: 74.48, H: 6.91. ^{1}H NMR (600 MHz, [D$_2$]-dichloromethane, 298 K): δ 9.58 (d, ^3J = 8.0 Hz, 1H, 17-H); 8.37 (dd, ^3J = 15.5 Hz, J = 2.9 Hz, 1H, 15-H); 6.86 (d, $^4J_{HP}$ = 2.8 Hz, 2H, m-CH^{MesA}); 6.65 (d, $^4J_{HP}$ = 2.8 Hz, 2H, m-CH^{MesB}); 6.21 (ddd, ^3J = 15.5 Hz, 8.0 Hz, J = 1.8 Hz, 1H, 16-H); 4.55 (m, 1H, 13-H); 4.30 (m, 1H, 11-H); 4.29 (m, 1H, 12-H); 4.25 (m, 1H, C_5H_4); 4.04 (dt, ^3J = 12.6 Hz, 2.5 Hz, 1H, 9-H); 4.01 (m, 1H, C_5H_4); 3.93 (m, 1H, C_5H_4); 3.74 (m, 1H, C_5H_4); 2.66 (m, 1H, 6-H); 2.52 (s, 6H, o-CH$_3^{MesA}$); 2.38 (m, 1H, 8-H^A); 2.35 (s, 6H, o-CH$_3^{MesB}$); 2.24 (s, 3H, p-CH$_3^{MesA}$); 2.20 (m, 1H, 8-H^B); 2.12 (s, 3H, p-CH$_3^{MesB}$); 1.17 (d, ^3J = 7.2 Hz, 3H, 7-H). ^{13}C{^{1}H} NMR (151 MHz, [D$_2$]-dichloromethane, 298 K): δ 193.4 (C-17); 157.7 (d, $^4J_{CP}$ = 17.4 Hz, C-15); 143.5 (d, $^2J_{CP}$ = 16.3 Hz, o-C^{MesA}); 143.1 (d, $^2J_{CP}$ = 15.2 Hz, o-C^{MesB}); 138.9 (p-C^{MesA}); 138.1 (p-C^{MesB}); 132.6 (d, $^1J_{CP}$ = 28.7 Hz, i-C^{MesA}); 131.6 (d, $^1J_{CP}$ = 27.1 Hz, i-C^{MesB}); 130.3 (d, $^3J_{CP}$ = 3.7 Hz, m-CH^{MesA}); 130.0 (d, $^3J_{CP}$ = 3.3 Hz, m-CH^{MesB}); 126.2 (C-16); 93.4 (C-1); 89.0 (d, $^2J_{CP}$ = 22.5 Hz, C-10); 76.3 (m, C-14, C-11); 74.6 (C_5H_4); 70.7 (C-12); 70.5 (C_5H_4); 69.19 (C-13); 69.15 (C_5H_4); 69.10 (C_5H_4); 47.3 (d, $^2J_{CP}$ = 26.8 Hz, C-8); 28.0 (d, $^1J_{CP}$ = 23.6 Hz, C-9); 26.4 (d, $^3J_{CP}$ = 10.4 Hz, C-6); 23.5 (d, $^3J_{CP}$ = 13.4 Hz, o-CH$_3^{MesB}$); 23.3 (d, $^3J_{CP}$ = 14.4 Hz, o-CH$_3^{MesA}$); 20.9 (p-CH$_3^{MesA}$); 20.7 (p-CH$_3^{MesB}$); 16.5 (C-7). ^{31}P{^{1}H} NMR (243 MHz, [D$_2$]-dichloromethane, 298 K): δ −6.6 ($\nu_{1/2}$ ≈ 15 Hz).

X-ray crystal structure analysis of 23: formula $C_{35}H_{39}FeOP$, M = 562.48, red crystal, 0.35 × 0.15 × 0.15 mm, a = 9.9695(5) Å, b = 11.1347(5) Å, c = 13.5680(6) Å, α = 86.386(2)°, β = 75.787(2)°, γ = 80.391(3)°, V = 1439.18(12) Å^3, ρ_{calc} = 1.298 g cm^{-3}, μ = 0.606 mm^{-1}, empirical absorption correction (0.816 ≤ T ≤ 0.915), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 23 735 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.68 Å^{-1}, 7082 independent (R_{int} = 0.050) and 5268 observed reflections [$I \geq 2\sigma(I)$], 350 refined parameters, R = 0.044, wR^2 = 0.113, max. (min.) residual electron density 0.46 (−0.50) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 24. Compound **23** (100 mg, 0.178 mmol) and $B(C_6F_5)_3$ (91 mg, 0.178 mmol) were dissolved in dichloromethane (2 mL), and the resulting solution was stored at −32 °C for two days. The supernatant liquid was removed via syringe, and the yellow needles (182 mg, 0.169 mmol, 95%) were dried in vacuo. Anal. Calcd for $C_{53}H_{39}BF_{15}FeOP$: C: 59.19, H: 3.75. Found: C: 59.26, H: 3.94. ^{1}H NMR (600 MHz, [D$_2$]-dichloromethane, 298 K): δ 7.09 (br d, ^4J = 4.2 Hz, 1H, m-CH$^{MesA'}$); 6.98 (br, 1H, m-CH^{MesA}); 6.90 (br d, ^4J = 2.9 Hz, 1H, m-CH^{MesB}); 6.84 (br, 1H, m-CH$^{MesB'}$); 6.48 (dd, ^3J = 10.0 Hz, J = 2.9 Hz, 1H, 15-H); 6.14 (m, 1H, 17-H); 4.43 (m, 1H, 4-H); 4.39 (dt, ^3J = 13.5 Hz, 4.0 Hz, 1H, 9-H); 4.31 (m, 1H, 13-H); 4.26 (m, 1H, 12-H); 4.25 (m, 1H, 11-H); 4.12 (m, 1H, 2-H); 4.07 (m, 1H, 3-H); 3.99 (m, 1H, 5-H); 3.33 (ddd, ^3J = 10.0 Hz, 5.6 Hz, $^4J_{HP}$ = 6.9 Hz, 1H, 16-H); 2.85 (s, 3H, o-CH$_3^{MesA'}$); 2.45 (s, 3H, o-CH$_3^{MesB}$); 2.44 (m, 1H, 8-H^A); 2.34 (s, 3H, p-CH$_3^{MesA}$); 2.23 (s, 3H, p-CH$_3^{MesB}$); 2.02 (m, 1H, 6-H); 1.99 (s, 3H, o-CH$_3^{MesA}$); 1.86 (m, 1H, 8-H^B); 1.80 (s, 3H, o-CH$_3^{MesB'}$); 0.83 (d, ^3J = 6.7 Hz, 3H, 7-H). ^{1}H{^{31}P} NMR (600 MHz, [D$_2$]-dichloromethane,

298 K): δ 6.48 (d, ^3J = 10.0 Hz, 1H, 15-H); 6.14 (d, ^3J = 5.6 Hz, 1H, 17-H); 3.33 (dd, ^3J = 10.0 Hz, 5.6 Hz, 1H, 16-H) [selected resonances]. $^{13}C\{^1H\}$ NMR (151 MHz, $[D_2]$-dichloromethane, 298 K): δ 150.5 (d, $^3J_{CP}$ = 14.5 Hz, C-17); 148.4 (dm, $^1J_{CF} \approx$ 249 Hz, C_6F_5); 145.0 (d, $^2J_{CP}$ = 13.3 Hz, *o*-$C^{MesB'}$); 144.9 (*p*-C^{MesA}); 144.3 (d, $^4J_{CP}$ = 3.2 Hz, *p*-C^{MesB}); 144.0 (d, $^2J_{CP}$ = 11.0 Hz, *o*-$C^{MesA'}$); 141.9 (d, $^2J_{CP}$ = 8.9 Hz, *o*-C^{MesB}); 141.1 (d, $^2J_{CP}$ = 6.9 Hz, *o*-C^{MesA}); 139.1 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5); 137.0 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5); 133.1 (d, $^3J_{CP}$ = 11.3 Hz, *m*-$CH^{MesA'}$); 132.9 (d, $^3J_{CP}$ = 11.3 Hz, *m*-$CH^{MesB'}$); 132.7 (d, $^3J_{CP}$ = 12.0 Hz, *m*-CH^{MesB}); 132.0 (d, $^3J_{CP}$ = 9.9 Hz, *m*-CH^{MesA}); 123.1 (br, *i*-C_6F_5); 119.9 (d, $^1J_{CP}$ = 58.2, *i*-C^{MesA}); 117.5 (d, $^1J_{CP}$ = 67.8 Hz, *i*-C^{MesB}); 95.1 (C-14); 94.8 (d, $^2J_{CP}$ = 21.1 Hz, C-16); 90.3 (d, $^2J_{CP}$ = 14.6 Hz, C-10), 89.4 (C-1), 78.0 (C-5); 72.3 (C-12). 72.1 (C-4); 69.8 (C-3); 66.2 (d, $^3J_{CP}$ = 9.4 Hz, C-13); 65.8 (C-2); 63.9 (d, $^3J_{CP}$ = 9.4 Hz, C-11); 47.9 (C-8); 42.9 (d, $^1J_{CP}$ = 42.7 Hz, C-15); 34.7 (C-9); 28.6 (C-6); 25.0 (*o*-$CH_3{}^{MesA'}$); 24.1 (d, $^3J_{CP}$ = 4.3 Hz, *o*-$CH_3{}^{MesB'}$); 23.8 (d, $^3J_{CP}$ = 1.9 Hz, *o*-$CH_3{}^{MesB}$); 22.5 (d, $^3J_{CP}$ = 6.1 Hz, *o*-$CH_3{}^{MesA}$); 21.7 (C-7); 21.2 (d, ^5J = 1.6 Hz, *p*-$CH_3{}^{MesA}$); 20.9 (d, ^5J = 1.4 Hz, *p*-$CH_3{}^{MesB}$). ^{19}F NMR (564 MHz, $[D_2]$-dichloromethane, 298 K): δ −133.8 (m, 2F, *o*-C_6F_5); −161.9 (t ^3J = 20.0 Hz, 1F, *p*-C_6F_5); −166.6 (m, 2F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (192 MHz, $[D_2]$-dichloromethane, 298 K): δ −2.5 ($\nu_{1/2} \approx$ 120 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $[D_2]$-dichloromethane, 298 K): δ 73.8 ($\nu_{1/2} \approx$ 20 Hz).

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Supporting Information Available: Additional experimental and spectroscopic details. CIF files for compounds **9**, **10**, **12**, **16**, **17**, **20**, **22**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.