Ambiphilic Ligands

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Diferrocenophosphaborin: A Planar-Chiral, Redox-Active and Anion-Responsive Ambiphilic Ligand**

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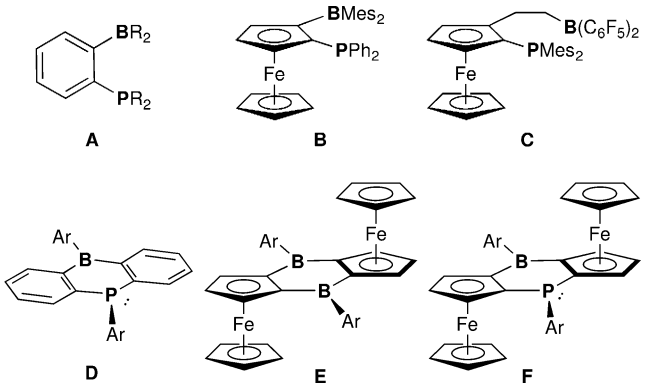
Abstract: *A new class of Janus-like ambiphilic ligands is introduced. The rigid diferrocene backbone in heterocycles* ***4-SnP*** *and* ***4-BP*** *creates an unprecedented chiral environment as demonstrated by multinuclear NMR and single-crystal X-ray studies. In addition, the ligands are redox-responsive and the Lewis acidic borane moiety in* ***4-BP*** *can be exploited to further tune the properties: a clear decrease in the CO stretching frequency of a Vaska-type Rh^I complex* ***5-BP*** *is observed upon addition of fluoride ions. Thus, the Lewis acid and Lewis base sites influence each other and their strength can be modulated by redox chemistry and anion binding.*

The concept of combining Lewis acids (LAs) and Lewis bases (LBs) without the formation of direct LA–LB interactions has inspired several emerging research areas. Different from classical Lewis pairs (CLPs), so-called "frustrated Lewis pairs" (FLPs) retain the high reactivity of the individual LA and LB moieties due to steric constraints.[1] If they are covalently linked to a rigid backbone, a bifunctional system is obtained, in which the LA and LB can interact with a substrate or a metal in a cooperative manner.[2] These types of "molecular pincers" have been successfully utilized in the activation of small molecules. Another application as ambiphilic ligands takes advantage of their ability to coordinate to transition metals in unique ways.[3] For example, by tuning the Lewis acidity of the boron center and nucleophilicity of the metal, ligand **A** (Scheme 1) can be tailored to bind to metals via P→Rh–Cl→B or P→Au→B interactions.[3a]

Lewis acids and Lewis pairs with a ferrocene (Fc) backbone have recently attracted attention, because they provide a rigid framework and also offer an opportunity to tune the reactivity by reversible oxidation of the Fe center.[3e,4] As an example, Aldridge reported the use of $FcB(C_6F_5)_2$ as a colorimetric and electrochemical indicator for N_2O binding.[5] Chiral B/P Lewis pairs (**B**) were developed by Aldridge[6] and Thilagar,[7] while Erker[8] demonstrated the use of ferrocenylalkylborane (**C**) in the activation of H_2. An alternative approach is to incorporate both the LA and LB moieties into a heterocyclic system. For example, Kawashima and Gabbaï reported that phosphaborins (**D**) display desirable charge-transfer characteristics and, upon alkylation at P, exhibit high affinity for fluoride anions.[9] Symmetric ferrocene-fused diboracycles (**E**)[4a,10] have been introduced as well, but despite the importance of ferrocenylphosphines in catalysis,[11] the corresponding phosphacycles remain elusive.[12] We envisioned that formal replacement of a single boron atom in **E** with phosphorus might offer access to a unique new ligand architecture. The rigid and highly unusual stereochemical environment at B and P would give rise to a Janus-like chiral ambiphilic ligand that is at the same time redox-active. We describe here the synthesis of the first example of such an ambiphilic diferrocenophosphaborin. We further demonstrate that the ligand properties can be tuned not only by switching the redox state of Fe, but also via anion binding to the Lewis acidic borane moiety.



Scheme 1.

We chose Kagan's ferrocenylsulfinate, (S_S)-FcS(O)Tol (**1**), as a building block to access the desired enantiopure diferrocenes.[13] Treatment of **1** with LDA followed by addition of 0.5 equiv Me_2SnCl_2 gave diferrocenylstannane **2** in 80% yield after purification by column chromatography and recrystallization (Scheme 2).[14] The sulfinate groups in **2** were then replaced by addition of 2 equivalents of *t*BuLi at −78°C. Metathesis of the dilithiated species with $PhPCl_2$, followed by addition of BH_3·THF gave the heterocycle **3-SnP** in an overall yield of 40%. Initial attempts at replacing the stannyl group in **3-SnP** by reaction with $PhBCl_2$ proved unsuccessful. Therefore, **3-SnP** was first treated with $HgCl_2$ in acetone to give a ring-opened species bearing Me_2ClSn and ClHg substituents. The latter reacted smoothly with $PhBCl_2$ to give phosphaborin **3-BP** in 49% yield after purification by column chromatography.

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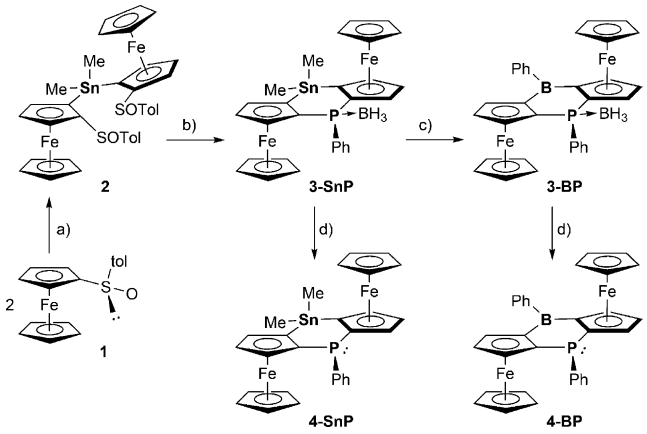

Scheme 2. Synthesis of chiral ambidentate ligands **4**. a) 1. 2 LDA, 2. Me_2SnCl_2; b) 1. 2 *t*BuLi, 2. $PhPCl_2$, 3. BH_3·THF; c) 1. $HgCl_2$, 2. $PhBCl_2$; d) DABCO. LDA = lithium diisopropylamide; DABCO = 1,4-diazabicyclo[2.2.2]octane.

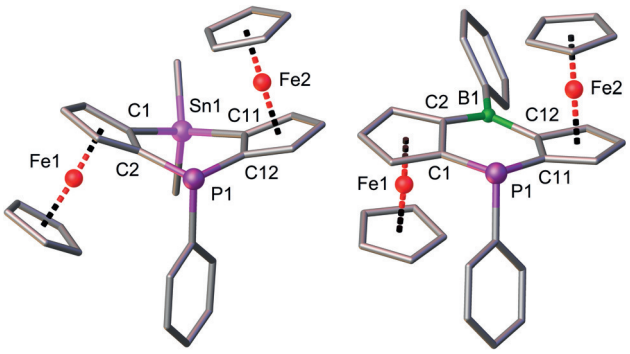

Figure 1. X-ray structure plots of **4-SnP** and **4-BP**; H atoms and a CH_3CN solvent molecule are omitted.

Table 1: Comparison of selected geometric parameters for **4-SnP**, **4-BP** and **5-SnP** (angles,°).

Compound	4-SnP	4-BP	5-BP
Bridge angle at Sn/B[a]	96.0(1)	117.2(2)	114.8(14)
Bridge angle at P[a]	104.5(2)	99.5(1)	101.1(7)
$\Sigma\sphericalangle_{C\text{-}B\text{-}C}$	–	360.0	359.9
$\Sigma\sphericalangle_{C\text{-}P\text{-}C}$	311.7	305.7	310.3
Dip angle for B[b]	–	14.6, 15.6	15.8, 18.1
Tilt angle[c]	4.1, 0.3	2.5, 2.2	2.1, 0.5
Cp//Cp[d]	44.1	15.1	19.2

[a] Endocyclic C-E-C angles (E = Sn, B, P). [b] 180° − $\sphericalangle(Cp_{centroid}\text{-}C\text{-}B)$. [c] Dihedral angles between Cp ring planes in the same Fc unit. [d] Dihedral angles between the substituted Cp ring planes of different Fc units.

Successful formation of the desired stanna- and boracycles was confirmed by multinuclear NMR, mass spectrometry, and single-crystal X-ray diffraction (Supporting Information). The tin atom in **3-SnP** gives rise to a doublet at $\delta(^{119}Sn) = -26.9$ ppm ($^3J(^{31}P,^{119}Sn) = 10$ Hz) and the bridging boron atom in **3-BP** shows a broad signal at $\delta(^{11}B) = 52.1$ ppm. Sharp ^{11}B NMR signals (**3-SnP**: −38.6; **3-BP**: −35.2 ppm) and a quartet signal in the ^1H NMR (**3-SnP**: 1.20; **3-BP**: 1.16 ppm) are assigned to the BH_3 group. In each case high-resolution MALDI-MS data showed a major signal corresponding to the loss of BH_3 from the molecular ion M^+, indicating the lability of the protecting group. To preparatively remove the BH_3, **3-SnP** and **3-BP** were reacted with a slight excess of DABCO at elevated temperature. The products were purified by crystallization or alumina gel column chromatography under N_2 atmosphere. BH_3 removal was confirmed by a shift of the ^{31}P NMR resonance from +10.3 ppm to −28.6 ppm for **4-SnP** and from +11.2 ppm to −24.9 ppm for **4-BP**. The pyramidal geometry at P manifests itself in two distinct sets of Fc resonances in the ^1H NMR, which showed no signs of coalescence at temperatures up to 80 °C.

All these compounds are chiral and the stereoselectivity for each reaction step was examined. Compounds **3-SnP** and **3-BP** were subjected to optical rotation and chiral HPLC measurements,[15] which showed only one major band. In addition, the Flack parameters from single-crystal X-ray analyses confirmed the formation of the expected enantiomer. The X-ray structures of **4-SnP** and **4-BP** (Figure 1, Table 1) offer important additional insights into the chiral environment. When looking down the P–E (E = Sn, B) vector, an unusual paddlewheel-like[16] axial-chiral structure is evident. The central phosphastannin cycle adopts a boat conformation whereas the phosphaborin cycle is more planar but strongly puckered. These structural differences arise from the fact that the Sn atom in **4-SnP** is in a tetrahedral environment, but the boron atom in **4-BP** adopts a perfectly trigonal planar geometry ($\Sigma\sphericalangle_{C\text{-}B\text{-}C} = 360.0°$). In addition, interaction of the electron-deficient boron atom with the ferrocene moiety in **4-BP** results in pronounced bending of the boryl group[17] toward the iron atoms (dip angles $\alpha = 14.6$, 15.6°). The angle sums at P are similar for **4-SnP** ($\Sigma\sphericalangle_{C\text{-}P\text{-}C} = 311.7°$) and **4-BP** ($\Sigma\sphericalangle_{C\text{-}P\text{-}C} = 305.7°$) and consistent with a pyramidal geometry. We emphasize that these ligands display no central chirality at P, but the chiral environment is determined solely by the orientation of the ferrocene "paddles".

An intriguing aspect is the potential utility of **4-SnP** and **4-BP** as responsive and tunable chiral phosphine ligands. To investigate this possibility, we reacted the free ligands with 0.25 equiv of $[\{Rh(CO)_2Cl\}_2]$ to give the corresponding Vaska-type rhodium complexes $[L_2Rh(CO)Cl]$, **5-SnP** and **5-BP** (Figure 2).

The ^{31}P NMR resonances at 15.8 and 7.6 ppm, respectively, are downfield shifted when compared to those of the free ligands **4-SnP** (−28.6 ppm) and **4-BP** (−24.9 ppm) and the direct attachment to Rh is reflected in doublet splitting with $^2J(^{103}Rh,^{31}P)$ coupling constants of 127 and 121 Hz. The presence of only one set of ^1H NMR signals is consistent with the expected *trans*-arrangement,[18] which was further corroborated by a single-crystal X-ray diffraction analysis of **5-BP** (Figure 2c, Table 1).

All the ligands and complexes are redox-active and the electrochemical properties were studied by cyclic and square wave voltammetry (SWV, Table 2). For the BH_3-protected species **3-SnP**, a reversible 1st oxidation at $E_{1/2}(1) = +138$ mV and quasi-reversible 2nd oxidation at $E_{1/2}(2) = +557$ mV were recorded ($\Delta E = 419$ mV). Replacement of the Sn bridge with the electron-deficient B bridge in **3-BP** caused an anodic shift

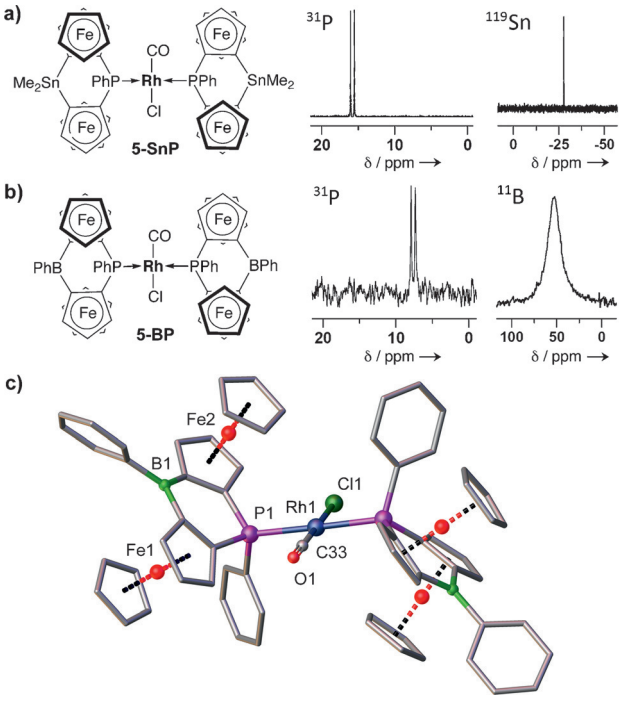

Figure 2. a,b) Selected NMR data (CD_2Cl_2) for **5-SnP** and **5-BP**. c) X-ray structure plot of **5-BP**; H atoms and disordered CH_3CN solvent molecules are omitted; selected bond distances [Å]: Rh1–P1 2.336(3), Rh1–C33 1.79(2), C33–O1 1.16(2).

Table 2: Comparison of ^{31}P NMR chemical shifts (ppm) and electrochemical (SWV) data (mV, vs. Fc/Fc^+ couple).

Compound	δ (^{31}P)	$E_{1/2}$ (**1**)	$E_{1/2}$ (**2**)	ΔE
3-SnP	+10.3	+138	+557	419
3-BP	+11.2	+255	+940	685
4-SnP	−28.6	−50	+318 (650)[a]	368
4-BP	−24.9	−2	+591 (787)[a]	593
5-SnP	+15.8	−2/+146[b]	+522/+706[b]	540[c]
5-BP	+7.6	+130/+254[b]	+862/+1000[b]	739[c]

[a] Additional process attributed to P oxidation. [b] Values correspond to ferrocene oxidation on different ligands. [c] Redox splitting calculated using averaged values for 1st/2nd and 3rd/4th redox process.

and a greatly increased peak separation of $\Delta E = 685$ mV that indicates more effective electronic communication of the ferrocenes via the tricoordinate borane moiety.[10] Upon removal of BH_3 an increase in electron density is expected, which is reflected in much higher cathodic potentials for **4-SnP** and **4-BP**. For the free ligands, additional redox processes are observed at higher potentials and based on literature precedents[19] they are likely due to electron transfer between the ferrocene and "free" phosphine moieties, followed by reaction with traces of water. This is supported by the fact that they are neither observed for the BH_3 nor the Rh complexes. The Vaska-type Rh complexes show four separate redox waves (Figure 3), which is consistent with additional (weak) interactions between the individual ligands. Thus, oxidation occurs first at one ferrocene moiety of each ligand and then at significantly higher potential on the second ferrocene moieties. Overall the potentials are quite similar to those recorded for the BH_3 complexes.

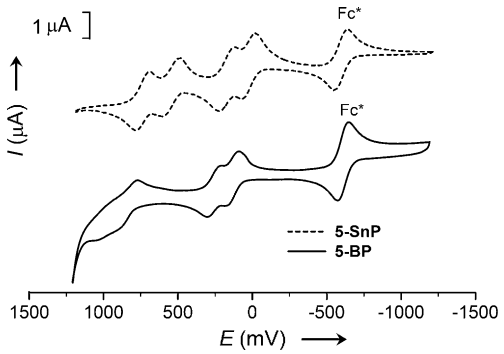

Figure 3. Cyclic voltammograms for **5-SnP** and **5-BP** (0.05 M $Bu_4N[B(C_6H_3(CF_3)_2)_4]$ in CH_2Cl_2, 50 mVs^{-1}; Fc^*/Fc^{*+} as internal reference, Fc^* = decamethylferrocene).

Table 3: Comparison of CO stretching frequencies (ν_{CO}) for Vaska-type complexes $[(L)_2Rh(CO)Cl]$.

PPh_2Fc	$PPhFc_2$	PCy_3	4-SnP	4-BP	$[4\text{-BP-F}]^-$
[a] 1970	[a] 1957	[b] 1943	[c] 1962	[c] 1967	[c] 1948

[a] Ref. [18]. [b] Ref. [22]. [c] This work (solid sample, ATR).

The Vaska-type Rh^I complexes offer an opportunity to probe the steric and electronic properties of the phosphine ligands by monitoring the CO stretching frequency, ν(CO).[18] The stretching frequency of **5-SnP** is 1962 cm^{-1} and that of **5-BP** 1967 cm^{-1} (Table 3), indicating a slightly more electron-rich character of the phosphastannin ligand **4-SnP**. These values are in-between those for PPh_2Fc and $PPhFc_2$. However, upon addition of an excess of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) to the rhodium complex **5-BP**, ν(CO) shifted dramatically to lower energy (1948 cm^{-1}), suggesting a stronger electron-donating effect of the ligand after fluoride ion binding. Presumably, the weakening of the C≡O bond is caused by both enhanced d–π* backbonding due to the increased electron density at the metal center and electrostatic polarization triggered by complexation with the negatively charged fluoride anion.[20,21] In a control experiment, the addition of F^- to $[(PPh_3)_2Rh(CO)Cl]$ did not affect ν(CO), which eliminates other possible reasons such as halide ligand exchange.

In conclusion, the first examples of planar-chiral ferrocene-fused phosphacycles were synthesized and their unique chiral structure was confirmed by multinuclear NMR spectroscopy, X-ray crystallography, chiral HPLC and optical rotation measurements. As a novel type of ambidentate ligand the phosphaborin **4-BP** is not only redox-active but also responsive to the presence of fluoride anions. Binding of F^- to B in the corresponding Vaska-type Rh complex **5-BP** shifts ν(CO) from 1967 to 1948 cm^{-1}, a value that is approaching that for the highly electron-rich alkylphosphine PCy_3. Given the importance of phosphines in a large array of catalytic processes we envision broad utility of this new class of rigid, chiral, and stimuli-responsive ligands in catalysis.

Keywords: ambiphilic ligands · ferrocenes · Lewis acids · planar chirality · redox activity

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[1] a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; c) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252–12262; d) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541.

[2] a) F. Schulz, V. Sumerin, S. Heikkinen, B. Pedersen, C. Wang, M. Atsumi, M. Leskelä, T. Repo, P. Pyykkö, W. Petry, B. Rieger, *J. Am. Chem. Soc.* **2011**, *133*, 20245–20257; b) M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Petersen, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2012**, *134*, 10156–10168; c) E. Theuergarten, D. Schluens, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Commun.* **2010**, *46*, 8561–8563; d) M. Lindqvist, K. Borre, K. Axenov, B. Kótai, M. Nieger, M. Leskelä, I. Pápai, T. Repo, *J. Am. Chem. Soc.* **2015**, *137*, 4038–4041.

[3] a) S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057; b) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem. Int. Ed.* **2007**, *46*, 8583–8586; *Angew. Chem.* **2007**, *119*, 8737–8740; c) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C. H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729–16738; d) A. Amgoune, S. Ladeira, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2012**, *134*, 6560–6563; e) B. E. Cowie, D. J. H. Emslie, *Chem. Eur. J.* **2014**, *20*, 16899–16912.

[4] a) K. Venkatasubbaiah, I. Nowik, R. H. Herber, F. Jäkle, *Chem. Commun.* **2007**, 2154–2156; b) R. Boshra, A. Doshi, F. Jäkle, *Angew. Chem. Int. Ed.* **2008**, *47*, 1134–1137; *Angew. Chem.* **2008**, *120*, 1150–1153; c) L. Kaufmann, H. Vitze, M. Bolte, H. W. Lerner, M. Wagner, *Organometallics* **2008**, *27*, 6215–6221; d) J. Chen, K. Venkatasubbaiah, T. Pakkirisamy, A. Doshi, A. Yusupov, Y. Patel, R. A. Lalancette, F. Jäkle, *Chem. Eur. J.* **2010**, *16*, 8861–8867; e) M. W. P. Bebbington, S. Bontemps, G. Bouhadir, M. J. Hanton, R. P. Tooze, H. van Rensburg, D. Bourissou, *New J. Chem.* **2010**, *34*, 1556–1559; f) H. Braunschweig, F. Breher, C. W. Chiu, D. Gamon, D. Nied, K. Radacki, *Angew. Chem. Int. Ed.* **2010**, *49*, 8975–8978; *Angew. Chem.* **2010**, *122*, 9159–9162; g) J. Chen, R. A. Lalancette, F. Jäkle, *Organometallics* **2013**, *32*, 5843–5851; h) J. Chen, R. A. Lalancette, F. Jäkle, *Chem. Commun.* **2013**, *49*, 4893–4895; i) J. Chen, R. A. Lalancette, F. Jäkle, *Chem. Eur. J.* **2014**, *20*, 9120–9129; j) Y. L. Rao, T. Kusamoto, R. Sakamoto, H. Nishihara, S. N. Wang, *Organometallics* **2014**, *33*, 1787–1793.

[5] M. J. Kelly, J. Gilbert, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2013**, *52*, 14094–14097; *Angew. Chem.* **2013**, *125*, 14344–14347.

[6] a) I. Siewert, D. Vidovic, S. Aldridge, *J. Organomet. Chem.* **2011**, *696*, 2528–2532; b) I. R. Morgan, A. Di Paolo, D. Vidovic, I. A. Fallis, S. Aldridge, *Chem. Commun.* **2009**, 7288–7290.

[7] P. Sudhakar, P. Thilagar, *J. Chem. Sci.* **2013**, *125*, 41–49.

[8] X. W. Wang, G. Kehr, C. G. Daniliuc, G. Erker, *J. Am. Chem. Soc.* **2014**, *136*, 3293–3303.

[9] a) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima, F. P. Gabbai, *Chem. Commun.* **2007**, 1133–1135; b) T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbai, *J. Am. Chem. Soc.* **2008**, *130*, 10890–10891.

[10] a) K. Venkatasubbaiah, L. N. Zakharov, W. S. Kassel, A. L. Rheingold, F. Jäkle, *Angew. Chem. Int. Ed.* **2005**, *44*, 5428–5433; *Angew. Chem.* **2005**, *117*, 5564–5569; b) K. Venkatasubbaiah, T. Pakkirisamy, R. A. Lalancette, F. Jäkle, *Dalton Trans.* **2008**, 4507–4513; c) T. Pakkirisamy, K. Venkatasubbaiah, W. S. Kassel, A. L. Rheingold, F. Jäkle, *Organometallics* **2008**, *27*, 3056–3064; d) P. Thilagar, D. Murillo, J. Chen, F. Jäkle, *Dalton Trans.* **2013**, *42*, 665–670.

[11] a) R. G. Arrayás, J. Adrio, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 7674–7715; *Angew. Chem.* **2006**, *118*, 7836–7878; b) *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Stepnicka), Wiley, Chichester, **2008**; c) *Chiral Ferrocenes in Asymmetric Catalysis: Synthesis and Applications* (Eds.: L.-X. Dai, X.-L. Hou), Wiley-VCH, Weinheim, **2010**; d) E. K. Sarbisheh, J. C. Green, J. Müller, *Organometallics* **2014**, *33*, 3508–3513.

[12] Racemic mixtures of diferrocenylphosphine oxide derivatives were reported by Mathey; see: L. Eberhard, J. P. Lampin, F. Mathey, *J. Organomet. Chem.* **1974**, *80*, 109–118.

[13] O. Riant, G. Argouarch, D. Guillaneux, O. Samuel, H. B. Kagan, *J. Org. Chem.* **1998**, *63*, 3511–3514.

[14] The alternative approach of introducing P first resulted in complex product mixtures that could not be easily separated.

[15] Compounds **3-SnP** and **3-BP** were used because of their better oxidative stability.

[16] M. P. Doyle, D. Shabashov, L. Zhou, P. Y. Zayalij, C. Welch, Z. Pirzada, *Organometallics* **2011**, *30*, 3619–3627.

[17] M. Scheibitz, M. Bolte, J. W. Bats, H.-W. Lerner, I. Nowik, R. H. Herber, A. Krapp, M. Lein, M. Holthausen, M. Wagner, *Chem. Eur. J.* **2005**, *11*, 584–603.

[18] A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.* **2003**, *245*, 121–137.

[19] K. S. Gan, T. S. A. Hor, A. Togni, T. Hayashi, *Ferrocenes: Homogeneous Catalysis, Organic Synthesis Materials Science*, Wiley-VCH, Weinheim, **1995**.

[20] a) K. G. Caulton, R. F. Fenske, *Inorg. Chem.* **1968**, *7*, 1273–1284; b) A. S. Goldman, K. Krogh Jespersen, *J. Am. Chem. Soc.* **1996**, *118*, 12159–12166.

[21] Caution needs to be exercised when gauging the electronic structure of systems with different formal charges based on ν(CO) (J. C. Thomas, J. C. Peters, *Inorg. Chem.* **2003**, *42*, 5055–5073), but it is reasonable to assume that the anionic borate complex is more electron-releasing given also that the ^{31}P NMR signal of ligand **4-BP** experiences an upfield shift of 1.2 ppm upon fluoride binding.

[22] M. R. Wilson, A. Prock, W. P. Giering, A. L. Fernandez, C. M. Haar, S. P. Nolan, B. M. Foxman, *Organometallics* **2002**, *21*, 2758–2763.

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