Dalton Transactions

PAPER

Check for updates

Cite this: DOI: 10.1039/c6dt04791b

Planar-chiral ferrocenylphosphine-borane complexes featuring agostic-type B-H---E (E = Hg, Sn) interactions†

Alain C. Tagne Kuate,^{a,b} Roger A. Lalancette*^a and F. Jäkle^b*^a

The synthesis of ferrocenylphosphine-borane adducts $1,2-fc(E)(PPh_2 \cdot BH_3)$ (E = SnR₂R', HgX; 1,2-fc = 1,ferrocenediyl) that are substituted with organotin or organomercury Lewis acid moieties in ortho-position is presented. Several compounds that feature two ferrocenylphosphine-borane moieties bridged by Sn or Hg are also introduced. The products are fully characterized by multinuclear NMR spectroscopy, highresolution MALDI-TOF mass spectrometry and elemental analysis. The attachment of the Lewis acid substituent to the same Cp ring of the ferrocene results in planar-chirality and the close proximity between the boron hydride group and the Lewis acid is expected to allow for agostic-type $B-H\cdots E$ (E = Sn, Hg) interactions. Structural investigations by X-ray diffraction reveal a short B-H...Sn contact of 2.755(4) Å for 1,2-fc(SnMe₂Cl)(PPh₂·BH₃), which is only the second reported example of such a short agostic-type contact involving a coordinatively saturated tin(iv) center. In contrast, for the tetraorganotin derivatives 1,2-fc(SnMe₃)(PPh₂·BH₃) and [1,2-fc(PPh₂)](µ-SnMe₂)[1,2-fc(PPh₂·BH₃)], in which the Lewis acidity of the tin atom is weaker than in $1,2-fc(SnMe_2Cl)(PPh_2BH_3)$, the B-H...Sn distances are much longer but still within the sum of the van der Waals radii of Sn and H (\sum_{vdW} = 3.27 Å). The chloromercury-substituted ferrocenylphosphine-borane 1,2-fc(HgCl)(PPh2·BH3) shows a similarly short B-H···Hg contact of 2.615(5) Å $(\sum_{vdW} = 3.15 \text{ Å})$. Inspection of the extended structure of 1,2-fc(HgCl)(PPh₂·BH₃) reveals that the Lewis acidic mercury atom is also involved in intermolecular Hq...Cl interactions with a neighboring molecule. An analysis of ³¹P and ¹¹B NMR data reveals a correlation between the chemical shifts and the Lewis acidity of the adjacent organotin/mercury substituent. Structure optimization of 1,2-fc(SnMe₃)(PPh₂·BH₃) and 1,2-fc(SnMe₂Cl)(PPh₂·BH₃) by density functional theory (DFT) indicates B-H...Sn contacts respectively of 3.129 and 2.631 Å that are close to the experimental values. Natural bond orbitals (NBO) and atom in molecules (AIM) analyses reveals a B-H \rightarrow Sn donor-acceptor interaction energy of 5.46 kcal mol⁻¹ and a B-H...Sn bond path for the chlorodimethyltin-substituted derivative with a modest electron density $\rho(r)$ of 0.0082 a.u. and a positive Laplacian at the bond critical point.

Received 20th December 2016, Accepted 11th April 2017

DOI: 10.1039/c6dt04791b

rsc.li/dalton

Introduction

Investigations into bonding situations where an X–H σ bond coordinates to a metal center are of fundamental importance for understanding catalytic processes that involve organometallic complexes. Indeed, the formation of 3c–2e inter-

actions is relevant to bond activation processes, can help describe various reaction mechanism, and is critical to the development of new synthetic pathways. In the case of intramolecular bonding situations, these σ -interactions have been termed "agostic".¹⁻⁴ This description originally referred specifically to coordination of C–H σ bonds to low valent transition metals. Over time, the term has been applied more generally and any X–H σ -bonded intramolecularly to low-valent or electron-deficient elements is nowadays frequently referred to as "agostic".

The coordination chemistry of phosphine-borane adducts of type BH_3 ·L (L = PMe₃, PPh₃) or B_2H_4 ·2PMe₃ has been extensively studied in regards to the nature of the B–H bonding to transition metals and the ensuing complex stabilization.⁵ The formation of a σ complex has been postulated as an intermediate in the C–H bond activation of the corresponding isoelectro-



View Article Online

^aDepartment of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102, USA. E-mail: fjaekle@andromeda.rutgers.edu,

rogerlal@andromeda.rutgers.edu

^bDepartment of Chemistry, Faculty of Sciences, University of Dschang, P.O. Box 67, Dschang, Cameroon

[†]Electronic supplementary information (ESI) available: Details for the synthesis and characterization of FcPPh₂·BH₃, NMR and mass spectra of all new compounds (PDF), FT-IR spectral data, computational details. CCDC 1523540–1523543. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt04791b

Paper

nic alkanes.⁶ In view of the importance of reactions involving alkanes to the petroleum industry, phosphine-borane adducts serve as easy-to-handle alternatives for investigating this σ -bonding character.⁷ The first observation of a B-H···E interaction in a complex between a metal and a phosphine-borane, B_2H_4 ·2PMe₃ and ZnCl₂, has been reported three decades ago by Snow et al.8 This important discovery has provided the basis for further exploration of the coordination of transition metals with mono- or bidentate phosphine-borane adducts. Several structurally characterized neutral complexes have since been described, including [CpMo(CO)₂{BH₃·PPh[N(SiMe₃)₂]}],⁹ $[M(CO)_n(B_2H_4 \cdot 2PMe_2)]$ (M = Cr, Mo, W; n = 4, 5),¹⁰ $[M(CO)_5(BH_3 \cdot L)]$ (M = Cr, Mo, W; L = PMe_3, PPh_3),¹¹ [CpMn $(CO)_{2}(BH_{3} \cdot PMe_{3})]^{12} [Cp*M(CO)_{2}(BH_{3} \cdot PMe_{3})] (M = Fe, Ru);^{13} in$ these complexes the B-H bond acts as a two-electron donor to stabilize the central metal atom in an η^{1} - or η^{2} -binding mode. Bisphosphine-borane adducts that feature both a BH₃-protected phosphine and a free phosphine moiety have emerged as bidentate ligands that are able to further stabilize the B-H···E interaction. An example of such a ligand is $BH_3 \cdot PPh_2 CH_2 PPh_2$ ($BH_3 \cdot dppm$), which was first introduced by Martin et al.¹⁴ and used for the synthesis of Co, Cr, Ru and Rh compounds. In these complexes the metal is chelated by the BH₃ (η^1) and free PPh₂ group.¹⁵ Recently, Weller *et al.* described an ionic variant, $[Ph_2HP-BH_2-PHPh_2]X$ (X = counter anion), with BH2 as a linker between two phosphines; they used this ligand in the formation of a Rh complex that displays a β B–H…Rh agostic interaction.¹⁶

In main group chemistry, agostic-type B–H…E interactions are comparatively much less studied. Short B–H…Sn(π)/Pb(π) contacts in the monomeric dialkyltetrylene species I (Fig. 1) are thought to prevent dimerization into the corresponding bis (tetrylene).¹⁷ Kawachi *et al.* postulated a weak interaction between the borate hydrogen and an adjacent electrondeficient silicon center in II (Fig. 1).¹⁸ On the other hand, interactions of the type R₃Si–H…ER₃ and R₃Sn–H…ER₃ (E = electron-deficient Group 13 element) have attracted consider-



Fig. 1 Examples of species with $B-H\cdots E$ and $B\cdots H-E$ (E = Si, Sn, Hg) contacts.

able interest. Wrackmeyer *et al.* proposed the first intramolecular Si-H···B interaction for compound **III** (Fig. 1)¹⁹ and Chen *et al.* recently confirmed an intermolecular interaction for Et₃Si-H···Al(C₆F₅)₃ by single crystal X-ray diffraction.²⁰ Müller *et al.* reported multiple Si-H···Al interactions, resulting in a formally hexacoordinate Al species.²¹ These interactions have frequently been referred to as agostic or three-center interactions, based on the significant covalent character derived from theoretical calculations.^{18,21,22} The term "charge-inverted hydrogen bond" has been proposed by Jablonski to be more appropriate considering the X^{$\delta+$}-H^{$\delta-$} donation to a lone pair vacancy.²³

The coordination chemistry of ferrocenyl-substituted phosphine-borane adducts remains scarcely developed despite potential advantages, including the robustness and unique steric demand of ferrocene, and the opportunity for further studies on the electronic and redox properties of such complexes. A literature search shows only two reports on the parent ferrocenyldiphenylphosphine-borane adduct $(FcPPh_2 \cdot BH_3, Fc = ferrocenyl)$ ²⁴ while related derivatives have been used as intermediates for ligands applied in asymmetric catalysis.^{25,26} Notably, ferrocenylphosphine-boranes FcCH₂PH₂·BH₃, FcPH₂·BH₃, FcP(tBu)H·BH₃, and corresponding planar-chiral derivatives have been explored by Hey-Hawkins et al. as precursors to redox-active phosphinoborane oligomers and polymers via metal-catalyzed dehydrocoupling and cross-dehydrocoupling processes.²⁷ Structural studies on ferrocenyldiphenylphosphine-borane adducts with Lewis acidic metal centers in ortho position are exceedingly rare. Recently we reported the structures of BH3-adducts of ferrocene-fused phosphastannin and phosphaborin species formed en-route to ambiphilic P,Sn and P,B ligands; however, the complex geometry was such that B-H···E (E = Sn, B) agostictype interactions are not feasible.²⁸ In earlier work, we also examined intramolecular B-Cl...Sn contacts in ferrocene based heteronuclear bidentate Lewis acids 1,2-fc(BRCl) $(SnMe_2Cl)$ (R = Me, Ph; fc = ferrocenediyl).²⁹ In continuation of our studies on ferrocene-based Lewis pair systems, we report here a new series of planar-chiral organostannyland chloromercurio-substituted ferrocenylphosphine-borane adducts (IV, V) and discuss the possibility of agostic-type interactions through coordination of B-H bonds to the Lewis acidic tin and mercury atoms. We postulate that these interactions are similar in nature to those involving coordination of silanes or stannanes to electron-deficient Group 13 elements discussed above.

Results and discussion

The planar-chiral ferrocenylsulfinate-substituted phosphineborane (pS,S_s)-2, first prepared by Kagan from (S_s)-ferrocenyl *p*-tolyl sulfoxide (1) and LDA followed by quenching with PPh₂Cl/BH₃·THF,^{25*a*} was chosen as starting material owing to the possibility to easily replace the tolylsulfinate moiety and attach Lewis acid groups in *ortho*-position to the phosphineborane through lithiation and reaction with a metal halide as electrophile. Thus, slow addition of *t*BuLi to a solution of (pS,S_s) -2 in THF at -78 °C and subsequent treatment with trimethyltin chloride afforded after purification by column chromatography and recrystallization from hexanes the trimethylstannyl-substituted ferrocenylphosphine-borane (pS)-3 as an orange crystalline solid in 58% yield (Scheme 1).

The ¹H NMR spectrum of (pS)-3 displayed the typical resonances for a 1,2-substituted Cp ring, as well as a singlet with tin satellites and a broad resonance at low frequency consistent respectively with the attachment of the SnMe₃ group at the ferrocene moiety and retention of BH3 at the phosphorus atom. The formation of (pS)-3 is also reflected in a broad, nonresolved resonance at δ = 18.1 ppm in the ³¹P NMR, a sharp signal at $\delta = -37.5$ ppm in the ¹¹B NMR which is indicative of the Ph₂P·BH₃ adduct, and a single resonance at $\delta = -5.6$ ppm in the ¹¹⁹Sn NMR spectrum that is slightly low field compared to the chemical shift measured for ortho-(diphenylphosphino) ferrocenyl stannane ($\delta = -7.2$ ppm).³⁰ Relative to the sulfinate precursor both the ³¹P ((p*S*,*S*_s)-2, δ = 16.7 ppm (ref. 31)) and the ¹¹B NMR signal ((pS,S_s)-2, $\delta = -36.5$ ppm) experienced slight low field shifts. The high resolution MALDI-TOF mass spectrum of (pS)-3 showed a major peak at m/z = 534.0228 a.u. that corresponds to $[(pS)-3 - BH_3]^+$ and demonstrates the lability of the BH₃ group.

Enhancement of the Lewis acidity at tin was achieved by methyl/chloride substituent exchange reaction. Treatment of (pS)-3 with PhBCl₂ in benzene at 50 °C overnight resulted in quantitative conversion to a new product. Solvent evaporation and recrystallization of the crude material from hexanes at -30 °C gave a yellow-orange crystalline solid that was identified as the chlorodimethylstannyl-substituted ferrocenylphosphine-borane (pS)-4 (Scheme 1) by multinuclear NMR spectroscopy and high resolution MALDI-TOF MS. The methyl/ chloride exchange reaction occurs selectively and in high yield (96%) without any sign of borodestannylation or decomplexation of BH₃. The ¹H NMR spectrum of (pS)-4 showed two distinct resonances with tin satellites at $\delta = 1.27$ ppm (${}^{2}J_{\text{Sn,H}} =$ 67/70 Hz) and $\delta = 0.49$ ppm (${}^{2}J_{\text{Sn,H}} = 62/64$ Hz) assigned to the diastereotopic methyl groups generated upon halogenation. The ${}^{2}J_{Sn,H}$ coupling constants are much larger than that for (pS)-3, which is indicative of an enhanced s-character of the equatorial Sn-C(Me) bonds as typically observed for hypercoordinate organotin species.³² The presence of the chloride substituent induces a strong low field shift of the Cp proton close to the tin atom with a signal appearing at $\delta = 5.34$ ppm, whereas the corresponding Cp proton in (pS)-3 appears at δ = 4.56 ppm. A single broad resonance is observed at higher field for the BH₃ protons, which is consistent with fast rotation about the P-B bond on the NMR time scale. It is not surprising that a separate signal for a bridging H atom involved in an agostic-type interaction cannot be detected considering that dynamic exchange persists even at very low temperature according to previous studies. For instance, an activation energy of only $\Delta G^{\#} = 30$ kJ mol⁻¹ was estimated for the BH₃ hydrogen exchange in the transition metal complex $[M(CO)_5(\eta^1-H_3BPMe_3)]$ (M = Cr, Mn, W).^{17a,b,11} Importantly, the ¹¹⁹Sn NMR signal of (pS)-4 at δ = 67.0 ppm is split into a doublet with a coupling constant of J = 12.3 Hz; the signal splitting is tentatively assigned to coupling of ¹¹⁹Sn with ³¹P as a similar coupling has been reported for the hypercoordinated ferrocenylstannane Fc(PPh2O)(SnMe2Cl) with a bridging phosphine oxide moiety (29 Hz).³³ This is in contrast to the precursor (pS)-3, for which only a singlet could be resolved. The 31 P (δ = 15.9 ppm) and 11 B (δ = -36.7 ppm) NMR chemical shifts are slightly upfield relative to those of (pS)-3, possibly as a result of a weak B-H...Sn agostic-type interaction (vide infra). A high resolution MALDI-TOF mass spectrum of (pS)-4 displayed peaks at m/z = 568.0015 a.u. and 553.9666 a.u. respectively assigned to $[(pS)-4]^+$ and $[(pS)-4 - BH_3]^+$.

The molecular structures of (p*S*)-3 and (p*S*)-4 in the solid state were determined by X-ray diffraction analysis and are depicted in Fig. 2. The H1A···Sn1 distance of 3.104(3) Å in (p*S*)-3 is only slightly shorter than the sum of the van der Waals radii ($\sum_{vdW} = 3.27$ Å (ref. 34)) of H and Sn, indicative of the absence of an agostic-type interaction or a very weak interaction that does not significantly impact the geometry about the tin atom. The Sn atom adopts a monocapped tetrahedral coordination geometry with H1A approaching *via* the tetrahedral face C1, C24 and C25. In contrast, the enhanced Lewis acidity of the tin center in (p*S*)-4 results in an H1A···Sn1 distance of 2.755(4) Å, which is considerably shorter than that



Scheme 1 Synthesis of ferrocenylphosphine-borane adducts with organotin and mercury substituents in ortho position (only one enantiomer shown for rac-5).



Fig. 2 (a) Molecular structure of enantiomerically pure (pS)-3 (50% ellipsoids, H atoms omitted for clarity except for B-H). Selected bond lengths, interatomic distances (Å) and angles (°): Sn1-C1 2.141(3), Sn1-C23 2.155(3), Sn1-C24 2.154(3), Sn1-C25 2.137(3), P1-C2 1.791(3), P1-B1 1.924(4), B1...Sn1 3.912(4), H1A...Sn1 3.104(3), C1-Sn1-C24 116.80(13), C1-Sn1-C25 109.88(12), C24-Sn1-C25 109 13(13) H1A...Sn1-C23 174.51(5), P1-C2-C1-Sn1 -2.00(5); the B-H distances were fixed at 1.19 Å. Flack parameter 0.038(3). (b) Molecular structure of enantiomerically pure (pS)-4 (50% ellipsoids, H atoms omitted for clarity except for B-H). Selected bond lengths, interatomic distances (Å) and angles (°): Sn1-Cl1 2.4022(9), Sn1-C1 2.133(3), Sn1-C23 2.143(3), Sn1-C24 2.127(4), P1-C2 1.793(3), P1-B1 1.925(4), B1-H1A 1.13(4), B1-H1B 1.13(4), B1-H1C 1.11(4), B1...Sn1 3.585(5), H1A...Sn1 2.755(4), C1-Sn1-C23 121.17(14), C1-Sn1-C24 112.94(13), C23-Sn1-C24 115.20(14), H1A...Sn1-Cl1 177.22(7), B1-H1A...Sn1 129.32(7), P1-C2-C1-Sn1 -2.42(5); the B-H distances were fully refined. Flack parameter: 0.020(3).

found for (pS)-3. As a consequence, the tin atom in (pS)-4 is pyramidalized (\sum equatorial angles = 349.3°) and adopts a distorted trigonal bipyramidal coordination geometry with H1A and Cl1 in axial positions. The P1-B1 bond in (pS)-4 (1.925(4) Å) is similar in length to the corresponding bond in (pS)-3 (P1-B1 = 1.924(4) Å). The hydrogen atoms on boron were found on the difference map and refined, yielding B-H distances of 1.11(4), 1.13(4) and 1.13(4) Å for (pS)-4. To the best of our knowledge, compound (pS)-4 represents only the second reported example of such a short B-H...Sn agostic-type interaction involving a tin(w) center. In a previous report, an even shorter B-H...Sn contact of 2.349 Å was found for the anion [10-endo-(SnPh3)-10-i-H-7,8-nido-C2B9H10], indicative of an α -agostic interaction, but in this case the tin atom is directly bound to a boron atom of the carborane.³⁵ Other known examples involve (cyclic) dialkylstannylenes (I, Fig. 1) having low-valent tin(II) centers stabilized by short B-H···Sn contacts.17

We next turned our attention to the replacement of the trimethylstannyl group in (p*S*)-3 by a Lewis acidic mercury chloride with the aim of structurally investigating a possible agostic-type B–H···Hg interaction. The synthesis was achieved by reacting (p*S*)-3 with a slight excess of HgCl₂ in acetone for 1 h. Precipitation in water and recrystallization from CH₂Cl₂/ hexanes afforded the chloromercurio-substituted ferrocenylphosphine-borane *rac*-5 as a yellow crystalline solid in 62% yield (Scheme 1). The ³¹P and ¹¹B NMR spectra display resonances at δ = 14.6 and δ = -36.4 ppm while the ¹H NMR spectrum exhibits the expected pattern for a 1,2-disubstituted ferrocene with the most downfield shifted Cp-proton observed at δ = 4.74 ppm. A MALDI-TOF mass spectrum confirmed the identity of 5 with a major peak at m/z = 605.9874 a.u. for [5 – BH₃]⁺.

X-ray diffraction analysis of a single crystal of *rac*-5 (Fig. 3) was performed in order to identify any short B–H…Hg contacts in the solid state. The H1C…Hg1 distance in the structure of *rac*-5 is 2.615(5) Å ($\sum_{vdW} = 3.15$ Å (ref. 34)), indicative of an agostic-type interaction similar to the one observed for (*pS*)-4. In addition, inspection of the extended structure revealed the formation of dimers *via* short intermolecular Hg1…Cl1 contacts of 3.191(1) Å ($\sum_{vdW} = 3.80$ Å (ref. 34)). This dimerization brings about significant steric strain, because the Cl1 atom comes into close proximity of the free Cp ring of the second molecule as reflected in a short intermolecular Cl1–CpH6 distance of 2.666(9) Å (Fig. 3). Consequently the Hg1–Cl1 moiety is bending away from the ferrocene framework, resulting in a distortion of the linear geometry at the mercury atom (C1–Hg1–Cl1 = 174.34(11)°).

We next pursued the synthesis of corresponding organotin and mercury-bridged diferrocenes. Lithiation of (pS,S_s) -2 and subsequent reaction with 0.5 equiv. of HgCl₂ at low temperature gave the mercury-substituted bis(ferrocenylphosphineborane) (pSpS)-6 in 27% yield (Scheme 2). Retention of the BH₃ groups in (pSpS)-6 is evidenced by a single, broad resonance at $\delta = 16.8$ ppm in the ³¹P NMR spectrum, which is slightly low field shifted relative to that of the chloromercury derivative *rac*-5, whereas the boron signal at $\delta = -36.0$ ppm appears at an almost identical chemical shift. The ¹H NMR spectrum shows three signals for the substituted and one for the free Cp rings, which is consistent with the formation of a single enantiomer with C_2 -symmetry. As in the case of the monoferrocenes, the Ph groups are chemically inequivalent



Fig. 3 Molecular structure of *rac*-5 (50% ellipsoids, H atoms omitted for clarity except for B–H); a pair of enantiomers is displayed. Selected bond lengths, interatomic distances (Å) and angles (°): Hg1–C1 2.038(4), Hg1–Cl1 2.3274(9), P1–C2 1.781(4), P1–B1 1.933(5), B1–H1A 1.00(5), B1–H1B 1.18(5), B1–H1C 1.16(5), H1C…Hg1 2.615(5), B1–H1A 1.00(5), H1B…Hg1 2.929(5), Hg1…Cl1# 3.191(1) Å and Cp–H6…Cl1# 2.666(9) Å. C1–Hg1–Cl1 174.34(11), P1–C2–C1–Hg1 0.21(4); the B–H distances were fully refined.



Scheme 2 Synthesis of bis(ferrocenylphosphine-borane) adducts with organotin and mercury bridges.

and thus give rise to two sets of resonances. The formation of (p*S*p*S*)-**6** was further confirmed by peaks in the MALDI-TOF mass spectrum for $[(pSpS)-6 - BH_3]^+$ at m/z = 954.1053 a.u. and $[(pSpS)-6 - 2BH_3]^+$ at m/z = 940.0734 a.u. In order to investigate the presence of an agostic-type B–H…Hg interaction in (p*S*p*S*)-**6** in the solid state, X-ray diffraction data were collected on a single crystal obtained by recrystallization from hexanes, but all attempts to solve the structure proved unsuccessful.

The successful synthesis of (pSpS)-6 by salt elimination reaction starting from (pS, S_s) -2 prompted us to apply a similar method for the preparation of the corresponding dimethylstannyl-bridged bis(ferrocenylphosphine-borane). Lithiation of (pS,S_s) -2 and subsequent reaction with 0.5 equiv. of Me₂SnCl₂ gave after aqueous workup an oily red residue. The latter was subjected to column chromatography on silica gel using hexanes: Et₂O: Et₃N as the eluent. One of the later fractions was concentrated and repeated recrystallization of the residue in hexanes at low temperature allowed deposition of a first crop of orange solid that appeared to be the parent ferrocenylphosphine-borane, FcPPh₂·BH₃, according to an ¹H NMR analysis (see ESI[†] for full characterization). A second crop containing very few orange crystals was collected after some days and its analysis revealed the formation of the expected dimethylstannyl-substituted bis(ferrocenylphosphine-borane), but with only one remaining BH₃ group ((pSpS)-7, Scheme 2). The ¹H NMR spectrum exhibits eight proton resonances for the inequivalent ferrocene fragments and two independent signals at δ = 1.20 ppm (²J_{Sn,H} = 62 Hz) and δ = 0.02 ppm (²J_{Sn,H} = 56 Hz) for the diastereotopic methyl groups. Peaks at m/z =889.0534 a.u. and m/z = 905.0495 a.u. corresponding to $[\{(pSpS)-7\} - BH_3 + H]^+$ and the oxidized species $[\{(pSpS)-7\} - BH_3 + H]^+$ $BH_3 + O^{\dagger}$ were identified by MALDI-TOF MS.

The structure was finally confirmed by single crystal X-diffraction analysis (Fig. 4). The ferrocene units in (pS,pS)-7 are positioned almost perpendicular to each other with an interplanar angle between the substituted Cp-rings of 82.7(1)°. The molecular structure is marked by an B1–H1A···Sn1 contact that is slightly shorter than for the tetraorganostannane (pS)-3, but still much longer than for the chlorostannane (pS)-4. Consistent with a rather weak B–H···Sn interaction is the small sum of the equatorial angles at Sn of 337.5° (involving C1, C23, C24), which is closer to the value expected for a tetrahedral than a trigonal bipyramidal configuration. A relatively short P2···Sn1 contact of 3.882(9) Å that is in the range of the sum of the van der Waals radii of P and Sn ($\sum_{vdW} = 3.97$ Å (ref. 34)) appears to also contribute to distortions of the tetrahedral geometry at Sn.

An earlier band from the chromatographic separation gave after recrystallization from hexanes a yellow crystalline solid in low yield (6%) that was identified as the hydridodimethylstannyl-substituted ferrocenylphosphine-borane (pS)-8 (Scheme 2). High resolution MALDI-TOF MS analysis confirmed the formation of (pS)-8 with a dominant peak at m/z =520.0041 a.u. assigned to $[{(pS)-8} - BH_3]^+$. (pS)-8 most likely originates from initial formation of (pS)-4 as an intermediate by 1:1 reaction between the lithio derivative of (pS,S_s) -2 and dimethyltin chloride. The latter may then be reduced to the hydride either by tert-butyllithium or FcPPh₂·BH₃, which was identified as a major product of the reaction. Literature precedents describe the synthesis of 1,1'-fc(SnMe₂H)₂ by reduction of the chloro precursor with LiAlH4.36 The 119Sn NMR spectrum of (pS)-8 in CDCl₃ exhibits a single resonance at $\delta = -96.3$ ppm close to that reported for 1,1'-fc(SnMe₂H)₂



Fig. 4 Molecular structure of enantiomerically pure (pSpS)-7 (50% ellipsoids, H atoms omitted for clarity except for B–H). Selected bond lengths, interatomic distances (Å) and angles (°): Sn1–C1 2.158(4), Sn1–C23 2.150(3), Sn1–C24 2.147(3), Sn1–C25 2.151(4), P1–C2 1.801(4), P2–C26 1.815(4), P1–B1 1.914(4), B1…Sn1 3.732(5), H1A…Sn1 3.006, P2…Sn1 3.882(9), C1–Sn1–C23 107.14(14), C1–Sn1–C24 118.73(13), C1–Sn1–C25 103.22(13), C23–Sn1–C24 111.62(15), C23–Sn1–C25 104.62(14), C24–Sn1–C25 110.31(14), C25–Sn1…H1A 173.97(5), P2–Sn1…H1A 136.72(7), P1–C2–C1–Sn1 3.44(5), P2–C26–C25–Sn1 –8.67(5); the B–H distances were fixed at 1.19 Å. Flack parameter: 0.027(2).

Paper

 $(\delta = -102.4 \text{ ppm}, C_6 D_6)$ ³⁶ Due to coupling to the methyl protons, the Sn–H proton is split into a septet resonance at δ = 5.27 ppm in the ¹H NMR spectrum. Similar to (pS)-4, the methyl groups in (pS)-8 are diastereotopic and give rise to two close but independent doublet resonances at $\delta = 0.18$ ppm $({}^{3}J_{HH} = 1.8 \text{ Hz}, {}^{2}J_{Sn,H} = 55/58 \text{ Hz})$ and 0.17 ppm $({}^{3}J_{HH} = 1.8 \text{ Hz},$ ${}^{2}J_{\text{Sn,H}}$ = 58/60 Hz). The ${}^{2}J_{\text{Sn,H}}$ coupling constants, however, are much smaller than those for (pS)-4, indicative of less s-character of the corresponding Sn-C bonds. The ³¹P and ¹¹B NMR spectra offer evidence that the BH₃ is still attached to the phosphine moiety, given that broad resonances are observed in the expected range at δ = 18.5 ppm and δ = -38.5 ppm. They are more similar to those of (pS)-3 than (pS)-4, suggesting that agostic-type B-H...Sn contacts are not present. We were unable to further assess the molecular structure of (pS)-8, because the refinement of a dataset for crystals obtained from hexanes failed.

The desired dimethylstannyl-bridged bis(ferrocenylphosphine-borane) is more readily obtained by first introducing the dimethyltin bridge and then adding the PPh₂·BH₃ moieties, thereby avoiding undesirable side reactions such as the reduction processes discussed above. We recently reported a high yield synthesis of the enantiomerically pure dimethylstannyl-substituted bis(ferrocenylsulfinate) (pRS_spRS_s)-9.^{28a} Treatment of (pRS_spRS_s) -9 with two equiv. of *t*BuLi at -78 °C followed by addition of Ph2PCl and BH3 THF furnished the dimethylstannyl-bridged bis(ferrocenylphosphine-borane) (pRpR)-10 in 38% yield (Scheme 2). The formation of (pRpR)-10 was further confirmed by high resolution MALDI-TOF MS with a dominant peak at m/z = 889.0544 a.u. for [(pRpR)-10 – $2BH_3 + H^{\dagger}$. The ¹H NMR spectrum of (pRpR)-10 displays only four signals for the ferrocene fragments and one signal for the methyl groups, suggesting that a single isomer is generated. Signals at δ = 17.9 ppm in the ³¹P NMR and at δ = -37.7 ppm in the ¹¹B NMR spectrum are close to those of (pS)-**3.** The ¹¹⁹Sn NMR spectrum of (p*R*p*R*)-**10** shows a singlet at δ = -13.1 ppm, a resonance that is shifted to high field when compared with that of the SnMe₂-bridged diferrocenylphosphineborane $fc_2(\mu$ -SnMe₂)(μ -PPh·BH₃) ($\delta = -29.6$).^{28a} Unfortunately, despite several attempts, single crystals suitable for analysis of the structure of (pRpR)-10 in the solid state by X-ray diffraction could not be obtained.

The stereoselectivity of the transformations described in here deserves a further comment. Except for *rac*-5 all X-ray diffraction studies were performed on single enantiomers. Refinement of the Flack parameter gave values of 0.038(3), 0.020(3), and 0.027(2) respectively for (p*S*)-3, (p*S*)-4, and (p*S*p*S*)-7 (Fig. 2 and 4), demonstrating their planar-chirality with the expected p*S* configurations according to the CIP (Cahn–Ingold–Prelog) protocol. Although no proof of enantiomeric purity, the chirality of the bulk samples was further established by measurement of the specific rotations in CHCl₃, which is respectively [α]_D²⁰ = +167 (*c* 0.25), +74 (*c* 0.16), +50 (*c* 0.22) and -47 (*c* 0.18) for (p*S*)-3, (p*S*)-4, (p*S*)-8 and (p*R*p*R*)-10. The reasons for racemization in the conversion of (p*S*)-3 to *rac*-5 have not been established. One possibility is that the BH₃ group directs attack of the HgCl₂ electrophile into the less hindered C–H *ortho*-position, opening up a competing pathway to the direct mercuriodestannylation at the sterically more hindered C–Sn position.³⁷

The structural studies in this manuscript reveal a relatively long B-H...Sn contact in the structures of (pS)-3 and (pSpS)-7 containing a tetraorganotin moiety, which is known to be a poor Lewis acid. The selective conversion of (pS)-3 into (pS)-4 with PhBCl₂ induces a shorter B-H...Sn contact as a result of the enhanced Lewis acidity of the tin atom. Similarly, rac-5 exhibits a short B-H...Hg contact, but the Lewis acidic mercury center is also involved in intermolecular Hg...Cl interactions that result in formation of discrete dimers in the solid state. Looking at the heteronuclear solution NMR data we find that within the series of stannyl- and mercury-substituted compounds, the ³¹P NMR signals are shifted upfield and the ¹¹B NMR signals shifted downfield in the order (pS)-8 < (pS)-3 \approx (pRpR)-10 < (pSpS)-6 < (pS)-4 \approx rac-5 (Table 1). This trend tracks well with the expected Lewis acidity of the stannyl/ mercury group (highest for (pS)-4 and rac-5).³⁸ It is also in good agreement with the magnitude of the agostic-type B-H…E interactions as determined by X-ray crystallography. Interestingly, in the ¹H NMR spectra we observe distinct downfield shifts for the BH₃ protons of (pS)-4, rac-5, and (pSpS)-6 (1.7-2.0 ppm) relative to the parent FcPPh₂·BH₃ (1.25 ppm). This is in sharp contrast to the upfield shifts typically observed upon complexation of phosphine-borane ligands to transition metal complexes.¹⁰ Looking at prior NMR spectroscopic studies on main group species, in several cases upfield shifts have been reported (e.g., Et₃SiH···Al(C₆F₅)₃; III in Fig. 1);^{19,20} however, there is also precedent for downfield shifts for complexes with proposed Si-H...Al contacts.²¹ It is possible that in our case spin-orbit effects due to the heavy metals play an important role.

Table 1	Comparison of heteronuclear	NMR data for compounds	1,2-fc(PPh ₂ ·BH ₃)(R)	with different substituents	R in <i>ortho</i> position to phosphorous

Compound (R)	δ (¹¹⁹ Sn) (ppm)	$J(^{117/119}\text{Sn}, {}^{1}\text{H}) \text{Sn-Me} (\text{Hz})$	$\delta \left(^{31}\mathrm{P}\right) \left(\mathrm{ppm}\right)$	δ (¹¹ B) (ppm)	δ (¹ H) BH ₃ (ppm)
FcPPh ₂ ·BH ₃			16.0	-38.4	1.25
(pS)-8 (SnMe ₂ H)	-96.3	55/58, 58/60	18.5	-38.5	1.37
(pS)-3 (SnMe ₃)	-5.6	55	18.1	-37.5	1.32
(pRpR)-10 (SnMe ₂ Fc')	-13.1	60	17.9	-37.7	1.34
(pS)-4 (SnMe ₂ Cl)	+67.0	62/64, 67/70	15.9	-36.7	1.70
(pSpS)-6 (HgFc')		,	16.8	-36.0	1.91
rac-5 (HgCl)			14.6	-36.4	1.99

An unexpected result is seen for (pS)-8, for which the NMR data would seem to indicate very weak agostic-type interactions. This suggests that the structure of the Sn-H derivative (pS)-8 resembles more that of (pS)-3 than the Sn-Cl derivative (pS)-4 with the small H atom positioned close to the BH₃ moiety rather than in *trans*-position. The smaller steric demand of the hydrogen in comparison to a Me group may result in even less distortions at the Sn atom ultimately placing this compound at the top of the list.

The nature of the B-H...Sn interactions was further investigated for compounds (pS)-3 and (pS)-4 using computational tools. The optimized geometries obtained by density functional theory (DFT) calculations at the B3LYP/dgdzvp level of theory, indicated interatomic B-H...Sn distances of 3.129 and 2.631 Å for (pS)-3 and (pS)-4 respectively, which are close to those determined by X-ray diffraction analysis (3.104(3) and 2.755(4) Å). Thus, as observed experimentally, a much stronger B-H···Sn interaction is predicted for (pS)-4, in accordance with an increased Lewis acidity and pyramidalization (\sum equatorial angles = 350.8°) of the tin atom. Only a small difference in the P-B bond lengths (1.939 Å for (pS)-3; 1.944 Å for (pS)-4) is found. However, the B-H bond that is pointing toward Sn in compound (pS)-4 is elongated by ca. 1% relative to the other B-H bonds (1.217 vs. 1.208 Å), giving rise to a bent B-H…Sn linkage (131.86°; experimental value: 129.32°). Examination of the B1-H1→Sn1 second order perturbation in the optimized structures of (pS)-3 and (pS)-4 by NBO analysis indicated interaction energies $(E^{(2)})$ of 0.20 and 5.46 kcal mol⁻¹, respectively. The latter suggests a significant donor-acceptor interaction between the B1–H1A moiety and the Sn center only in (pS)-4. For comparison, a deletion calculation for a R₃C-H…SiR₂FR' interaction increased the total energy of the molecule by



Fig. 5 AIM contour plots of (a) the electron density and (b) the calculated Laplacian for **4**. The bond path between Sn1 and the bridging hydrogen (H6) is indicated by a dashed black line and the corresponding BCP as a green circle.

3.069 kcal mol⁻¹,^{22c} and the interaction energies determined by NBO analysis of strongly hydrogen-bonded organic compounds were found to be within 4.7–12.8 kcal mol⁻¹.³⁹ On the other hand, the B–H···Sn donor–acceptor interaction energies in tin(π) compound I (Fig. 1, X = CH₂CH₂) were calculated to be 20 and 30 kcal mol⁻¹ for the *rac*- and *meso*-isomers, indicating much stronger interactions.^{17a}

In good agreement with the NBO calculations and X-ray diffraction analyses, atoms in molecules (AIM) analysis of the optimized structure of (p*S*)-4 indicated a B–H…Sn bond path (Fig. 5), which is characterized by an electron density $\rho(r)$ of 0.0082 e/a_0^3 at the bond critical point (BCP) and a positive Laplacian of $\nabla^2 \rho(r) = +0.040694 e/a_0^5$. In contrast, no BCP was found during AIM analysis of the optimized structure of (p*S*)-3, consistent with no or unremarkable secondary interactions. The calculated electron density value at the BCP in (p*S*)-4 is slightly lower than that reported by Kawachi for the B–H…Si interaction in compound **II** (0.0156 e/a_0^3 , Fig. 1)¹⁸ and the R₃C–H…SiR₂FR' interaction reported by Gabbai^{22c} (0.0168 e/a_0^3).

Conclusions

We have prepared a series of ferrocene-based planar-chiral organostannyl and mercury-substituted ferrocenylphosphineborane adducts, in which the BH₃ group at the phosphorus atom is involved in B–H···E interactions with Lewis acidic tin or mercury atoms in close proximity. The nature of the interaction was investigated in the solid state by X-ray structural analyses and in solution by multinuclear NMR spectroscopy. DFT calculations on (p*S*)-3 and (p*S*)-4, and corresponding NBO and AIM analyses further support the notion that an increase in the Lewis acidity of the tin atom results in a B–H \rightarrow Sn donor–acceptor interaction with a perturbation energy typical of compounds with moderately strong hydrogen bonding.

Thus, our investigations provide new insights into the nature of agostic-type interactions involving phosphineboranes and organotin(IV) and chloromercury moieties, and attempts to synthesize the corresponding organoborylsubstituted ferrocenylphosphine-boranes, which may feature B–H···B agostic-type interactions, are currently in progress. As planar-chiral bidentate ligands with a Lewis acid moiety in the bridge, the diferrocenes (p*S*p*S*)-**6** and (p*R*p*R*)-**10** are also promising for use in coordination chemistry with transition metals and asymmetric synthesis.

Experimental section

General methods

All reactions were carried out under an atmosphere of dry nitrogen using high vacuum Schlenk-line techniques or in an inert-atmosphere glove box (Innovative Technologies). Commercial-grade solvents (toluene, hexanes) were purified by a solvent purification system from Innovative Technologies,

degassed and stored over sodium-potassium (NaK) alloy prior to use. Tetrahydrofuran was distilled from sodium/benzophenone and dichloromethane from CaH2, degassed and stored under nitrogen atmosphere. 499.9/599.7 MHz ¹H NMR, 125.7/150.8 MHz ¹³C NMR, 192.4 MHz ¹¹B NMR, 202.5 MHz ³¹P NMR, and 223.6 MHz ¹¹⁹Sn NMR spectra were recorded on a Bruker Avance III HD NMR spectrometer (Bruker BioSpin, Billerica, MA) equipped with a 5 mm broadband gradient SmartProbe (Bruker, Billerica, MA) or a 600 INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Chemicals shifts (δ) are given in ppm and were referenced internally to deuterated solvent signals (CDCl₃ 7.26 (¹H), 77.36 (¹³C); C₆D₆ 7.15 (¹H), 128.62 (^{13}C)). Coupling constants (J) are reported in Hertz (Hz) and splitting patterns are indicated as s (singlet), d (doublet), pt (pseudo triplet), t (triplet), brs (broad singlet), nr (not resolved), brm (broad multiplet) and m (multiplet), and the following abbreviations are used for signal assignments: Ph = phenyl, Fc = ferrocenyl, Cp = cyclopentadienyl, Me = methyl. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR device. Optical rotation analyses were performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at λ = 589 nm. Highresolution matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) data were acquired on a Bruker Ultraflextreme. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. Structural optimization with full NBO analysis and frequency calculations of the optimized structures were performed using the Gaussian 09 suite of programs^{40,41} with the B3LYP functional⁴² and dgdzvp basis set⁴³ for all elements. The dgdzvp basis set has been employed for DFT studies on tin containing compounds.44 The AIM analysis was performed with the AIMAll professional program applying wavefunctions obtained from DFT calculations at the B3LYP/dgdzvp level of theory.45

Materials

Me₃SnCl, PhBCl₂, Me₂SnCl₂, HgCl₂, BH₃·THF (1.0 M in THF), *n*-butyllithium (1.6 M in hexanes), and *t*-butyllithium (1.7 M in pentane) were purchased from commercial sources and used without further purification. Ph₂PCl was purchased from Aldrich and distilled prior to use. Lithium diisopropylamide (LDA) was freshly prepared by addition of *n*-butyllithium (1.6 M in hexanes) to a THF solution of diisopropylamine (distilled from sodium/benzophenone prior to use) at 0 °C. Ferrocenylphosphine-borane sulfinate ((pS, S_s)-2) and trimethylstannyl-substituted bis(ferrocenylphosphine-borane) disulfinate ((pRS_spRS_s)-9) have been previously reported.^{25a,28}

X-ray diffraction analysis

Reflections were collected on a Bruker SMART APEX II CCD Diffractometer using CuK α (1.54178 Å) radiation at 100 K. Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs.⁴⁶⁻⁴⁸ The structures were

solved by direct methods and refined by full-matrix least squares based on F^2 with all reflections using the SHELXTL V6.14 program package.^{49,50} Non-hydrogen atoms were refined with anisotropic displacement coefficients. All H atoms were found in electron-density difference maps and carbon-bound H atoms were treated as idealized contribution unless noted differently. For (p*S*)-3 and (p*S*p*S*)-7 the boron-bound H atoms were allowed to refine positionally, but were constrained to be at a fixed distance to the boron atom; for (p*S*)-4, and *rac*-5 they were allowed to refine freely. Structural data have been deposited with the Cambridge Structure Database as supplementary publications CCDC 1523540–1523543.

Synthesis of trimethylstannyl-substituted ferrocenylphosphine-borane (p*S*)-3

To a solution of (pS, S_s) -2 (1.023 g, 1.96 mmol) in THF (40 mL) that was cooled to -78 °C, was added slowly a solution of tBuLi in pentane (1.7 M, 1.3 mL, 2.20 mmol, 1.1 equiv.). The mixture was stirred for 10 min and a solution of Me₃SnCl (0.43 g, 1.1 mmol, 1.1 equiv.) in THF (10 mL) was slowly added. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm up to room temperature overnight. The THF solvent was removed in vacuum and the residue dissolved in Et₂O (50 mL) and quenched by addition of aqueous sodium bicarbonate. The combined organic layer was then separated, washed with water, brine, dried with sodium sulfate, and the solvent was removed in vacuum to leave an orange viscous oil. The latter was purified by column chromatography on silica gel with hexanes/Et₃N (100:1) and recrystallized in hexanes at −27 °C to give orange X-ray quality crystals. Yield 0.62 g (58%). $[\alpha]_{D}^{20}$ (*c* = 0.25, CHCl₃) = +167°. ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.69 (t, ${}^{3}J_{H,H}$ = 8.8 Hz, 2H, Ph), 7.51 (t, ${}^{3}J_{H,H}$ = 7.3 Hz, 1H, Ph), 7.45 (t, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, Ph), 7.45-7.30 (m, 5H, Ph), 4.56 (nr, 1H, Cp), 4.48 (nr, 1H, Cp), 4.23 (s, 5H, free Cp), 3.99 (nr, 1H, Cp), 1.32 (brm, 3H, BH₃), 0.16 (s, ${}^{2}J_{\text{Sn,H}}$ = 55 Hz, 9H, SnMe₃). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (158.8 MHz, CDCl₃, 25 °C): δ = 133.7 (d, ²*J*_{P,C} = 10 Hz, *o*-Ph), 133.0 (d, ²*J*_{P,C} = 10 Hz, o-Ph), 132.3 (d, ¹*J*_{C,P} = 61 Hz, i-Ph), 131.2 (s, *p*-Ph), 131.1 (d, ${}^{1}J_{P,C} = 62$ Hz, i-Ph), 130.9 (s, *p*-Ph), 128.6 (d, ${}^{3}J_{P,C} = 10$ Hz, *m*-Ph), 80.4 (d, $J_{P,C}$ = 13 Hz, $J_{Sn,C}$ = 49 Hz, Cp), 76.5 (d, $J_{P,C}$ = 7.1 Hz, Cp), 75.9 (d, ${}^{2}J_{P,C}$ = 25 Hz, i-Cp–Sn), 75.6 (d, ${}^{1}J_{P,C}$ = 77 Hz, i-Cp-P), 73.3 (d, $J_{P,C}$ = 5.7 Hz, $J_{Sn,C}$ = 39 Hz, Cp), 69.9 (s, free Cp), -5.8 (s, ${}^{1}J_{\text{Sn,C}}$ = 370/377 Hz, SnMe). ${}^{31}P{}^{1}H$ NMR (202.5 MHz, CDCl₃, 25 °C): δ = 18.1 (nr). ¹¹⁹Sn{¹H} NMR (223.6 MHz, CDCl₃, 25 °C): $\delta = -5.6$ (s). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -37.5 (nr). High-resolution MALDI-TOF MS (positive mode, anthracene): m/z 534.0228 $([(pS)-3 - BH_3]^+, 100\%, \text{ calcd for } {}^{12}C_{25}{}^{1}H_{27}{}^{31}P^{56}Fe^{120}Sn$ 534.0222). Elem. anal. for C₂₅H₃₀BFePSn: calcd C 54.91, H 5.53; found C 55.09, H 5.45.

Synthesis of chlorodimethylstannyl-substituted ferrocenylphosphine-borane (p*S*)-4

To a solution of $PhBCl_2$ (0.095 g, 0.060 mmol, 1.1 equiv.) in C_6D_6 (1 mL) was added (pS)-3 (0.030 g, 0.055 mmol) in an NMR tube. The mixture was left standing for two hours at

room temperature and heated to 50 °C overnight. Analysis by ¹¹⁹Sn and ¹¹B NMR showed full conversion to a new ferrocene species and PhMeBCl as a byproduct (δ (¹¹B) = 65.3 ppm, δ (¹H) = 1.08 ppm for Me). The solvent was evaporated under vacuum to leave an orange residue that was dissolved in hexanes and stored at -30 °C. X-ray quality crystals of (pS)-4 were obtained after 24 h. Yield 0.030 g (96%). $[\alpha]_{D}^{20}$ (c = 0.16, CHCl₃) = +74°. ¹H NMR (599.7 MHz, C₆D₆, 25 °C): δ = 7.67 (m, 2H, Ph), 7.26 (m, 2H, Ph), 7.04 (m, 1H, Ph), 6.98 (m, 2H, Ph), 6.91 (m, 1H, Ph), 6.83 (m, 2H, Ph), 5.34 (m, 1H, Cp), 4.30 (pt, ${}^{3}J_{H,H}$ = 2.4 Hz, 1H, Cp), 4.04 (s, 5H, free Cp), 3.96 (m, 1H, Cp), 1.70 (brm, 3H, BH₃), 1.27 (s, ${}^{2}J_{Sn,H}$ = 67/70 Hz, 3H, SnMe), 0.49 (s, ${}^{2}J_{\text{Sn,H}} = 62/64$ Hz, 3H, SnMe). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (158.8 MHz, C₆D₆, 25 °C): δ = 134.3 (d, ²*J*_{P,C} = 10 Hz, *o*-Ph), 132.9 (d, ²*J*_{P,C} = 10 Hz, o-Ph), 132.4 (d, ${}^{1}J_{P,C}$ = 64 Hz, i-Ph), 132.2 (s, p-Ph), 131.5 (s, *p*-Ph), 130.2 (d, ${}^{1}J_{P,C}$ = 64 Hz, i-Ph), 129.2 (d, ${}^{3}J_{P,C}$ = 12 Hz, *m*-Ph), 128.8 (d, one peak overlapping with C_6D_6 , *m*-Ph), 81.6 (d, $J_{P,C}$ = 12 Hz, Cp), 79.9 (d, ${}^{2}J_{P,C}$ = 26 Hz, i-Cp–Sn), 76.0 (d, $J_{P,C}$ = 4.3 Hz, $J_{Sn,C}$ = 43 Hz, Cp), 75.2 (d, $J_{P,C}$ = 5.9 Hz, Cp), 74.4 (d, ${}^{1}J_{P,C}$ = 77 Hz, i-Cp–P), 71.0 (s, free Cp), 6.1 (s, ${}^{1}J_{Sn,C}$ = 509/ 535 Hz, SnMe), 3.5 (s, $J_{Sn,C}$ = 450/468 Hz, SnMe). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25 °C): δ = 15.9 (nr). ¹¹⁹Sn{¹H} NMR (223.6 MHz, CDCl₃, 25 °C): δ = 67.0 (d, ² $J_{Sn,P}$ = 12.3 Hz). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -36.7 (nr). Highresolution MALDI-TOF MS (positive mode, anthracene): m/z568.0015 ([(p*S*)-4]⁺, 5%, calcd for ${}^{12}C_{24}{}^{1}H_{27}{}^{11}B^{35}Cl^{31}P^{56}Fe^{120}Sn$ 568.0001); m/z 553.9666 ([M – BH₃]⁺, 100%, calcd for ${}^{12}C_{24}{}^{1}H_{24}{}^{35}Cl^{31}P^{56}Fe^{120}Sn 553.9669); m/z 534.9882 ([M - BH₃])$ - Cl + O]⁺, 45%, calcd for ${}^{12}C_{24}{}^{1}H_{24}{}^{16}O^{31}P^{56}Fe^{120}Sn 534.9936);$ m/z 518.9921 ([M - BH₃ - Cl]⁺, 30%, calcd for ${}^{12}C_{24}{}^{1}H_{24}{}^{31}P^{56}Fe^{120}Sn$ 518.9987). Elem. anal. for C₂₄H₂₇BClFePSn: calcd C 50.82, H 4.80; found C 51.00, H 4.64.

Synthesis of chloromercury-substituted ferrocenylphosphineborane *rac*-5

A solution of (pS)-3 (0.11 g, 0.20 mmol) in acetone (2 mL) was added to a solution of HgCl₂ (0.053 g, 0.20 mmol) in acetone (2 mL). The mixture was stirred for one hour at room temperature and then added to water (40 mL). Upon addition, a yellow precipitate formed that was collected by filtration, washed with hexanes and dried under high vacuum. Recrystallization from CH₂Cl₂/hexanes by slow solvent evaporation at room temperature gave X-ray quality yellow crystals of rac-5. Yield: 0.072 g (62%). $[\alpha]_{D}^{20}$ (c = 0.16, CHCl₃) = +14°. ¹H NMR (499.9 MHz, $CDCl_3$, 25 °C): δ = 7.76 (m, 2H, Ph), 7.57 (m, 1H, Ph), 7.51 (m, 2H, Ph), 7.43 (m, 1H, Ph), 7.35 (m, 4H, Ph), 4.74 (nr, 1H, Cp), 4.47 (nr, 1H, Cp), 4.45 (nr, 1H, Cp), 4.11 (s, 5H, free Cp), 1.99 (brm, 3H, BH₃). ¹³C{¹H} NMR (158.8 MHz, CDCl₃, 25 °C): δ = 133.6 (d, ${}^{2}J_{P,C}$ = 10 Hz, o-Ph), 132.3 (d, ${}^{2}J_{P,C}$ = 10 Hz, m-Ph), 132.0 (s, *p*-Ph), 131.8 (d, ${}^{1}J_{C,P}$ = 64 Hz, i-Ph), 131.3 (s, *p*-Ph), 129.8 (d, ${}^{1}J_{P,C} = 67$ Hz, i-Ph), 129.1 (d, ${}^{3}J_{P,C} = 10$ Hz, m-Ph), 129.0 (d, ${}^{3}J_{P,C}$ = 10 Hz, *m*-Ph), 88.7 (d, ${}^{2}J_{P,C}$ = 25 Hz, i-Cp-Hg), 78.2 (d, $J_{P,C}$ = 11 Hz, Cp), 74.9 (d, $J_{P,C}$ = 5.9 Hz, Cp), 74.3 (d, $J_{P,C}$ = 5.7 Hz, Cp), 74.3 (d, ¹ $J_{P,C}$ = 77 Hz, i-Cp–P), 70.6 (s, free Cp). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25 °C): δ = 14.6 (nr). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -36.4 (nr). Highresolution MALDI-TOF MS (positive mode, anthracene): m/z605.9874 ([rac-5 - BH₃]⁺, 100%, calcd for ${}^{12}C_{22}{}^{1}H_{18}{}^{35}Cl^{56}Fe^{200}Hg^{31}P$ 605.9880); m/z 940.0681 ([rac-6 -2BH₃]⁺, 50%, calcd for ${}^{12}C_{44}{}^{1}H_{36}{}^{56}Fe_{2}{}^{200}Hg^{31}P_{2}$ 940.0703). Elem. anal. for $C_{22}H_{21}$ BClFeHgP: calcd C 42.68, H 3.42; found C 43.20, H 3.12.

Synthesis of mercury-bridged bis(ferrocenylphosphine-borane) (pSpS)-6

To a solution of (pS, S_s) -2 (0.52 g, 1.0 mmol) in THF (40 mL) that was cooled to -78 °C, was added slowly a solution of tBuLi in pentane (1.7 M, 0.65 mL, 1.1 mmol, 1.1 equiv.). The mixture was stirred for 10 min and a solution of HgCl₂ (0.12 g, 0.45 mmol, 0.45 equiv.) in THF (10 mL) was slowly added. After stirring for 1 h at this temperature, the reaction mixture was allowed to slowly warm up to 25 °C overnight. The THF solvent was removed in vacuum, the residue dissolved in toluene (20 mL) and filtered to remove insoluble solid. The toluene solvent was evaporated and the crude product was extracted with hexanes (20 mL) at 50 °C for two hours. After filtration and solvent evaporation, the remaining residue was subjected to column chromatography on silica gel with Et₂O/ hexanes (1:2) as eluent. The first band was concentrated, washed with hexanes and dried in vacuum. Recrystallization from CH₂Cl₂/hexanes by slow evaporation at room temperature afforded a yellow crystalline solid consisting of a mixture of (pSpS)-6 (ca. 90%) and a small amount of byproducts, which proved to be impossible to remove despite many efforts to obtain (pSpS)-6 in analytically pure form. Yield: 0.26 g (27%). ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.82 (m, 4H, Ph), 7.55 (m, 2H, Ph), 7.51 (m, 4H, Ph), 7.36 (m, 6H, Ph), 7.30 (m, 4H, Ph), 4.67 (nr, 2H, Cp), 4.65 (pt, ³J_{H,H} = 2.3 Hz, 2H, Cp), 4.27 (s, 10H, free Cp), 4.25 (nr, 2H, Cp), 1.91 (brm, 6H, BH₃). ¹³C{¹H} NMR (158.8 MHz, CDCl₃, 25 °C): δ = 133.7 (d, ²J_{P,C} = 10 Hz, o-Ph), 133.3 (d, ${}^{1}J_{P,C}$ = 62 Hz, i-Ph), 132.4 (d, ${}^{2}J_{P,C}$ = 10 Hz, o-Ph), 131.4 (s, p-Ph), 131.1 (d, ¹J_{P,C} = 65 Hz, i-Ph), 130.6 (s, *p*-Ph), 128.7 (nr, *m*-Ph), 128.6 (nr, *m*-Ph), 105.9 (d, ${}^{2}J_{P,C}$ = 29 Hz, i-Cp-Hg), 81.8 (d, $J_{P,C}$ = 13 Hz, Cp), 75.6 (d, ${}^{1}J_{P,C}$ = 80 Hz, i-Cp-P), 74.7 (nr, Cp), 74.6 (nr, Cp), 69.8 (s, free Cp). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25 °C): δ = 16.8 (nr). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -36.0 (nr). High-resolution MALDI-TOF MS (positive mode, anthracene): m/z 954.1053 $([(pSpS)-6 - BH_3]^+)$, 20%, calcd for ${}^{12}C_{44}{}^{1}H_{39}{}^{11}B^{56}Fe_2{}^{200}Hg^{31}P_2$ 954.1037; m/z 940.0734 ([(pSpS)-6 - 2BH₃]⁺), 100%, calcd for ${}^{12}\mathrm{C}_{44}{}^{1}\mathrm{H}_{36}{}^{56}\mathrm{Fe}_{2}{}^{200}\mathrm{Hg}{}^{31}\mathrm{P}_{2} \ 940.0703.$

Attempted synthesis of dimethylstannyl-bridged bis(ferrocenylphosphine-borane) from (pS,S_s) -2: isolation of (pSpS)-7 and (pS)-8

To a solution of (pSS_s) -2 (1.01 g, 1.94 mmol) in THF (60 mL) that was cooled to -78 °C, was added slowly a solution of *t*BuLi in pentane (1.7 M, 1.26 mL, 2.13 mmol, 1.1 equiv.). The mixture was stirred for 10 min and a solution of Me₂SnCl₂ (0.26 g, 1.16 mmol, 0.6 equiv.) in THF (10 mL) was slowly added. After stirring for 1 h at this temperature, the reaction mixture was allowed to slowly warm up to 25 °C overnight. The

THF solvent was removed in vacuum and the residue dissolved in Et_2O (50 mL) and quenched by addition of aqueous sodium bicarbonate. The combined organic layer was then separated, washed with water, brine, dried with sodium sulfate, and the solvent was removed in vacuum to leave a red oily residue. The latter was purified by column chromatography on silica gel with hexanes/ Et_2O/Et_3N (80:20:1).

The first orange band gave an oily residue after evaporation that did not show evidence for the expected product by ¹H NMR. A second band was concentrated and the residue recrystallized in hexanes at -27 °C to give an orange crystalline solid, which was identified to be the hydridodimethylstannylsubstituted ferrocenylphosphine-borane (pS)-8 by multinuclear NMR and MALDI-TOF MS analyses. Yield 0.060 g (6%). $[\alpha]_{D}^{20}$ (c = 0.22, CHCl₃) = +50°. ¹H NMR (599.7 MHz, CDCl₃, 25 °C): δ = 7.67 (m, 2H, Ph), 7.51 (m, 1H, Ph), 7.45 (m, 2H, Ph), 7.44–7.38 (m, 5H, Ph), 7.34 (m, 2H, Ph), 5.27 (sept, ${}^{3}J_{H,H} =$ 2.4 Hz, 1H, SnH), 4.59 (pt, ${}^{3}J_{H,H}$ = 2.4 Hz, 1H, Cp), 4.48 (m, 1H, Cp), 4.24 (s, 5H, free Cp), 4.08 (m, 1H, Cp), 1.37 (brm, 3H, BH₃), 0.18 (d, ${}^{3}J_{H,H}$ = 1.8 Hz, ${}^{2}J_{Sn,H}$ = 55/58 Hz, 3H, SnMe), 0.17 (d, ${}^{3}J_{H,H} = 1.8$ Hz, ${}^{2}J_{Sn,H} = 58/60$ Hz, 3H, SnMe). ${}^{13}C{}^{1}H{}$ NMR (158.8 MHz, CDCl₃, 25 °C): δ = 133.6 (d, ²J_{P,C} = 10 Hz, *o*-Ph), 133.1 (d, ²*J*_{P,C} = 9 Hz, *o*-Ph), 132.0 (d, ¹*J*_{P,C} = 61 Hz, i-Ph), 131.4 (s, *p*-Ph), 131.1 (s, *p*-Ph), 130.9 (d, ${}^{1}J_{P,C} = 65$ Hz, i-Ph), 128.7 (m, *m*-Ph), 81.1 (d, $J_{P,C}$ = 12 Hz, $J_{Sn,C}$ = 51 Hz, Cp), 76.7 (d, $J_{P,C}$ = 8.7 Hz, Cp), 75.8 (d, ${}^{1}J_{P,C}$ = 77 Hz, i-Cp–P), 73.7 $(d, J_{C,P} = 5.9 \text{ Hz}, J_{Sn,C} = 40 \text{ Hz}, \text{Cp}), 72.9 (d, {}^{2}J_{P,C} = 23 \text{ Hz}, \text{ i-Cp-}$ Sn), 70.4 (s, free Cp), -7.4 (s, SnMe), -8.9 (s, SnMe). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25 °C): δ = 18.5 (nr). ¹¹⁹Sn{¹H} NMR (223.6 MHz, CDCl₃, 25 °C): $\delta = -96.3$ (s). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -38.5 (nr). High-resolution MALDI-TOF MS (positive mode, anthracene): m/z 534.9943 BH_3 - H + O⁺₁, 50%, calcd for ([(pS)-8 _ ${}^{12}C_{24}{}^{1}H_{24}{}^{16}O^{56}Fe^{31}P^{120}Sn 534.9936; m/z 520.0041 ([(pS)-8 -$ $BH_3]^+$), 100%, calcd for ${}^{12}C_{24}{}^{1}H_{25}{}^{56}Fe^{31}P^{120}Sn$ 520.0065. Elem. anal. for C24H28BFePSn: calcd C 54.10, H 5.80; found C 54.50, H 5.10.

The third band was collected from the column and concentrated. Repeated recrystallization in hexanes at -27 °C gave first a crop of crystals corresponding to FcPPh₂·BH₂ (0.20 g, 27% yield). A second crop of just a few orange crystals was obtained from the hexanes solution after a few more days and identified to be the dimethyl(ferrocenylphosphino)stannylsubstituted ferrocenylphosphine-borane adduct (pSpS)-7 by X-ray, MALDI-TOF MS and ¹H NMR analysis. Yield: 0.005 g (3%). ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.68 (m, 2H, Ph), 7.63 (m, 2H, Ph), 7.20-7.28 (m, 14H, Ph), 7.24 (m, 2H, Ph), 4.54 (nr, 1H, Cp), 4.23 (nr, 1H, Cp), 4.19 (nr, 1H, Cp), 4.17 (nr, 1H, Cp), 3.98 (nr, 1H, Cp), 3.95 (s, 5H, free Cp), 3.83 (s, 5H, free Cp), 3.81 (nr, 1H, Cp), 1.38 (brm, 3H, BH₃), 1.20 (s, ${}^{2}J_{Sn,H}$ = 62 Hz, 3H, SnMe₃), 0.02 (s, ${}^{2}J_{Sn,H} = 56$ Hz, 3H, SnMe₃). High-resolution MALDI-TOF MS (positive mode, anthracene): m/z 905.0495 ([(pSpS)-7 – BH₃ + O]⁺), 100%, calcd ${}^{12}\text{C}_{46}{}^{1}\text{H}_{43}{}^{16}\text{O}^{56}\text{Fe}_{2}{}^{31}\text{P}_{2}{}^{120}\text{Sn} \quad 905.0517; \quad \textit{m/z} \quad 889.0534$ for $([(pSpS)-7 - BH_3 + H]^+, 45\%, calcd for {}^{12}C_{46}{}^{-1}H_{43}{}^{-56}Fe_2{}^{-31}P_2{}^{-120}Sn$ 889.0568).

Synthesis of dimethylstannyl-bridged bis (ferrocenylphosphine-borane) (pRpR)-10

To a solution of (pRSspRSs)-9 (0.18 g, 0.23 mmol) in THF (40 mL) that was cooled to -78 °C, was added slowly a solution of tBuLi in pentane (1.7 M, 0.27 mL, 0.46 mmol, 2.1 equiv.). The mixture was stirred for 10 min and a solution of PPh₂Cl (0.087 g, 0.49 mmol, 2.2 equiv.) in THF (5 mL) was slowly added, followed by addition of a solution of BH3. THF (1.0 M in THF, 0.7 mL, 0.66 mmol, 3.0 equiv.). After stirring for 1 h at this temperature, the reaction mixture was slowly allowed to warm up to 25 °C overnight. The THF solvent was removed in vacuum and the residue dissolved in Et₂O (30 mL) and quenched by addition of aqueous sodium bicarbonate. The combined organic layer was then separated, washed with water, brine, dried with sodium sulfate, and the solvent was removed in vacuum to leave a yellow oily residue. Purification by column chromatography on silica gel with hexanes/THF/ Et_3N (80:20:1) afforded (pRpR)-10 as a yellow solid that was obtained in analytically pure form after washing several times with hot hexanes. Yield 0.070 g (38%). $[\alpha]_{D}^{20}$ (*c* = 0.18, CHCl₃) = -47° . ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.69 (m, 4H, Ph), 7.50 (m, 6H, Ph), 7.45 (m, 6H, Ph), 7.38 (m, 4H, Ph), 4.29 Cp), 3.88 (nr, 2H, Cp), 1.34 (brm, 6H, BH₃), 0.46 (s, ${}^{2}J_{Sn,H}$ = 60 Hz, 6H, SnMe₂). ¹³C¹H} NMR (125.7 MHz, CDCl₃, 25 °C): δ = 133.7 (d, ²J_{P,C} = 9 Hz, *o*-Ph), 133.2 (d, ²J_{P,C} = 9 Hz, *o*-Ph), 132.4 (d, ${}^{1}J_{P,C}$ = 56 Hz, i-Ph), 131.3 (d, ${}^{1}J_{P,C}$ = 60 Hz, i-Ph), 131.3 (s, p-Ph), 131.1 (s, p-Ph), 128.6 (m, m-Ph), 82.2 (d, J_{P,C} = 12 Hz, Cp), 78.0 (d, ${}^{2}J_{P,C}$ = 25 Hz, i-Cp–Sn), 76.2 (d, $J_{P,C}$ = 6.4 Hz, Cp), 74.9 (d, ${}^{1}J_{P,C}$ = 72 Hz, i-Cp–P), 73.2 (d, $J_{P,C}$ = 4.5 Hz, Cp), 70.3 (s, free Cp), -0.86 (s, SnMe₂). ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25 °C): δ = 17.9 (nr). ¹¹⁹Sn{¹H} NMR (223.6 MHz, CDCl₃, 25 °C): $\delta = -13.1$ (s). ¹¹B{¹H} NMR (160.4 MHz, CDCl₃, 25 °C): -37.7 (nr). High-resolution MALDI-TOF MS (positive mode, anthracene): m/z 905.0513 ([(pRpR)-10 - 2BH₃ + O]⁺, 30%, calcd for ${}^{12}C_{46}{}^{1}H_{43}{}^{16}O^{56}Fe_2{}^{31}P_2{}^{120}Sn 905.0517$); m/z 889.0544([(p*R*p*R*)-**10** - 2BH₃ 100%, calcd + H^{+} for ${}^{12}C_{46}{}^{1}H_{43}{}^{56}Fe_{2}{}^{31}P_{2}{}^{120}Sn$ 889.0568). Elem. anal. for C₄₆H₄₈B₂Fe₂P₂Sn: calcd C 60.39, H 5.29; found C 60.07, H 4.95.

Acknowledgements

A. C. T. K. thanks the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship. A 500 MHz NMR spectrometer used in these studies was purchased with support from the NSF-MRI program (1229030). The X-ray diffractometer was purchased with support from the NSF-CRIF program (0443538) and Rutgers University (Academic Excellence Fund).

References

1 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, 250, 395–408.

- 2 M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 6908–6914.
- 3 W. Scherer and G. S. Mcgrady, *Angew. Chem., Int. Ed.*, 2004, 43, 1782–1806.
- 4 E.-L. Zins, B. Silvi and M. E. Alikhani, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9258–9281.
- 5 G. J. Kubas, Metal Dihydrogen and σ -bond complexes, Kluwer Academic/Plenum Publishers, New York, 2001, pp. 365–415.
- 6 (a) A. E. Shilov and G. B. Shul'pin, Catalysis by Metal Complexes: Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, 2000, vol. 21;
 (b) F. M. Chadwick, T. Krämer, T. Guttmann, N. H. Rees, A. L. Thompson, A. J. Edwards, G. Buntkowsky, S. A. Mcgregor and A. S. Weller, J. Am. Chem. Soc., 2016, 138, 13369-13378.
- 7 Alkane C-H Activation by Single-Site Metal Catalysis, ed.
 P. J. Perez, in Catalysis by Metal Complexes, D. J. Cole-Hamilton, P. W. N. M. van Leuven Perez, series eds, vol. 38, Springer, Dordrecht, 2012.
- 8 S. A. Snow, M. Shimoi, C. D. Ostler, B. K. Thompson, C. Kodama and R. W. Parry, *Inorg. Chem.*, 1984, 23, 512– 515.
- 9 W. F. Mcnamara, E. N. Duesler, R. T. Paine, J. V. Ortiz, P. Kölle and H. Nöth, *Organometallics*, 1986, 5, 380–383.
- 10 (a) K. Katoh, M. Shimoi and H. Ogino, *Inorg. Chem.*, 1992,
 31, 670-675; (b) M. Shimoi, K. Katoh and H. Ogino,
 J. Chem. Soc., Chem. Commun., 1990, 811; (c) M. Shimoi,
 K. Katoh, Y. Kawano, G. Kodama and H. Ogino,
 J. Organomet. Chem., 2002, 659, 102-106; (d) Y. Kawano,
 K. Yamaguchi, S.-Y. Miyake, T. Kakizawa and M. Shimoi,
 Chem. Eur. J., 2007, 13, 6920-6931.
- 11 M. Shimoi, S.-I. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi and H. Ogino, *J. Am. Chem. Soc.*, 1999, **121**, 11704–11712.
- 12 (a) T. Kakizawa, Y. Kawano and M. Shimoi, Organometallics, 2001, 20, 3211; (b) T. Yasue, Y. Kawano and M. Shimoi, Angew. Chem., Int. Ed., 2003, 42, 1727–1730.
- 13 T. Yasue, Y. Kawano and M. Shimoi, *Chem. Lett.*, 2000, **29**, 58–59.
- 14 D. R. Martin, C. M. Merkel and J. P. Ruiz, *Inorg. Chim. Acta*, 1986, **115**, L29–L30.
- 15 (a) M. Ingleson, N. J. Patmore, G. D. Ruggiero, C. G. Frost, M. F. Mahon, M. C. Willis and A. S. Weller, *Organometallics*, 2001, 20, 4434–4436; (b) O. Volkov, R. Macías, N. P. Rath and L. Barton, *Inorg. Chem.*, 2002, 41, 58327–55843; (c) N. Merle, G. Koicok-köhn, M. F. Mahon, C. G. Frost, G. D. Ruggiero, A. S. Weller and M. C. Willis, *Dalton Trans.*, 2004, 3883–3892.
- 16 T. A. Shuttleworth, M. A. Huertos, I. P. Pernik, R. D. Young and A. S. Weller, *Dalton Trans.*, 2013, 42, 12917–12925.
- 17 (a) K. Izod, W. Mcfarlane, B. V. Tyson, I. Carr, W. Clegg and R. W. Harrington, *Organometallics*, 2006, 25, 1135–1143;
 (b) K. Izod, C. Wills, W. Clegg and R. W. Harrington, *Organometallics*, 2009, 28, 2211–2217; (c) K. Izod,

C. M. Dixon, R. W. Harrington and M. R. Probert, *Chem. Commun.*, 2015, **51**, 679–681; (*d*) K. Izod, C. Wills, S. Elhamruni, R. W. Harrington and P. G. Waddell, *Organometallics*, 2015, **34**, 2406–2414; (*e*) K. Izod, C. Wills, M. R. Probert and R. W. Harrington, *Main Group Met. Chem.*, 2014, **37**, 113–117.

- 18 A. Kawachi, H. Morisaki, A. Tani, M. Zaima and Y. Yamamoto, *Heteroat. Chem.*, 2011, **22**, 471–475.
- 19 B. Wrackmeyer, O. L. Tok and Y. N. Bubnov, Angew. Chem., Int. Ed., 1999, 38, 124–126.
- 20 J. Chen and E. Y.-X. Chen, Angew. Chem., Int. Ed., 2015, 54, 6842–6846.
- 21 H. Großekappenberg, N. Lühmann, W. Saak and T. Müller, *Z. Anorg. Allg. Chem.*, 2015, 641, 2543–2548.
- 22 (a) N. Kordts, C. Borner, R. Panisch, W. Saak and T. Müller, Organometallics, 2014, 33, 1492–1498; (b) R. Panisch, M. Bolte and T. Müller, J. Am. Chem. Soc., 2006, 128, 9676– 9681; (c) C. L. Dorsey and F. P. Gabbaï, Organometallics, 2008, 27, 3067–3069.
- 23 (a) M. Jabłonski, Chem. Phys., 2014, 433, 76–84;
 (b) M. Jabłonski, Comput. Theor. Chem., 2016, 1096, 54–65.
- 24 (a) V. D. Vil'chevskaya, N. K. Baranetskaya, A. S. Peregudov,
 V. D. Makhaev and A. I. Krylova, *Russ. J. Coord. Chem.*,
 1998, 24, 307–308; (b) J. C. Kotz, C. L. Nivert and
 J. M. Lieber, *J. Organomet. Chem.*, 1975, 91, 87–95.
- 25 (a) O. Riant, G. Argouarch, D. Guillaneaux, O. Samuel and H. B. Kagan, J. Org. Chem., 1998, 63, 3511-3514;
 (b) D. Enders, R. Peters, R. Lochtman and J. Runsink, Eur. J. Org. Chem., 2000, 2839-2850; (c) C.-O. Turin, J. Chiffre, J.-C. Daran, D. de Montauzon, A.-M. Caminade, E. Manoury, G. Balavoine and J.-P. Majoral, Tetrahedron, 2001, 57, 2521-2536; (d) E. B. Kaloum, R. Merdès, J.-P. Genêt, J. Uziel and S. Jugé, J. Organomet. Chem., 1997, 529, 455-463.
- 26 (a) P. Štěpnička and I. Císařová, Dalton Trans., 2013, 42, 3373–3389; (b) J. Bayardon, J. Bernard, E. Rémond, Y. Rousselin, R. Malecea-kabbara and S. Jugé, Org. Lett., 2015, 17, 1216–1219; (c) J. Bayardon, H. Laureano, V. Diemer, M. Dutartre, U. Das, Y. Rousselin, J.-C. Henry, F. Colobert, F. R. Leroux and S. Jugé, J. Org. Chem., 2012, 77, 5759–5769; (d) K. D. Reichl, D. H. Ess and A. T. Radosevich, J. Am. Chem. Soc., 2013, 135, 9354–9357; (e) E. A. Colby and T. F. Jamison, J. Org. Chem., 2003, 68, 156–166.
- 27 (a) S. Pandey, P. Lönnecke and E. Hey-Hawkins, *Inorg. Chem.*, 2014, 53, 8242–8249; (b) S. Pandey, P. Lönnecke and E. Hey-hawkins, *Eur. J. Inorg. Chem.*, 2014, 2456–2465.
- 28 (a) J. Chen, D. A. Murillo, R. A. Lalancette and F. Jäkle, Angew. Chem., Int. Ed., 2015, 54, 10202–10205; (b) J. Chen, A. C. Tagne Kuate, R. A. Lalancette and F. Jäkle, Organometallics, 2016, 35, 64–72.
- 29 J. A. Gamboa, A. Sundararaman, L. Kakalis, A. J. Lough and F. Jäkle, *Organometallics*, 2002, **21**, 4169–4181.
- 30 A. C. Tagne Kuate, R. A. Lalancette and F. Jäkle, unpublished results.

- 31 In our hands, the ³¹P NMR spectrum of the planar-chiral ferrocenyl-substituted phosphine-borane sulfinate (p*S*,*S*_s)-2 recorded at 202.5 MHz in CDCl₃ showed a broad resonance at δ = 16.7 ppm.
- 32 T. P. Lockhart and W. F. Manders, *J. Am. Chem. Soc.*, 1987, 23, 7015–7020.
- 33 S. Hoppe, H. Weichman, K. Jurkschat, C. Schneider-koglin and M. Dräger, J. Organomet. Chem., 1995, 505, 63–72.
- 34 The following van der Waals radii are used: H 1.10, B 1.92, O 1.52, P 1.80, Cl 1.75, Sn 2.17, Hg 2.05 Å; seeM. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. A*, 2009, 113, 5806–5812. The value of 2.05 Å for Hg is taken from S. S. Batsanov, *J. Mol. Struct.*, 1999, 468, 151–159.
- 35 J. Kim, S. Kim and Y. Do, *J. Chem. Soc., Chem. Commun.*, 1992, 938–939.
- 36 M. Herberhold, U. Steffl, W. Milius and B. Wrackmeyer, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1803–1804.
- 37 J. Chen, R. A. Lalancette and F. Jäkle, Organometallics, 2013, 32, 5843–5851.
- 38 We note that spin-orbit effects may influence the NMR shifts and replacing Sn by Hg may result in different spinorbit effects on the ³¹P and ¹¹B NMR shifts. As a result, the position of the Hg compounds 5 and 6 in this series does not necessarily mean that the strength of the B-H…Hg interaction falls onto this position relative to the Sn compounds in the series.
- 39 P. Kolandaivel and V. Nirmala, *J. Mol. Struct.*, 2004, **694**, 33–38.
- 40 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda,

J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09, Revision S.05*, Gaussian, Inc., Wallingford CT, 2016.

- 41 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO Version 3.1*.
- 42 (a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652;
 (b) P. J. Stephens, F. J. Devlin, C. F. Chablowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623-11627;
 (c) R. H. Hertwig and W. Koch, Chem. Phys. Lett., 1997, 268, 345-351.
- 43 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560–571.
- 44 (a) D. Martínez-Otero, B. Flores-Chávez, J. G. Alvarado-Rodríguez, N. Andrade-López, J. Cruz-Borbolla, T. Pandiyan, V. Jancik, E. González-Jiménez and C. Jardinez, *Polyhedron*, 2012, 40, 1–10; (b) J. Vrána, S. Ketkov, R. Jambor, A. Růžička, A. Lyčkad and L. Dostál, *Dalton Trans.*, 2016, 45, 10343–10354.
- 45 T. A. Keith, *AIMAll (Version 17.01.25)*, T. K. Gristmill Software, Overland Park KS, USA, 2017 (http://aim.tkgrist-mill.com).
- 46 Bruker, *SAINT Version 7.23a*, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
- 47 Bruker, *APEX 2 Version 2.0-2*, Bruker AXS Inc., Madison, Wisconsin, USA, 2006.
- 48 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 2008.
- 49 G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112–122.
- 50 G. M. Sheldrick, SHELXL, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2015, 71, 3-8.