Supporting Information

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2,2'-Diborabiphenyl: A Lewis Acid Analog of 2,2'-Bipyridine.**

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**General Procedures.** All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene, hexane and THF solvents were dried and purified by passing through activated alumina and Q5 columns. CH2Cl2 was dried and distilled from CaH2. HC2=CHC2SiMe3 was purchased from GFS Chemicals and stored under argon prior to use. Solid lithium diisopropylamide was prepared by addition of a 1.6 M n-hexane solution of nBuLi (100 ml, 0.16 mol) to HN iPr2 (30 ml, 0.21 mol) in n-hexane (40 ml), followed by evaporation to dryness. H2SnBu2 was prepared from (Bu2SnO)n and (MeHSiO)n as previously reported. 2 (Bu2SnO)n, (MeHSiO)n, PMe3, pyridine, 1PrI, LiNMe2, BCl3 and CuI were purchased from Aldrich. Pyridine was dried over CaH2, and PMe3 was stored over activated molecular sieves (4 Å).

All NMR spectra were performed in dry, oxygen-free C6D6, CD2Cl2 or d8-THF. 1H, 2H, 13C{1H}, DEPT, 11B, 19F, 31P, 119Sn, COSY, NOESY, HMQC and HMBC NMR experiments were performed on Bruker AC-200, AMX-300 or DRX-400 spectrometers. Data are given in ppm relative to SiMe4 for 1H and 13C NMR spectra, and BF3(OEt2), CFCl3, 85 % H3PO4 in D2O, and SnMe4 for 11B, 19F, 31P and 119Sn NMR spectra respectively. All 1H and 13C NMR spectra were referenced to SiMe4 through the resonance of the employed solvent; C6D6 (δ 7.15 ppm), CD2Cl2 (δ 5.32 ppm) or d8-THF (δ 3.58, 1.73 ppm) for 1H NMR, and C6D6 (δ 128.39 ppm), CD2Cl2 (δ 54.00 ppm) or d8-THF (δ 67.57, 25.37 ppm) for 13C NMR. 11B, 19F, 31P and 119Sn NMR spectra were referenced using an external standard of BF3(OEt2) (0.0 ppm), C6F6 (-163.0 ppm relative to CFCl3), 85 % H3PO4 in D2O (0.0 ppm), and Bu3SnH (-83 ppm relative to SnMe4) respectively.

Electrochemical studies were carried out using an EG&G model 283 potentiostat in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire, the pseudo-reference electrode a silver wire, and the working electrode a platinum disc (1.6 mm diameter). Solutions were 1 x 10⁻³ mol dm⁻³ in the test compound and 0.1 mol dm⁻³ in [NnBu4][PF6] as the supporting electrolyte. Under these conditions, E⁰ versus SCE for redox couples added to the test solution as internal calibrants are: [FeCp2]⁰/+1 (0.47 V CH2Cl2, 0.54 V THF), [FeCp*2]⁰/+1 (-0.08 V CH2Cl2, 0.08 V THF), [CoCp2]⁰/+1 (-0.87 V CH2Cl2, -0.82 V THF), and [CoCp*2]⁰/+1 (-1.47 V CH2Cl2). Unless specified, all Ep red, Ep ox and E⁰ values are quoted at ν = 200 mVs⁻¹.
X-band ESR spectra were recorded with on a Bruker spectrometer equipped with a Bruker variable temperature accessory and a Bruker microwave frequency counter. The field calibration was checked by measuring the resonance of the dpph radical. UV-Visible spectra were recorded between 190 and 900 nm on a Varian Cary-1E spectrophotometer. High resolution mass spectra were performed by Mrs. D. Fox of this department on a Kratos MS-80 spectrometer. Elemental analyses were performed by Mrs. Dorothy Fox or Ms. Roxanna Simank of this department. A Fischer Scientific Ultrasonic FS-14 bath was used to sonicate reaction mixtures where indicated. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a Rigaku AFC6S diffractometer (University of Calgary).


**[Li(THF)][Bu2SnC2H4(SiMe3)].** A solution of lithium diisopropylamide (5.77 g, 53.9 mmol) in THF (200 ml) was added to a –78°C solution of 1,1-Di-n-butyl-2-(trimethylsilyl)stannacyclohexa-2,5-diene (20 g, 53.9 mmol) in THF (200 ml), stirred at –78°C for 30 min., and then at 25°C for 20 minutes. An aliquot of the resulting brown-orange solution was evaporated to dryness *in vacuo* and redissolved in C6D6. 1H NMR (C6D6): δ 7.44 (d, 1H, 3JH,H 7.5 Hz, CH3), 7.32 (dd, 1H, 3JH,H 13, 7.5 Hz, CH5), 5.07 (d, 1H, 3JH,H 13 Hz, CH6), 4.94 (dd, 1H, 3JH,H 7.5, 7.5 Hz, CH4), 3.19 (m, 4H, THF), 1.75 (m, 4H, SnBu2), 1.48 (dt, 4H, J7, 7 Hz, SnBu2), 1.17 (m, 4H, SnBu2), 1.11 (m, 4H, THF), 0.98 (t, 2 x 3H, J7 Hz, SnBu2), 0.32 (s, 9H, SiMe3). 13C NMR (C6D6): δ 145.55 (s, CH3), 143.21 (s, CH3), 94.25 (s, CH4), 89.07 (s, CH6), 69.31 (s, THF), 30.35 [s, Sn(CH2CH2CH2Me)2], 28.08 [s, Sn(CH2CH2CH2Me)2], 25.52 [s, Sn(CH2CH2CH2Me)2], 16.04 (s, THF) 14.47 [s, Sn(CH2CH2CH2Me)2], 12.27, 11.98
[s, 2 Sn(CH₂CH₂CH₂Me)₂], 2.04 (s, SiMe₃).

**1,1-Di-n-butyl-2-(trimethylsilyl)-4-(iso-propyl)stannacyclohexa-2,5-diene.**

A solution of lithium diisopropylamide (5.77 g, 53.9 mmol) in THF (200 ml) was added to a –78°C solution of 1,1-Di-n-butyl-2-(trimethylsilyl)stannacyclohexa-2,5-diene (20 g, 53.9 mmol) in THF (200 ml), stirred at –78°C for 30 min., then 25°C for 20 minutes. The resulting brown-orange solution was cooled to –78°C and iPrI (5.60 ml, 56.1 mmol) was added dropwise. The solution was stirred for 20 min. at –78°C to give an orange-peach slurry and then at 25°C for 2 hours. The resulting pale yellow solution was evaporated to dryness *in vacuo* and the product distilled at 126-129°C / 0.02 Torr to give a colourless oil. Yield 18.1 g (81 %).

**1H NMR (C₆D₆):** δ 6.89 (dd, 1H, 3 Jₕ,H 4 Hz, 4 Jₕ,H 1.5 Hz, CH₃), 6.58 (ddd, 1H, 3 Jₕ,H 14, 4 Hz, 4 Jₕ,H 1.5 Hz, CH₃), 6.39 (dd, 1H, 3 Jₕ,H 14 Hz, 4 Jₕ,H 1.5 Hz, CH₅), 2.99 (ddd, 1H, 3 Jₕ,H 4, 4 Hz, 4 Jₕ,H 1.5 Hz, CH₄), 1.79 (d, sept., 1H, 3 Jₕ,H 4, 7 Hz, CHMe₂), 1.61 (m, 4H, SnBu₂), 1.37 (d, t, 4H, J 7, 7 Hz, SnBu₂), 0.94 (d, 6H, J 7 Hz, CHMe₂) 0.91, 0.91 (t, 2 x 3H, 7 Hz, SnBu₂), 0.19 (s, 9H, SiMe₃).

**13C NMR (C₆D₆):** δ 156.38 (s, CH₃), 148.85 (s, CH₅), 142.08 (s, C₂-SiMe₃), 127.99 (s, CH₆), 52.38 (s, CH₄), 33.94 (s, CHMe₂), 30.27, 30.09 [s, 2 Sn(CH₂CH₂CH₂Me)₂], 27.89, 27.87 [s, 2 Sn(CH₂CH₂CH₂Me)₂], 20.09, 19.65 (s, 2 CHMe₂), 14.25, 14.22 [s, 2 Sn(CH₂CH₂CH₂Me)₂], 12.27, 11.98 [s, Sn(CH₂CH₂CH₂Me)₂], 0.09 (s, SiMe₃).

**119Sn NMR (C₆D₆):** δ -140 (s). HRMS for C₁₉H₃₇Si₁₂₀Sn (M⁻-H); Found 413.1659, Calcd. 413.1687.

**1-chloro-2-(trimethylsilyl)-4-(iso-propyl)boracyclohexa-2,5-diene.**

BCl₃ gas (6.09 g, 52.0 mmol) was condensed into a CH₂Cl₂ (150 ml) solution of 1,1-Di-n-butyl-2-(trimethylsilyl)-4-(iso-propyl)stannacyclohexa-2,5-diene (18.0 g, 43.6 mmol) at
–78°C. After stirring for 30 minutes at –78°C, the temperature was raised to 0°C for 4 hours and then to 25°C for 12 hours. The resulting yellow solution was evaporated to dryness in vacuo and the product distilled at 45-50°C / 0.02 Torr to give the product as a colourless oil. Yield 9.71 g (98 %). 1H NMR (C6D6): δ 7.38 (dd, 1H, 3J H,H 2, 4J H,H 2 Hz, CH3), 6.86 (ddd, 1H, 3J H,H 12, 2, 4J H,H 2 Hz, CH5), 6.61 (dd, 1H, 3J H,H 12, 4J H,H 2 Hz, CH6), 2.51 (dddd, 1H, 3J H,H 4, 2, 2, 4J H,H 2 Hz, CH4-iPr), 1.76 (d, sept., 1H, 3J H,H 4, 7 Hz, CHMe2), 0.66, 0.62 (d, 2 x 3H, J 7 Hz, CHMe2) 0.33 (s, 9H, SiMe3). 13C NMR (C6D6): δ 168.83 (s, CH3), 159.49 (s, CH5), 135.5 (broad s, CH6), 53.07 (s, CH4), 31.95 (s, CHMe2), 20.10, 19.52 (s, 2 CHMe2), -0.14 (s, SiMe3). 11B NMR (C6D6): δ 52.99 (broad s). HRMS for C11H20Si11B35Cl (M+); Found 226.11000, Calcd. 226.11159.

[Li(THF)][Me2NBC5H3(SiMe3-2)(iPr].

A solution of (2) (10 mg, 44.1 µmol) in THF (0.5 ml) was added to a THF (0.5 ml) solution of LiNMe2 (4.5 mg, 88.2 µmol) at 25°C. After 1 hour, the mixture was evaporated to dryness in vacuo, and the resulting oily brown solid was redissolved in d8-THF. 1H NMR (d8-THF): δ 7.11 (d, 1H, 4J H,H 2 Hz, CH3), 6.94 (dd, 1H, 3J H,H 11, 4J H,H 2 Hz, CH5), 5.59 (d, 1H, 3J H,H 11 Hz, CH6), 2.60 (sept., 1H, 3J H,H 7 Hz, CHMe2), 2.37 (broad s, 6H, B-NMe2), 1.10 (d, 6H, J 7 Hz, CHMe2) 0.18 (s, 9H, SiMe3). 13C NMR (d8-THF): δ 139.45 (s, CH3), 134.11 (s, CH5), 120.90 (s, C4-iPr), 113.1 (broad s, CH6), 41.63 (broad s, B-NMe2), 35.26 (s, CHMe2), 25.85 (s, CHMe2), 3.59 (s, SiMe3). 11B NMR (d8-THF): δ 33.91 (broad s).

B-NMe2 coupled product.
A solution of 1-chloro-2-(trimethylsilyl)-4-(iso-propyl)boracyclohexa-2,5-diene (9.71 g, 42.8 mmol) in THF (50 ml) was canula transferred onto a THF (250 ml) solution of LiNMe2 (4.59 g, 89.9 mmol) at 25°C, stirred for 1 hour and evaporated to dryness in vacuo. The resulting oily brown [Li(THF)][Me2NBC5H3(SiMe3-2)(iPr-4)] was redissolved in THF (250 ml) and canula transferred onto CuBr (14 g, 97.6 mmol) to give a brown slurry which was stirred for 14 hours before being filtered to remove the majority of the solids. The mixture was then refiltered through 10 g of Celite (pre-slurried with toluene) to give an orange-brown solution which was evaporated to dryness in vacuo to leave the product as a viscous orange-brown oil. Yield 8.85 g (88%). The 2 diastereomers of the coupled product were produced in variable proportions. 1H NMR (C6D6): δ 6.59 (broad s, 1H, major CH4), 6.47 (d, 0.5H, 4JH,H 0.5 Hz, minor CH4), 6.01 (broad dd, 1H, 3JH,H 5, 4JH,H 0.5 Hz, major CH6), 5.94 (dd, 0.5H, 3JH,H 5, 4JH,H 0.5 Hz, minor CH6), 2.85, 2.55 (s, 2 x 3H, major BNMe2), 2.75, 2.57 (s, 2 x 1.5H, minor BNMe2), 2.48 (sept, 0.5H, J 7 Hz, minor CHMe2), 2.44 (sept, 1H, J 7 Hz, major CHMe2), 2.44 (d, 1H, 3JH,H 5 Hz, major CH1), 2.31 (d, 0.5H, 3JH,H 5 Hz, minor CH1), 1.19 (d, 3H, J 7 Hz, minor CHMe2), 1.15 (broad d, 6H, J 7 Hz, major CHMe2), 0.13 (s, 4.5H, minor SiMe3), 0.11 (broad s, 9H, major SiMe3). 13C NMR (C6D6): δ 151.44 (broad s, C3-SiMe3), 143.17 (s, major CH4), 140.77 (s, minor C5-Pr), 140.70 (s, minor CH4), 140.41 (s, major C5-Pr), 126.95 (s, major CH6), 125.63 (s, minor CH4), 43.24, 40.24 (s, 2 minor BNMe2), 43.04, 41.43 (broad s, major BNMe2), 35.27 (s, minor CHMe2), 35.16 (s, major CHMe2), 34.8 (broad s, major CH1), 33.7 (broad s, minor CH1), 23.71, 23.23 (s, 2 minor CHMe2), 23.42, 23.32 (s, 2 major CHMe2), 0.15 (s, major SiMe3), -0.34 (s, minor SiMe3). 11B NMR (C6D6): δ 40.15 (broad s). HRMS for C26H50N2Si2B2 (M+); Found 468.3682, Calcd. 468.3699.

**B-Cl coupled product, 1.**

BCl3 gas (6.36 g, 54.3 mmol) was condensed into an n-hexane (250 ml) solution of the diastereomers produced as described above (8.85 g, 18.9 mmol) at –78°C. After stirring for 20 minutes at –78°C, the temperature was raised to 0°C for 6 hours, after which time the red solution was decanted via canula to leave a small amount of oily black residue on the walls of the flask. The solution was evaporated to dryness in vacuo for 24 hours to
leave a viscous red oil. Yield 8.19 g (96 %). $^1$H NMR (C$_6$D$_6$): δ 7.45 (d, 1H, $^4$J$_{HH}$ 2 Hz, major CH$^4$), 7.33 (d, 0.2H, $^4$J$_{HH}$ 2 Hz, minor CH$^4$), 6.37 (dd, 0.2H, $^3$J$_{HH}$ 5, $^4$J$_{HH}$ 2 Hz, minor CH$^6$), 6.33 (dd, 1H, $^3$J$_{HH}$ 5, $^4$J$_{HH}$ 2 Hz, major CH$^6$), 3.51 (d, 1.2 Hz, $^3$J$_{HH}$ 5 Hz, CH$_1$), 2.49 (sept., 1.2H, $^7$J, C$_{Me2}$), 1.12, 1.11 (d, 2 x 3H, $^7$J, major CH$_{Me2}$), 1.10, 1.09 (broad s, 2 x 0.6H, minor CH$Me_2$), 0.16 (s, 1.8H, minor SiMe$_3$), 0.10 (s, 9H, major SiMe$_3$). $^{13}$C NMR (C$_6$D$_6$): δ 150.58 (s, major C$_H$$_4$), 149.89 (minor C$_H$$_4$), 147.80 (broad s, C$^3$-SiMe$_3$), 142.41 (s, minor C$^5$-iPr), 142.13 (s, major C$^5$-iPr), 135.61 (s, minor C$H$$_6$), 135.48 (s, major C$H$$_6$), 54.94 (broad s, minor C$H$$_1$), 54.33 (broad s, major CH$^1$), 35.05 (s, CHMe$_2$), 23.77, 23.48 (s, 2 CHMe$_2$), 0.08 (s, major SiMe$_3$), -0.08 (s, minor SiMe$_3$). $^{11}$B NMR (C$_6$D$_6$): δ 57.18 (broad s). HRMS for C$_{22}$H$_{38}$Si$_2$B$_2$Cl$_2$ (M$^+$); Found 450.2061, Calcd. 450.2075. Anal. for C$_{22}$H$_{38}$Si$_2$B$_2$Cl$_2$; Found C 58.71, H 8.55, Calcd. C 58.56, H 8.49 %.

Bis-PMe$_3$ adduct of 2,2'-diborabiphenyl, 2.

PMe$_3$ (101 mg, 1.33 mmol) was added to a toluene (20 ml) solution of 1 (152 mg, 0.336 mmol) at -78°C. The solution was then stirred for 10 min. at -78°C, 4 h at 0°C and 12 h at 25°C before evaporation to dryness in vacuo. The solid was slurried in n-hexane, sonicated, cooled to -78°C and then filtered to collect a pale peach-brown solid. Yield 92 mg (70 %). Crystals of 2 suitable for X-ray diffraction study were grown by allowing a concentrated solution of 2 in toluene to diffuse into n-hexane at -35°C. $^1$H NMR (C$_6$D$_6$): δ 7.73 (ddd, 2H, $^3$J$_{HH}$ 9 Hz, $^4$J$_{HP}$ 4 Hz, $^4$J$_{HH}$ 1 Hz, CH$^1$), 7.38 (dd, 2H, $^4$J$_{HP}$ 6 Hz, $^4$J$_{HH}$ 1 Hz, CH$^6$), 7.11 (dd, 2H, $^3$J$_{HH}$ 9 Hz, $^3$J$_{HP}$ 8 Hz, CH$^3$), 3.14 (sept., 2H, $^7$J, C$_{Me2}$), 1.49 (d, 12H, J 7 Hz, CHMe$_2$), 0.81 (d, 18H, $^2$J$_{HP}$ 11 Hz, PMe$_3$). $^{13}$C NMR (C$_6$D$_6$): δ 138.12 (s, C$^5$-Pr), 132.46 (d, $^3$J$_{CP}$ 15 Hz, CH$^6$), 128.83 (d, $^3$J$_{CP}$ 18 Hz, CH$^3$), 36.58 (s, CHMe$_2$), 26.18 (s, CHMe$_2$), 12.44 (s, $^1$J$_{CP}$ 42 Hz, PMe$_3$). $^{11}$B NMR (C$_6$D$_6$): δ 17.87 (broad s). $^{31}$P NMR (C$_6$D$_6$): δ -22.6 (broad s). Anal. for C$_{22}$H$_{38}$B$_2$P$_2$; Found C 67.93, H 10.06, Calcd. C 68.44, H 9.92 %.

* CH$^3$ not located even in long $^{13}$C NMR, DEPT or HMQC spectra.
Bis-pyridine adduct of 2,2′-diborabiphenyl, 3.

Dry, distilled pyridine (0.2 ml, 2.47 mmol) was added dropwise to a toluene (40 ml) solution of 1 (320 mg, 0.71 mmol) at –78°C. The resulting orange brown solution was allowed to warm to room temperature, and stirred for 12 h to give a purple-black solution which was evaporated to dryness in vacuo. The residue was slurried in n-hexane (15 ml), sonicated, and filtered at room temperature to collect a purple-black solid which was washed with n-hexane (x 2) and dried in vacuo. Yield 270 mg (97%). 1H NMR (CD2Cl2): δ 8.72 (dd, 4H, 3 J_H,H 5, 4 J_H,H 0.5 Hz, C_H7), 7.86 (tt, 2H, 3 J_H,H 8, 4 J_H,H 0.5 Hz, C_H9), 7.44 (dd, 4H, 3 J_H,H 8, 5 Hz, C_H8), 7.05 (dd, 2H, 3 J_H,H 10 Hz, 4 J_H,H 1 Hz, C_H4), 6.87 (d, 2H, 4 J_H,H 1 Hz, C_H6), 6.28 (d, 2H, 3 J_H,H 10 Hz, C_H3), 2.67 (sept., 2H, J 7 Hz, C_HMe2), 1.06 (d, 12H, J 7 Hz, CHMe2). 13C NMR (CD2Cl2): δ 146.39 (s, C_H7), 139.55 (s, C_H9), 136.53 (s, C_5-iPr), 135.39 (s, C_H6), 131.03 (s, C_H4), 125.88 (s, C_H8), 121 (v.broad s, C_H3) 35.37 (s, CHMe2), 25.57 (s, CHMe2). 11B NMR (CD2Cl2): δ 30.91 (broad s).

Pyridazine adduct of 2,2′-diborabiphenyl, 4.

A toluene (10 ml) solution of pyridazine (44 mg, 554 µmol) was added dropwise over 1 hour (syringe pump) to a toluene (10 ml) solution of 1 (250 mg, 554 µmol). The deep red solution was evaporated to dryness in vacuo and the residue slurried in n-hexane, sonicated, cooled to –78°C and filtered to collect a red-brown solid which was washed with cold hexane (x 3) and dried in vacuo. Yield 81 mg of ~ 90 % pure product. The bright red filtrate was evaporated to dryness in vacuo, slurred in O(SiMe3)2 (5 ml), sonicated, cooled to –45°C and filtered to collect more red-brown solid. Yield 71 mg (41 %) of pure product. 1H NMR (C6D6): δ 8.64 (s, 2H, CH6), 8.15 (app dd, 2H, J 6, 3 Hz, CH7), 7.85 (d, 2H, 3 J_H,H 12 Hz, CH8), 7.41 (d, 2H, 3 J_H,H 12 Hz, CH3), 5.30 (app dd, 2H, J 6, 3 Hz, CH8), 3.07 (sept., 2H, J 7 Hz, CHMe2), 1.39 (d, 12H, J 7 Hz, CHMe2). 13C NMR (C6D6): δ 148.38 (s, C_5-iPr), 140.68 (s, C_H4), 133.69 (s, C_H7), 128.66 (broad s, C_H3), 121.81 (s, C_H6), 108.61 (s, C_H8) 36.86 (s, CHMe2), 24.24 (s, CHMe2). 11B NMR (C6D6): δ 24.39 (broad s).
Benzo[c]cinnoline adduct of 2,2′-diborabiphenyl, 5.

A toluene (8 ml) solution of 1 (400 mg, 886 µmol) was added to benzo[c]cinnoline (160 mg, 886 µmol) in toluene (5 ml). After stirring at 25°C for 2 days, the deep red solution was evaporated to dryness *in vacuo* and the residue slurried in *n*-hexane, sonicated, cooled to -78°C and filtered to remove a red-brown impurity. The bright red filtrate was evaporated to dryness *in vacuo* to give the product as a deep red solid, which appears green-gold when light is reflected. Yield 340 mg (93 %) of pure product. $^1$H NMR ($C_6D_6$): δ 8.34 (s, 2H, $C_6H_6$), 7.63 (m, 4H, Hz, $CH^3 + CH^4$), 7.58 (m, 2H, $CH^5$), 7.39 (m, 2H, $CH^6$), 6.95 (m, 4H, $CH^{10} + CH^{11}$), 2.91 (sept., 2H, $J 7$ Hz, $CHMe_2$), 1.31 (d, 12H, $J 7$ Hz, $CHMe_2$). $^{13}$C NMR ($C_6D_6$): δ 149.94 (s, $C_5$-iPr), 142.84 (s, $C_H4$), 141.38 (s, $C_7$), 133.9 (broad s, $C_H3$), 129.08 (s, $CH^{10}$), 128.73 (s, $CH^{11}$), 126.10 (s, $CH^{11}$), 124.17 (s, $C_8$), 123.28 (s, $CH^9$), 122.06 (s, $CH^6$), 36.79 (s, $CHMe_2$), 23.60 (s, $CHMe_2$). $^{11}$B NMR ($C_6D_6$): δ 26.85 (broad s).

* Peak assignments from COSY, NOESY, HMQC and HMBC spectra.

**Radical anion, [Co$^{III}Cp^*_2][5^−]$·THF.**

A solution of dark red (8) (30 mg, 72.4 µmol) and [CoCp$^*_2$] (30 mg, 91.2 µmol) in THF (3 ml) was allowed to stand at -35°C for 4 days. The resulting purple solution was then decanted to leave purple-black crystals which were dried *in vacuo*. Yield 39 mg (66 %). Crystals of [CoCp$^*_2$][5$^−$]·2 CH$_2$Cl$_2$ suitable for X-ray diffraction study were grown by preparing a concentrated solution of [CoCp$^*_2$][5$^−$] in CH$_2$Cl$_2$ at -35°C [15 mg of 5 + 15 mg CoCp$^*_2$], layering with cold *n*-hexane, and allowing slow diffusion at -35°C. $^1$H NMR (d$^8$-THF): δ 3.01 (v.broad s, CoCp$^*_2$)$^+$,

*a* One equivalent of THF determined from the $^1$H NMR spectra of diamagnetic products resulting from room temperature decomposition of [Co$^{III}Cp^*_2$][5$^−$]·THF in CD$_2$Cl$_2$. 