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Ferrocene-based Lewis acids and Lewis pairs: Synthesis and structural characterization

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Abstract. Optically active Lewis acids and Lewis pairs were synthesized and characterized by multinuclear NMR, UV/Vis spectroscopy and elemental analysis. Optical rotation measurements were carried out and the absolute configuration of the new chiral molecules confirmed by single crystal X-ray diffraction.

Keywords. Ferrocene/Lewis acid; optical rotation; frustrated Lewis pairs; organoborane.

1. Introduction

The design and synthesis of molecules containing non-interacting Lewis base and Lewis acid groups [Frustrated Lewis pairs (FLP's)] have received intense attention due to their potential applications in the area of molecular catalysis.[1–3] For example, Stephen's and co-workers have demonstrated that the unquenched Lewis acidity and Lewis basicity of $(C_6H_2Me)_2PH(C_6F_4)BF(C_6F_5)_2$ reversibly activate molecular hydrogen, in the absence of transition metals.[2] FLP's can also be used to activate C-H, B-H and N-H bonds. Erker and co-workers have demonstrated the reversible activation of H_2 by metallocene based FLPs.[3] Surprisingly, there is no report on the synthesis of enantiomerically pure FLP's, which would be very important for chiral organic transformations.[1–3]

Lewis acidic organoboranes play key role both as reagents and catalysts in asymmetric organic synthesis.[4–9] The *rigid three-dimensional* structure and inherent planar chirality of 1,2-disubstituted ferrocenes bearing non-identical atoms provide excellent chiral environment for enantioselective synthesis.[9,10] Several planar chiral ferrocene based phosphines and amines are known and their catalytic activity in the presence of transition metals is well documented.[10] Piers,[8] Wagner[11] and Aldridge[12] have independently prepared various ferrocenylboranes and studied their applications in catalysis and as anion sensors. Jakle *et al.*[9,13] have prepared verious ferrocenylboranes and studied their applications in anion binding as well as in chiral synthesis. It is noteworthy to mention that Aldridge and co-workers recently have devised a simple route for the synthesis of planar chiral frustrated Lewis pairs (PCFLP's) from 1,1′-dibromoferrocene, but the final products were in racemic form.[14a] Instead, use of chiral ferrocenyl sulphoxide can be visualized as a precursor for optically pure isomers both 1-phosphino-2-borylferrocenes (S_P) and 2-phosphino-1-borylferrocenes (R_P). We anticipate that the preparation of PCFLP's could open up a new entry into enantioselective catalysts and also that the reversible redox chemistry at the metal centre can be used to fine tune the activity of the PCFLP's. While the work was under progress in our lab[14b–d] Siewert and coworkers[14e] have independently reported the syntheses of homochiral Sp-1,2-fc$(PPh_2)(BMes_2)$ using ferrocene sulphoxide as a precursor, but they have not explored the possibility of synthesis of Rp-1,2-fc$(BMes_2)(PPh_2)$ from the same precursor. Prior to the report of Siewert *et al.*, the preliminary accounts of our work reported in this manuscript have been presented in one international and two national conferences.[14b–d] In this communication, we report our independent results on the synthesis and characterization of both 1-phosphino-2-borylferrocene (S_P) and 2-phosphino-1-borylferrocene (R_P) from single precursor chiral ferrocenylsulphoxide.

2. Experimental

2.1 *General procedure*

n-Butyl lithium, *t*-butyl lithium (1.7M in hexanes), *bis*-mesitylfluroborane and PPh_2Cl & were purchased

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from Aldrich. Caution! Lithium reagents and Ph_2PCl are toxic and highly corrosive and should be handled appropriately with great care. All reactions and manipulations were carried out under an atmosphere of pre-purified nitrogen using Schlenk techniques. Due to the unpleasant odour of Ph_2PCl, most of the manipulations were carried out in a well-ventilated fume hood. Thin-layer chromatography (TLC) analyses were carried out on pre-coated silica gel plates (Merck), and spots were visualized by UV irradiation. Column chromatography was performed on glass columns loaded with silica gel. THF and hexane were distilled from sodium/benzophenone. Chlorinated solvents were stirred for 24 h over anhydrous CaH_2, then degassed via several freeze pump thaw cycles and stored over 3 Å molecular sieves. 400 MHz ^{1}H NMR, 100.613 MHz ^{13}C NMR, 128.378 MHz, ^{11}B NMR and 161.976 MHz ^{31}P NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Solution ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{11}B NMR spectra to $BF_3.OEt_2$ (δ = 0) in C_6D_6. Mass spectral studies were carried out using a Q-TOF micro mass spectrometer or Bruker Daltonics Esquire 6000 plus mass spectrometer with ESI-MS mode analysis. The melting point was determined in open capillary using an ANALAB melting-point apparatus. UV-visible absorption data were acquired on a UV-vis/NIR perkin Elmer Lambda 750 spectrophotometer. Solutions were prepared using a microbalance ($\pm$ 0.1 mg) and volumetric glassware and then charged into quartz cuvettes with sealing screw caps. Optical rotation analysis was performed on JASCO p-1020 III polarimeter, using a tungsten-halogen light source operating at λ = 589 nm. CCDC 823721–823724 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2 *Preparation of (**2**(S_P, S_S))*

To a solution of Ferrocenyl-p-tolylsulphoxide (1.00 g, 3.05 mmol) in THF (30 mL) at −78°C was added drop-wise LDA (2 mL, 0.34 mmol) and the reaction mixture was stirred for 1 h. A solution of dimesityl fluoroborane (1 g, 4.06 mmol) in THF (4 mL) was added. The mixture was allowed to warm up to room temperature and kept stirring for an additional 6 h. After standard aqueous work-up, the crude product was purified by column chromatography (EtOAc-hexane 1:3 ratio) to obtain orange crystal. Yield: 0.6 g, 80% $[\alpha]_D^{24}$ = −676. 1H NMR (400 MHz, $CDCl_3$, 25°C, δ (ppm)): 2.24 (s, 6H), 2.32 (s, 12H), 2.419 (s, 3H), 4.12 (s, 5H), 4.43 (m, 1H), 4.62 (m, 2H), 6.74 (s, 4H), 7.24 (s, 2H), 7.56–7.54 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, δ (ppm)), 21.54, 21.95, 25.25, 71.59, 72.33, 73.34, 81.01, 101.10, 125.65, 129.4, 129.6, 137.9, 140.3, 140.6, 141.4, 143.2: ESI Mass Spectrometry: Mcalc = 572.2 : found: 595.0 $[M + Na]^+$; 611.0 $[M + K]^+$, (UV-Vis) (CH_2Cl_2, 1.001 × 10–5 M): λ max = 496 nm (ε = 2.6 × 103). Elemental analysis for $C_{37}H_{52}BFeOS$: C, 72.67; H, 8.57, found C, 72.12; H, 8.25

2.3 *Preparation of (**3**(S_P, S_S))*

To a solution of **2**(S_P, S_S) in THF was added distilled water (0.1 mL). The reaction mixture was stirred for 6 h at room temperature. The product was extracted with diethyl ether and volatiles were removed *in vacuo* to obtain desired product. Yield: 60%. $[\alpha]_D^{24}$ = 463, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δppm): 2.01 (s, 1H), 2.20 (s, 3H), 2.26 (s, 8H), 4.09 (m, 1H), 4.45 (s, 5H), 4.52 (d, 1H), 4.99 (m, 1H), 6.77 (d, 2H), 7.17 (m, 2H), 7.41 (d, 2H). 10.74 (s, 1H) ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 21.67, 21.76, 71.27, 73.29, 74.76, 79.59, 100.25, 124.64, 127.60, 130.13, 137.76, 141.34, 142.17. ^{11}B NMR (160 MHz, $CDCl_3$, 25°C) δ : 46.21, ESI Mass Spectrometry: Mcalc: 470.1; found: 507.4 [M+ OMe+H];. Elemental analysis for $C_{26}H_{27}BFeO_2S$; C, 66.41; H, 5.79; found C, 66.10; H, 5.35. UV-Vis (CH_2Cl_2, 1.001 × 10–5 M): λmax = 438 nm ($\varepsilon = 1.0 \times 10^2$).

2.4 *Preparation of (**4**(S_P))*

To a solution of **2**(S_P, S_S) (100 µg, 0.17 mmol) in THF (10 mL) at −78°C was added *t*-BuLi (77 µL, 0.18 mmol) and the reaction mixture stirred for 1 h. Chlorodiphenylphosphine (33 µL, 0.64 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The reaction mixture was kept stirring overnight. Volatiles were removed *in vacuo* to yield crude product, which was purified by column chromatography (EtOAc-hexane) to give red solid. Yield: 10 mg, 10%. $[\alpha]_D^{21}$ = −694.92. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δppm) 2.21 (s, 12H), 2.27 (s, 3H), 2.38 (s, 3H), 4.07 (s, 1H), 4.18 (s, 5H), 4.26 (s, 1H), 4.66 (m, 1H), 6.59 (s, 3H), 6.64 (d, 1H), 6.81 (m, 3H), 7.09 (t, 2H), 7.19 (m, 1H), 7.32 (m, 4H), ^{13}C NMR(100 MHz, $CDCl_3$, 25°C: 21.36, 25.15, 30.42, 70.16, 73.45, 79.13, 83.79, 88.86, 89.04, 133.67, 133.89, 134.72, 134.93, 137.47, 139.86, 140.08, 143.81, ^{31}P NMR (160 MHz, $CDCl_3$, 25°C δ ppm): −21.5, ESI Mass Spectrometry:

Mcalc = 618.3, found: 619 $[M + H]^+$; 641$[M + Na]^+$; 656.9 $[M + K]^+$, UV-Vis (CH_2Cl_2, 1.001×10^{-5} M): $\lambda max = 506$ nm ($\varepsilon = 1.2 \times 10^3$). Elemental analysis for $C_{41}H_{52}BFeP$ calcd C, 76.65; H, 8.16; found C, 76.22; H, 7.98.

2.5 *Preparation of (**5**(S_P, S_S))*

To a solution of Ferrocenyl-p-tolylsulphoxide (1.0 g, 3.05 mmol) in freshly distilled THF (30 ml), was added LDA (1.7 ml, 3.36 mmol) at −78°C. The reaction mixture was stirred at −78°C for 1 h and PPh_2Cl (600 µl, 3.1 mmol) was added. The resulting solution was warmed to room temperature, stirred for 6 h and quenched with water (5 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic extracts were washed with brine (10 ml) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (60–120 mesh) using petether/diethyl ether (1:1) as eluent to obtain (S,S)-2-(Diphenylphosphino)-1-(*p*-tolylsulfinyl)ferrocene as a yellow solid in 27% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C) δ 2.35 (s, 3H), 4.05 (m, 5H), 4.30 (s, 1H), 4.50 (d, 1H), 4.51 (d, 1H), 7.17 (s, 2H), 7.37 (m, 6H), 7.74–7.57 (m, 6H). ^{31}P NMR (160 MHz, $CDCl_3$, 25°C): δ −24.

2.6 *Preparation of (**4**(R_P))*

To a solution of **5**(S_P, S_S) (0.09 g, 0.17 mmol) in THF (10 mL) at −78°C was added *t*-BuLi (77, 0.18 mmol) and the reaction mixture was stirred for 2 h. Dimesityl fluoroborane (33 µL, 0.64 mmol) was then added and the reaction mixture was warmed to room temperature and stirred for overnight. Volatiles were removed *in vacuo* to yield crude product which was purified by column chromatography (EtOAc-hexane) to give red solid. Yield: 20%. $[\alpha]_D^{21} = 674.9$. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δppm) 2.22 (s, 12H), 2.26 (s, 3H), 2.39 (s, 3H), 4.10 (s, 1H), 4.20 (s, 5H), 4.25 (s, 1H), 4.67 (m, 1H), 6.59 (s, 3H), 6.65 (d, 1H), 6.80 (m, 3H), 7.10 (t, 2H), 7.20 (m, 1H), 7.31 (m, 4H). ^{13}C NMR

Table 1. Details of X-ray crystal structure analyses of complexes **2**(S_P, S_S), **3**(S_P, S_S), **4**(S_P) and **5**(S_P, S_S).

Compound	**2**(S_P, S_S)	**3**(S_P, S_S)	**4**(S_P)	**5**(S_P, S_S)
Empirical formula	$C_{35}H_{37}BFeOS$	$C_{26}H_{27}BFeO_2S$	$C_{40}H_{40}BFeP$	$C_{29}H_{25}FeOPS$
MW	572.39	470.21	618.37	508.39
T, K	273(2)	273(2)	363(2)	293(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$
a, Å	9.360(2)	7.433(3)	13.8055(17)	7.727(5)
b, Å	11.884(3)	9.196(3)	14.9786(18)	14.233(8)
c, Å	25.331(6)	17.092	15.4878(19)	10.969(7)
V, Å^3	2817.8(11)	1166.8(7)	3202.7(7)	1196.5(12)
Z	4	2	3	2
ρ_{calc}, g cm^{-3}	1.349	1.338	1.282	2.386
μ (Mo/Cu K_α), mm^{-1}	0.637	0.756	0.548	0.861
Crystal size, mm	0.30 × 0.20 × 0.20	0.25 × 0.22 × 0.20	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.15
θ range, deg	1.89 to 28.11	2.39 to 28.07	1.89 to 28.01	1.87 to 26.37 deg
Limiting indices	−12 <=h<=12 −15 <=k<=15 −33 <=l<=33	−9 <=h<=9 −12 <=k<=11 −22 <=l<=22	−18 <=h<=18 −19 <=k<=19 −20 <=l<=20	−9 <=h<=9, −17 <=k<=17, −13 <=l<=13
Reflns collected	32711	13432	37168	12595
Independent reflns	6740 [R(int) = 0.0579]	5416 [R(int) = 0.0237]	7646 [R(int) = 0.0566]	4879 [R(int) = 0.0853]
Absorption correction	SADABS	SADABS	SADABS	SADABS
data/restraints/parameters	6740/0/359	5416/1/285	7646/0/394	4879/1/300
Goodness-of-fit on F^2	0.981	1.059	1.016	0.959
Final R indices [I >2 σ(I)][a]	R1 = 0.0339 wR2 = 0.0700	R1 = 0.0322, wR2 = 0.0832	R1 = 0.0379 wR2 = 0.0739	R1 = 0.0696, wR2 = 0.1372
R indices (all data)[a]	R1 = 0.0453 wR2 = 0.0719	R1 = 0.0338, wR2 = 0.0844	R1 = 0.0536 wR2 = 0.0778	R1 = 0.1409, wR2 = 0.1625
$Peak_{max}$/$hole_{min}$(e Å^{-3})	0.497 and −0.250	0.232 and −0.325	0.469 and −0.251	0.667 and −0.315
Absolute structure parameter	0.012(11)	0.075(11)	0.038(11)	0.07(3)

[a] $R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$; $wR2 = \left\{ \Sigma \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / \Sigma \left[w \left(F_o^2 \right)^2 \right] \right\}^{1/2}$

(100 MHz, $CDCl_3$, 25°C) δ 21.35, 25.16, 30.41, 70.14, 73.42, 79.11, 83.77, 88.87, 89.06, 133.66, 133.90, 134.71, 134.92, 137.41, 139.87, 140.10, 143.80. ^{31}P NMR (160 MHz, $CDCl_3$, 25°C δppm) −20.5. ESI Mass Spectrometry: Mcalc = 618.37, found: 619 $[M + H]^+$, 656.9 $[M + K]^+$, UV-Vis, (CH_2Cl_2, 1.001 × 10^{-5} M): λ max = 506 nm (ε = 1.2 × 10^3). Elemental analysis for $C_{41}H_{52}BFeP$ calcd C, 76.65; H, 8.16, found C, 76.20; H, 8.0.

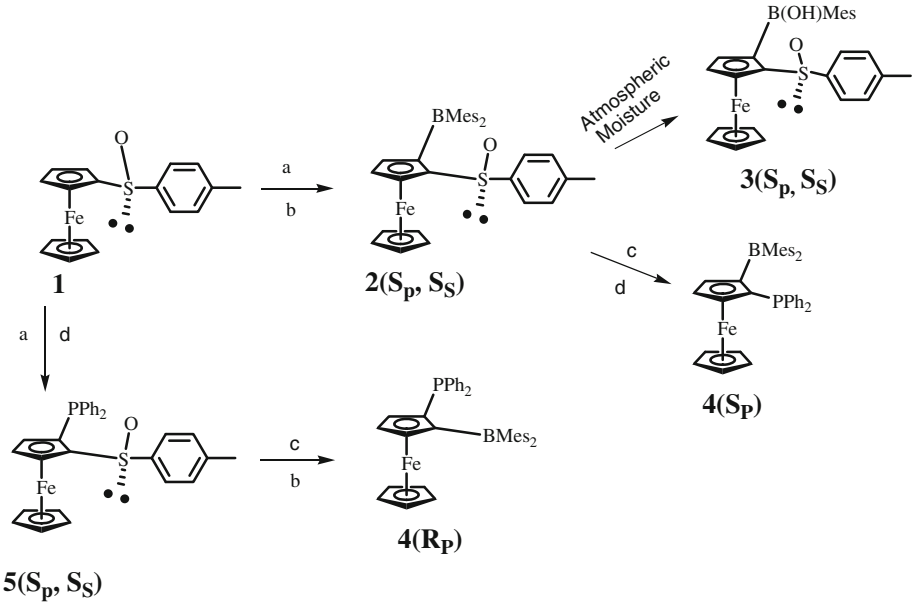
2.7 *Structure determination of compounds* ***2(S$_P$, S$_S$), 3(S$_P$, S$_S$), 4(S$_P$) and 5(S$_P$, S$_S$)***

Single-crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer equipped with 3-axis goniometer. The crystals were kept under a steady flow of cold dinitrogen during the data collection. The details regarding the data collection and refinement for compounds **2**($\mathbf{S_P}$, $\mathbf{S_S}$), **3**($\mathbf{S_P}$, $\mathbf{S_S}$), **4**($\mathbf{S_P}$) and **5**($\mathbf{S_P}$, $\mathbf{S_S}$) are given in table 1. The data were integrated using SAINT, and an empirical absorption correction was applied with SADABS. The structures were solved by direct methods and refined by full matrix least-squares on F2 using SHELXTL software. All the non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were refined isotropically on the positions calculated using a riding model.

3. Results and discussion

The synthetic strategy followed in the syntheses of compounds **2**($\mathbf{S_P}$, $\mathbf{S_S}$)-5 is described in scheme 1. The synthetic access to the chiral ferrocenylsulphoxide (**1**) was made possible by the principal studies of Kagan who converted stanylferrocene to **1** by the action of n-BuLi followed by (S,S)-menthyl-p-tolylsulphinate.[10e,10d,15] The second step of the process is the diastereo-selective ortholithiation of **1** by LDA at −78°C in THF and followed by quenching with Mes_2BF gave **2**($\mathbf{S_P}$, $\mathbf{S_S}$) in 80% yield after silica gel column purification (scheme 1). The ^{1}H and ^{13}C NMR spectra of **2**($\mathbf{S_P}$, $\mathbf{S_S}$) are consistent with a 1,2-disubstituted ferrocene derivatives, and a resonance at δ = 49 ppm in the ^{11}B NMR spectrum confirms the attachment of the $BMes_2$ group. The ^{11}B NMR signal is considerably upfield shifted compared to other triorganyl boranes (in general they resonate at 60–70 ppm).[8–13] This may be due to the interaction between the boron in -$BMes_2$ unit and the oxygen of tolylsulphinate moiety. The absolute configuration of **2**($\mathbf{S_P}$, $\mathbf{S_S}$) was assigned from the single-crystal X-ray structure, which confirms diastereoselective ortho lithiation of **1** (figure 1a).

The molecular structure of **2**($\mathbf{S_P}$, $\mathbf{S_S}$) also gives evidence for B—O (3.293 Å) interaction (figure 1a). Such kind of interaction was first noted by Aldridge and co-workers (B—O, 3.304 Å).[14] In contrast to the observation noted by Siewert *et al.*, compound **2**($\mathbf{S_P}$, $\mathbf{S_S}$) is not stable at atmospheric conditions and prone to



Scheme 1. Synthesis of compounds **2**($\mathbf{S_P}$, $\mathbf{S_S}$), **3**($\mathbf{S_P}$, $\mathbf{S_S}$), **4**($\mathbf{S_P}$), **4**($\mathbf{R_P}$) and **5**($\mathbf{S_P}$, $\mathbf{S_S}$) (a) LDA, (b) $FBMes_2$, (c) *t*-BuLi and (d) $ClPPh_2$.

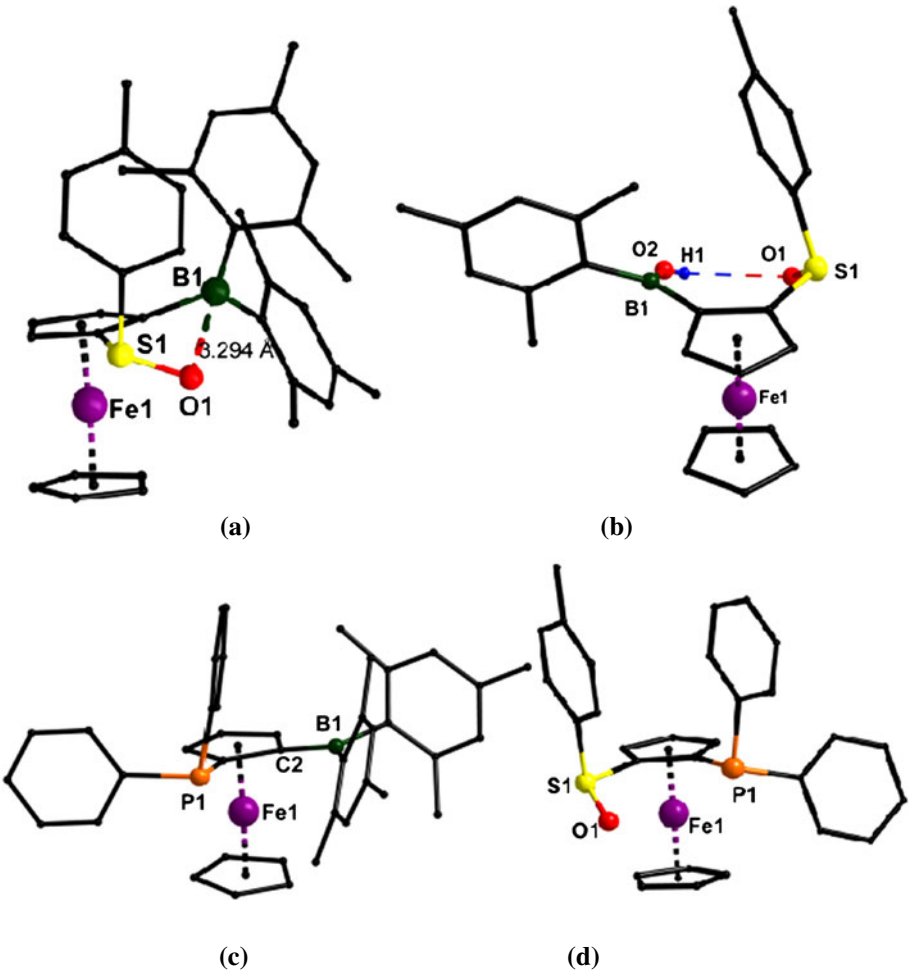
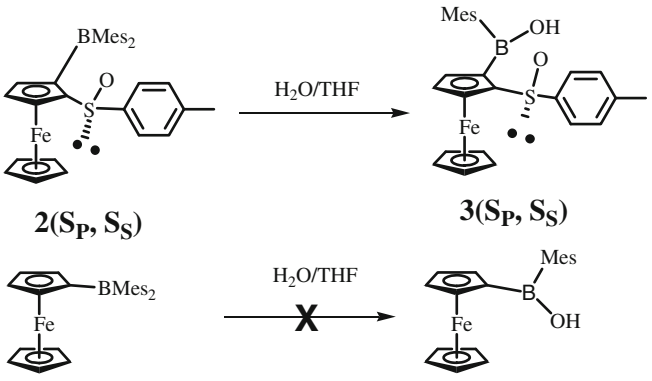


Figure 1. Molecular structures of (**a**) **2**(S_P, S_S), (**b**) **3**(S_P, S_S), (**c**) **4**(S_P) and (**d**) **5**(S_P, S_S). All the hydrogen atoms are omitted for clarity. (**a**) Molecular structure of **2**(S_P, S_S). Selected interatomic distances [Å] and angles [°]: C(1)-B(1) 1.573(3), C(20)-B(1) 1.584(3), C(11)-B(1) 1.589(3), S(1)-O(1) 1.5034(16), S(1)-C(2) 1.776(2), S(1)-C(29)1.804(2), O(1)-S(1)-C(2)107.67(9), O(1)-S(1)-C(29) 105.45(1), C(2)-S(1)-C(29) 99.16(9), C(1)-B(1)-C(20)119.60(2), C(1)-B(1)-C(11)116.83(2), C(20)-B(1)-C(11)122.01(2). (**b**) Molecular structure of **3**(S_P, S_S). Selected interatomic distances [Å] and angles [°]: S(1)-O(2) 1.5058(17), S(1)-C(1) 1.770(2), S(1)-C(11) 1.799(2), O(1)-B(1) 1.351(3), B(1)-C(18) 1.575(3), B(1)-C(2) 1.577(3), O(2)-S(1)-C(1) 109.39(10), O(2)-S(1)-C(11) 106.10(1), C(1)-S(1)-C(11) 96.93(9), O(1)-B(1)-C(2) 118.68(2), O(1)-B(1)-C(2) 121.04(2), C(18)-B(1)-C(2) 120.28(2). (**c**) Molecular structure of **4**(S_P), selected interatomic distances [Å] and angles [°]. P(1)-C(1)1.824(2), P(1)-C(11) 1.836(2), P(1)-C(17) 1.842(2), B(1)-C(2)1.557(3), B(1)-C(29)1.599(3), B(1)-C(23)1.599(3), C(1)-P(1)-C(11) 99.24(9), C(1)-P(1)-C(17) 99.26(1), C(11)-P(1)-C(17)100.48(1), C(2)-B(1)-(29)114.14(2), C(2)-B(1)-C(23)126.31(2), C(29)-B(1)-C(23)119.43(2). (**d**) Molecular structure of **5**. Selected interatomic distances [Å] and angles [°]: S(1)-O(1) 1.470(5), S(1)-C(2) 1.780(8), S(1)-C(23) 1.781(6), P(1)-C(1) 1.784(6), P(1)-C(11) 1.819(7), P(1)-C(18) 1.836(6), O(1)-S(1)-C(2) 109.6(3), O(1)-S(1)-C(23) 106.8(3), C(2)-S(1)-C(23) 98.0(3), C(1)-P(1)-C(11) 100.4(3), C(1)-P(1)-C(18) 101.9(3), C(11)-P(1)-C(18) 100.9(3).

hydrolysis. Over a period of a week it slowly underwent selective hydrolysis of one of the two B-Mes bonds by reacting with atmospheric moisture. The hydrolysed product was separated by using silica gel column chromatography technique and found to be compound **3**(S_P, S_S). Later, compound **3**(S_P, S_S) was prepared by a different route (scheme 2).

When compound **2**(S_P, S_S) was allowed to react with one equivalent of water in THF **3**(S_P, S_S), the quantitative yield was obtained. The ^{1}H NMR spectrum



Scheme 2. Synthesis of **3**(S_P, S_S) from **2**(S_P, S_S).

of **3**(S_P, S_S) shows three different resonances at 4.09, 4.52 and 4.99 ppm for substituted Cp and a single resonance for free Cp at 4.45 ppm. The hydrolysis might have occurred because of the intramolecular Tolyl-S-O—B interaction. The upfield shifted ^{11}B resonance of **3**(S_P, S_S) (46.2 ppm) (see Supporting Information Figure S9) relative to the parent compound **2**(S_P, S_S) (49 ppm) support the intramolecular interaction discussed *vide-supra*. In order to demonstrate the role of the B—O interaction in the hydrolysis reaction, control experiment was designed in which $FcBMes_2$, which lacks the Tolyl-S-O functionality, was tested for hydrolysis. $FcBMes_2$ was treated with 10 equiv of water for two days using THF as solvent (scheme 2). No B–C bond cleavage was observed and $FcBMes_2$ was completely recovered. The molecular structure of **3**(S_P, S_S) is shown in figure 1. Although free rotation is possible at the boron centre (due to the absence of one bulky mesityl group), we observed only one isomer. This might be due to the strong intramolecular OH—O (1.956 Å) interaction between sulphinate oxygen and B–OH moiety. The more downfield shifted resonance of B–OH (10.74 ppm) in solution state ^{1}H NMR clearly indicates that the intramolecular interaction also persists in solution state (see Supporting Information Figure S2).

Reaction of **2**(S_P, S_S) with *t*-BuLi in THF at −78°C generates chiral lithioferrocene, which was trapped with PPh_2Cl to give compound **4**(S_P). The ^{1}H NMR spectrum shows three signals at $\delta = 4.66$ (dd), 4.26 (pseudo triplet), and 4.07 ppm (dd), as expected for a 1,2-disubstituted Cp ring, and a singlet at $\delta = 4.18$ ppm for the free Cp ring. A signal at 77.6 ppm in the ^{11}B NMR spectrum confirms that $BMes_2$ is intact and a resonance at $\delta = -20.5$ ppm in the ^{31}P NMR spectrum confirms the attachment of PPh_2. The appearance of protonated molecular ion $[M + H]^+$ peak at 619 in the ESI mass spectrum confirms the formation of **4**(S_P). The ^{11}B and ^{31}P resonances clearly indicate the presence of unquenched tricoordinated phosphine and borane centres in **4**(S_P) in solution.[1–3,14] The optical purity of **4**(S_P) was confirmed by single crystal X-ray analysis and optical rotation studies. Compound **5**(S_P, S_S) was prepared by adopting known literature[15d] procedure (scheme 1). Compound **4**(R_P) was prepared from **5**(S_P, S_S) following a procedure similar to that used for **4**(S_P). Compound **4**(R_P) was characterized by multinuclear NMR (^{1}H, ^{13}C, ^{11}B and ^{31}P), ESI mass, optical rotation, and elemental analysis and UV-Vis spectroscopy. ^{1}H NMR integration and molecular ion peak in ESI Mass spectrum confirms the formation of **4**(R_P) and are consistent with **4**(S_P). The ^{11}B (77.2 ppm) and ^{31}P (−20.5 ppm) resonances are also in the range of free tricoordinated phosphine and borane, respectively.[1–3]

Molecular structure of compounds **2**(S_P, S_S), **3**(S_P, S_S), **4**(S_P) and **5**(S_P, S_S) are confirmed by single crystal X-ray diffraction studies. The molecular structures are shown in figure 1 with important geometric parameters. Recently, Aldrige and co-workers[14] reported the crystal structure of **2**(S_P, S_S) and **3**(S_P, S_S), but the inter and intramolecular bonding parameters vary considerably in the present report. In addition, the synthetic procedure for these compounds reported in the present study is different from the literature. The dihedral angle between BC2/BCO plane and plane of substituted Cp ring is considerably smaller for **4**(S_P) with 11.7° in comparison to the highly tilted **2**(S_P, S_S), (59.2°), while the angle found for **3**(S_P, S_S) lies in between at 27.7° (table 2). This might be due to the steric bulk of mesityl substituents in **2**(S_P, S_S), and **4**(S_P). Steric effects are also evident from a comparison of the Cp//Cp tiltangles of **2**(S_P, S_S)-**5**(S_P, S_S), which for **4**(S_P) is 8.6°, whereas for **2**(S_P, S_S), **3**(S_P, S_S) and **5**(S_P, S_S) they are 4.32, 1.18 and 3.19°, respectively. **3**(S_P, S_S) shows more pronounced Fe—B interaction (3.214 Å) compared to **2**(S_P, S_S) (3.44 Å) and **4**(S_P) (3.36 Å). This can be rationa-

Table 2. Selected intramolecular interactions (distance (Å) and angles (°)) involved in **2**(S_P, S_S), **3**(S_P, S_S), **4**(S_P), and **5**(S_P, S_S).

Compound	**2**(S_P, S_S)	**3**(S_P, S_S)	**4**(S_P)	**5**(S_P, S_S)
Cp//Cp	4.32	1.18	8.61	3.19
BC2/BCO//Cp	59.23	27.74	11.73	—
Fe—B	3.442	3.214	3.369	—

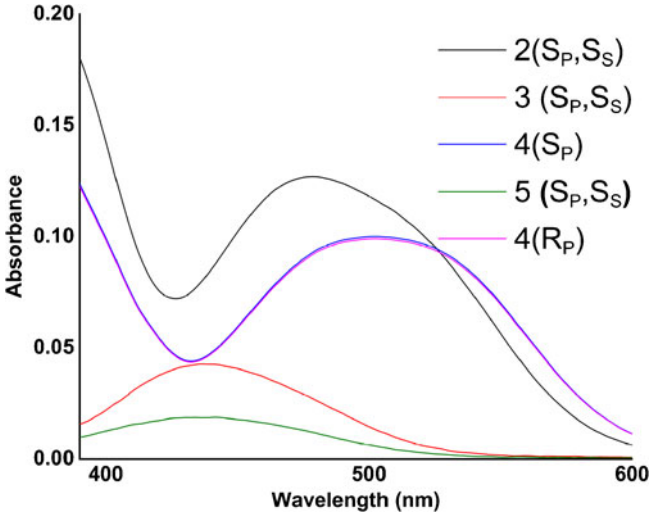


Figure 2. Uv-Vis spectra of **2**(S_P, S_S), **3**(S_P, S_S), **4**(S_P), **4**(R_P) and **5**(S_P, S_S).

lized by the electronic factor. The boron centre in **3**(S_P, S_S), (connected with OH and one mesityl group, respectively) is more electron deficient than in **2**(S_P, S_S) and **4**(S_P) (connected with two mesityl groups).

The boron centre in **3**(S_P, S_S), and **4**(S_P) is planar with the sum of angle around boron is 360°, in the case of **2**(S_P, S_S) little pyramidalization occurred.[14] The P-B separation of 3.567 Å in solid state together with ^{11}B and ^{31}P resonances (vide supra) in solution state clearly indicates the presence of an unquenched PCFLP in both forms. The electronic structure of compounds **2**(S_P, S_S) **-5**(S_P, S_S) has been studied by UV-Vis spectroscopy (figure 2). The longest wavelength absorption has been observed for **4**(S_P) and **4**(R_P), followed by **2**(S_P, S_S), **3**(S_P, S_S) and **5**(S_P, S_S) (figure 2). This band can be attributed to a d–d transition of the ferrocene moiety with considerable charge-transfer character.[13] The particular order may suggest that electronic interactions between the d-orbitals of the ferrocenyl and the empty *p*-orbital on boron are promoted by sterically bulky substituents on boron.

4. Conclusions

In conclusion, the novel planar chiral Lewis acids **3**(S_P, S_S), 1-phosphino-2-borylferrocenes **4**(S_P) and 2-phosphino-1-borylferrocenes **4**(R_P) are readily accessible from ferrocene sulphinate precursor. Adopting a simple synthetic approach and a single precursor, we have synthesized enentiomerically pure S_P and R_P isomers. We are currently investigating the catalytic properties of compounds **3**(S_S), **4**(S_P) and **4**(R_P). We are also trying to replace the mesityl groups on boron with other electron deficient groups like pentafluorophenyl and 1,3,5-trifluoromethylphenyl to fine tune the Lewis acidity of boron centre and to set-up a general route to enantiomerically pure Planar Chiral Frustrated Lewis Pairs (PCFLP's).

Supporting information

^{1}H NMR and ^{13}C NMR, ^{11}B and ^{31}P spectra and HRMS of compounds **2**(S_P, S_S), **3**(S_P, S_S), **4**(S_P), **4**(R_P) and **5**(S_P, S_S). CCDC 823721 - 823724 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary figures S1–S13 are given as supplementary material (see www.ias.ac.in/chemsci).

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