

More Electron Rich than Cyclopentadienyl: 1,2-Diaza-3,5-diborolyl as a Ligand in Ferrocene and Ruthenocene Analogs

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Experimental Section

General Considerations. All operations were performed under an argon atmosphere using standard Schlenk and glove box techniques. Solvents were dried and deoxygenated prior to use. Pyrazolidine hydrochloride,¹ as well as [Cp**RuCl*]₄² and FeCl₂(thf)₂³ were prepared according to reported procedures. NMR spectra were recorded on Bruker Advance DRX-400 and AMX-300 spectrometers and calibrated with respect to C₆D₅H (¹H, 7.15 ppm), THF-d₇ (¹H, 3.58 ppm), C₆D₆ (¹³C, 128.39 ppm), THF-d₈ (¹³C, 67.57 ppm) and BF₃·Et₂O (¹¹B, 0 ppm). The electron impact (EI), electrospray ionization (ESI) and high-resolution mass spectrometry (HRMS) were performed by the Analytical Instrumentation Laboratory, Department of Chemistry, University of Calgary.

4-Methyl-3,5-diphenyl-1,2-pyrazo-3,5-diborolidine (1). A colorless solution of potassium bis(trimethylsilyl)amide (2.987 g, 14.97 mmol) in THF (20 mL) was slowly added to a stirred suspension of pyrazolidine hydrochloride¹ (1.086 g, 7.488 mmol) in THF (30 mL). The mixture was stirred at room temperature overnight and subsequently triethylamine (1.515 g, 14.97 mmol) was added, followed by a solution of 1,1-bis(chlorophenylboryl)ethane (2.058 g, 7.488 mmol) in hexane (20 mL). The yellow suspension was stirred at room temperature for 5 h and the resulting white precipitate was filtered off. Volatiles were removed under full vacuum and the pale yellow residue was washed a few times with pentane (25 mL), yielding **1** as a colorless solid (1.605 g, 71 %). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 1.44 (d, 3H, ³J_{HH} = 8.4 Hz, HCCH₃), 1.55 (m, 2H, NCH₂CH₂), 1.73 (q, 1H, ³J_{HH} = 8.4 Hz, HCCH₃), 3.21 (m, 4H, NCH₂CH₂), 7.31 (t, 2H, ³J_{HH} = 7.5 Hz, *p*-C₆H₅), 7.40 (t, 4H, ³J_{HH} = 7.5 Hz, *m*-C₆H₅), 7.77 (d, 4H, ³J_{HH} = 7.5 Hz, *o*-C₆H₅); ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 11.7 (s, HCCH₃), 22.5 (s, br, HCCH₃), 30.9 (s, NCH₂CH₂), 44.2 (s, NCH₂CH₂), 128.6 (s, *m*-C₆H₅), 129.3 (s, *p*-C₆H₅), 134.9 (s, *o*-C₆H₅), 137.6 (s, br, *i*-C₆H₅); ¹¹B NMR (128 MHz, THF-d₈, 25 °C): δ = 39.3 (s, br); EI⁺-MS (70 eV): m/z(%): 274(45) [M]⁺; HRMS for H₂₀C₁₇N₂¹¹B₂ calcd. 274.18126, found 274.18256; Anal. Calcd for H₂₀C₁₇N₂B₂: C, 74.53; H, 7.36; N, 10.22. Found: C, 74.02; H, 7.55; N, 10.13.

4-Methyl-3,5-diphenyl-1,2-pyrazo-3,5-diborolyllithium (2). A yellow solution of lithium 2,2,6,6-tetramethylpiperidide was formed by mixing the 1.6 M *n*BuLi in hexane (2.52 mL, 4.03 mmol) with tetramethylpiperidine (570 mg, 4.03 mmol) in THF (3 mL). This solution was cooled to -35 °C and added to a pre-cooled solution of **1** (1.10 g, 4.03 mmol) in THF (10 mL). The orange mixture was kept at low temperature for 1 h and then stirred at room temperature for 2 h. The solvent was removed in vacuum leaving behind a pale yellow residue, which was washed with hexane (30 mL) and dried under vacuum. The product was obtained as a colorless powder (1.02 g, 91 %). ¹H NMR (400 MHz, THF-d₈, 25 °C): δ = 2.18 (quint, 2H, ³J_{HH} = 6.4 Hz, NCH₂CH₂), 2.23 (s, 3H, CCH₃), 3.63 (t, 4H, ³J_{HH} = 5.9 Hz, NCH₂CH₂), 6.99 (t, 2H, ³J_{HH} = 7.1 Hz, *p*-C₆H₅), 7.13 (t, 4H, ³J_{HH} = 7.3 Hz, *m*-C₆H₅), 7.58 (d, 4H, ³J_{HH} = 7.3 Hz, *o*-C₆H₅); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ = 15.7 (s, CCH₃), 31.5 (s, NCH₂CH₂), 46.0 (s, NCH₂CH₂), 91.6 (s, br, B₂CCH₃), 125.1 (s, *p*-C₆H₅), 127.4 (s, *m*-C₆H₅), 134.7 (s, *o*-C₆H₅), 145.5 (s, br, *i*-C₆H₅); ¹¹B NMR (128 MHz, THF-d₈, 25 °C): δ = 31.5 (s, br); ⁷Li NMR (155 MHz, THF-d₈, 25 °C): δ = -2.16 (s); EI⁺-MS (70 eV): m/z(%): 312(5) [M - Li + K]⁺, 274(8) [M - Li + H]⁺; HRMS for H₂₀C₁₇N₂¹¹B₂ calcd. 274.18126, found 274.18037.

4-Methyl-3,5-diphenyl-1,2-pyrazo-3,5-diboroly-pentamethylcyclopentadienylruthenium (3). A solution of **2** (0.10 g, 0.36 mmol) and [Cp**Ru*Cl]₄ (0.093 g, 0.089 mmol) in THF (20 mL) was stirred at -78 °C for 1 h, slowly warmed to ambient temperature and stirred for an additional 30 min. Volatiles were removed under vacuum and the dark brown solid was extracted with pentane (20 mL). LiCl was filtered off and the volatiles were removed, leaving behind the product as a light yellow solid (0.15 g, 80 %). Yellow crystals of **3** were obtained by slow evaporation of a hexane solution at ambient temperature. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 1.34 (m, 1H, NCH₂CH₂), 1.51 (s, 15H, C₅(CH₃)₅), 1.91 (m, 1H, NCH₂CH₂), 2.36 (s, 3H, CCH₃), 2.55 (m, 2H, NCH₂CH₂), 3.20 (m, 2H, NCH₂CH₂), 7.29 (t, 2H, *p*-C₆H₅), 7.43 (t, 4H, *m*-C₆H₅), 7.78 (d, 4H, *o*-C₆H₅); ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ = 11.0 (s, C₅(CH₃)₅), 15.9 (s, CCH₃), 26.5 (s, NCH₂CH₂), 47.0 (s, NCH₂CH₂), 80.0 (s, br, B₂CCH₃), 81.6 (s, C₅(CH₃)₅), 127.6 (s, *p*-C₆H₅), 128.1 (s, *m*-C₆H₅), 134.7 (s, *o*-C₆H₅), 139.1 (s, br, *i*-C₆H₅); ¹¹B{¹H} NMR (128 MHz, C₆D₆, 25 °C): δ = 14.7 (s, br); MS (EI⁺, 70 eV): m/z(%): 509(100)

$[\text{Cp}^*\text{RuL}]^+$, 495(62) $[\text{Cp}^*\text{RuL} - \text{Me}]^+$; HRMS for $\text{H}_{34}\text{C}_{27}\text{N}_2\text{Ru}^{11}\text{B}_2$ calcd. 510.19516, found 510.19853; Anal. Calcd for $\text{H}_{34}\text{C}_{27}\text{N}_2\text{RuB}_2$: C, 63.68; H, 6.73; N, 5.50. Found: C, 63.81; H, 6.80; N, 5.50.

Bis(4-methyl-3,5-diphenyl-1,2-pyrazo-3,5-diboroly)iron (4). THF (15 mL) was added to a mixture of **2** (0.10 g, 0.36 mmol) and $\text{FeCl}_2(\text{thf})_2$ (0.048 g, 0.18 mmol) at $-78\text{ }^\circ\text{C}$. The red mixture was slowly warmed to ambient temperature and stirred for 2 h. Volatiles were removed under full vacuum yielded dark brown residue, which was extracted with a mixture of hexane (15 mL) and THF (5 mL). The LiCl was filtered off and the solvent was removed in vacuum, leaving behind the product as a reddish-brown solid (0.095 g, 89 %). Thin red crystals of **4** were obtained by slow evaporation of a hexane solution at ambient temperature. ^1H NMR (400 MHz, CD_2Cl_2 , $25\text{ }^\circ\text{C}$): $\delta = 1.55$ (s, 3H, CCH_3), 2.20 (m, 1H, NCH_2CH_2), 2.36 (m, 1H, NCH_2CH_2), 2.94 (q, br, 2H, NCH_2CH_2), 3.75 (t, br, 2H, NCH_2CH_2), 7.33 – 7.37 (m, 6H, m - + p - C_6H_5), 7.68 (d, br, 4H, o - C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , $25\text{ }^\circ\text{C}$): $\delta = 15.5$ (s, CCH_3), 27.7 (s, NCH_2CH_2), 46.2 (s, NCH_2CH_2), 65.5 (s, br, B_2CCH_3), 128.0 (s, m - + p - C_6H_5), 134.9 (s, o - C_6H_5), 137.9 (s, br, i - C_6H_5); $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2 , $25\text{ }^\circ\text{C}$): $\delta = 13.6$ (s, br, $\text{LW}_{1/2} = 5647\text{ Hz}$); MS (EI^+ , 70 eV): $m/z(\%)$: 602(28) $[\text{FeL}_2]^+$, 328(10) $[\text{FeL}]^+$, 274(100) $[\text{L}]^+$; HRMS for $\text{H}_{38}\text{C}_{34}\text{N}_4^{11}\text{B}_4\text{Fe}$ calcd. 602.28181, found 602.28500; Anal. Calcd for $\text{H}_{38}\text{C}_{34}\text{N}_4\text{FeB}_4$: C, 67.86; H, 6.36; N, 9.31. Found: C, 67.48; H, 6.48; N, 9.26.

(1) Boros, E. E.; Bouvier, F.; Randhawa, S.; Rabinowitz, M. H. *J. Heterocyclic Chem.* **2001**, *38*, 613.

(2) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

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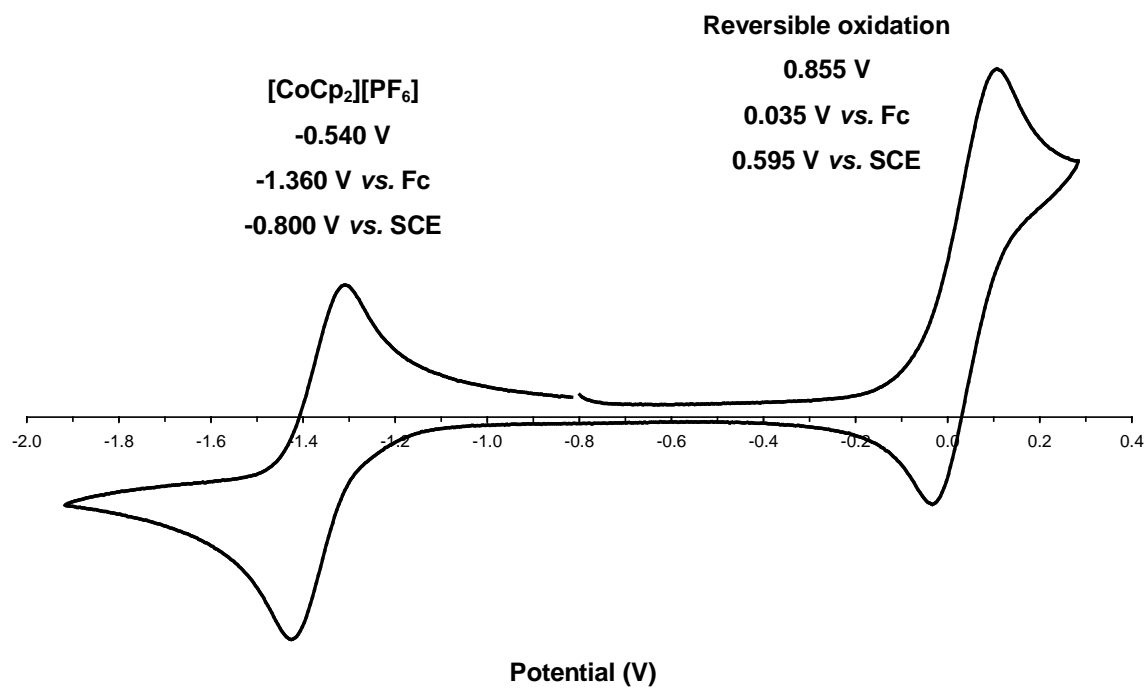
Cyclic voltammetry of 3 and 4

Measurements were performed in the absence of oxygen, in anhydrous dichloromethane at an analyte concentration of 1 mM, using 0.1 M $[n\text{Bu}_4\text{N}]\text{PF}_6$ as a supporting electrolyte. A PARstat 2273 potentiostat was used at scan rates between 50 to 500 mVs^{-1} . The cell had a platinum disk working electrode, a platinum wire auxiliary electrode and a silver wire pseudo-reference electrode. $[\text{Cp}_2\text{Co}]^{0/+1}$ with $E = -1.34 \text{ V vs. ferrocene}$ and -0.88 V vs. SCE in CH_2Cl_2 and $E = -1.36 \text{ V vs. ferrocene}$ and -0.80 V vs. SCE in THF was used as an internal standard.

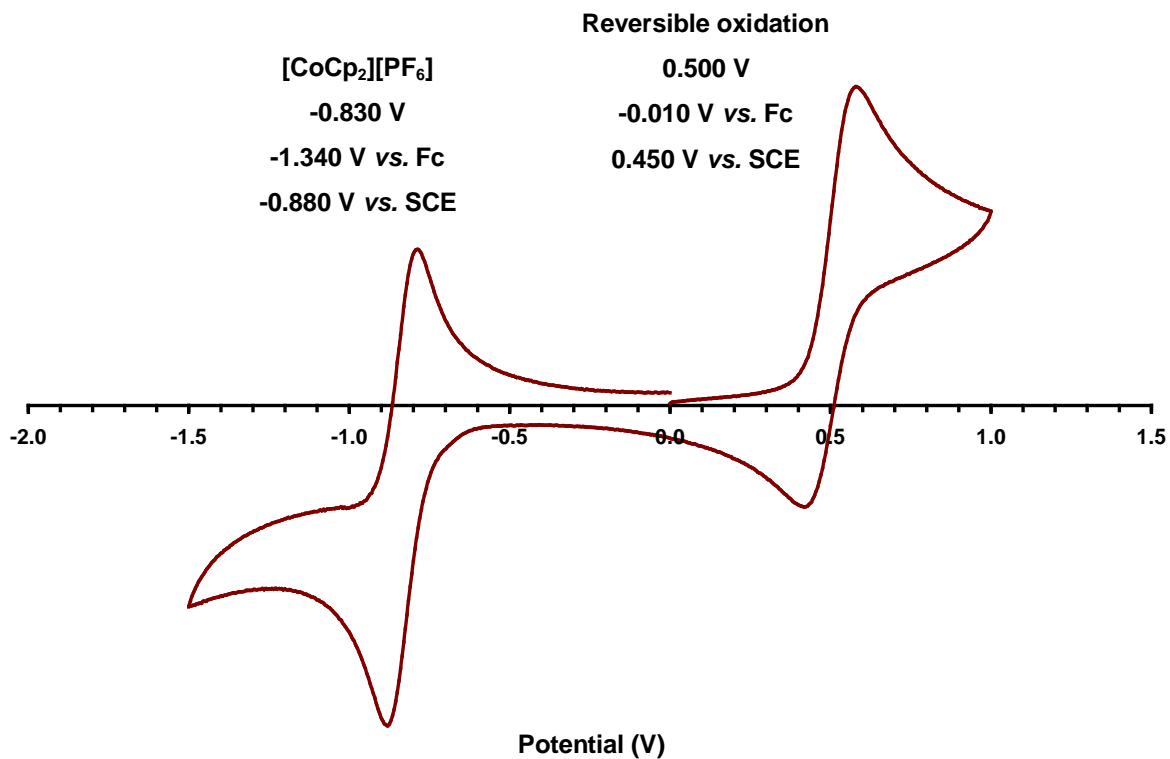
Compound	Reversible oxidation vs. ferrocene (V)	Reversible oxidation vs. SCE (V)
3 in THF	0.035	0.595
3 in CH_2Cl_2 ^a	-0.010	0.450
4 in THF	-0.530	-0.030
4 in CH_2Cl_2	-0.495	-0.035

^a Irreversible oxidation was observed at a peak potential of 1.090 V vs. Fc and 1.550 V vs. SCE.

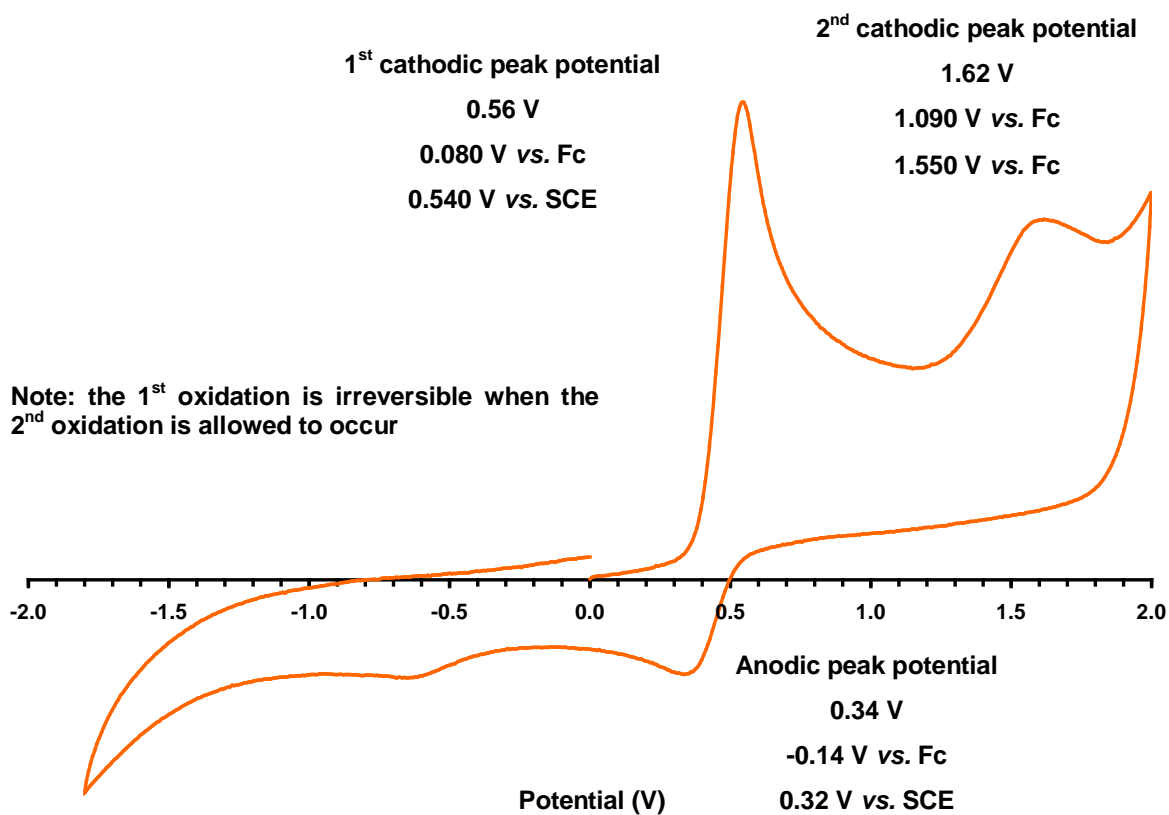
Cyclic voltammetry of **3** in the presence of $[\text{Cp}_2\text{Co}][\text{PF}_6]$ standard in THF at 50 mV/s



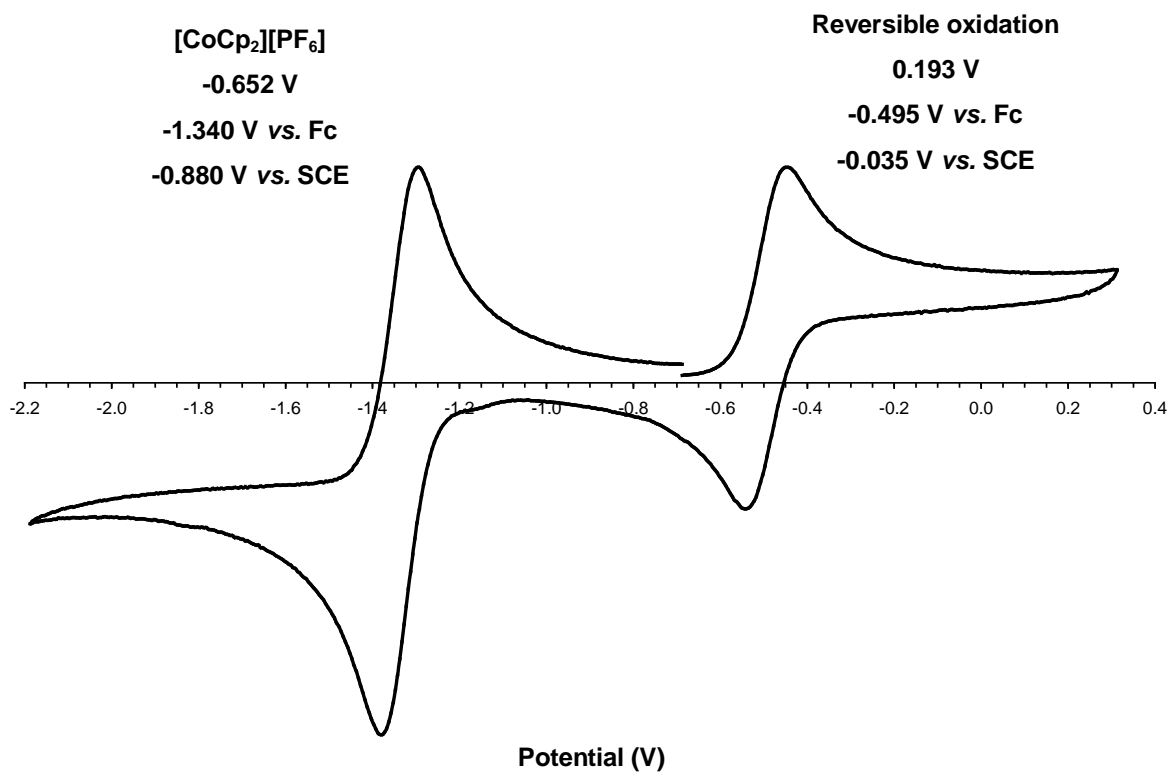
Cyclic voltammetry of **3** in the presence of $[\text{Cp}_2\text{Co}][\text{PF}_6]$ standard in CH_2Cl_2 at 50 mV/s



Cyclic voltammetry of **3** in CH₂Cl₂ at 200 mV/s



Cyclic voltammetry of **4** in the presence of [Cp₂Co][PF₆] standard in CH₂Cl₂ at 50 mV/s



Crystallographic details for 3 and 4

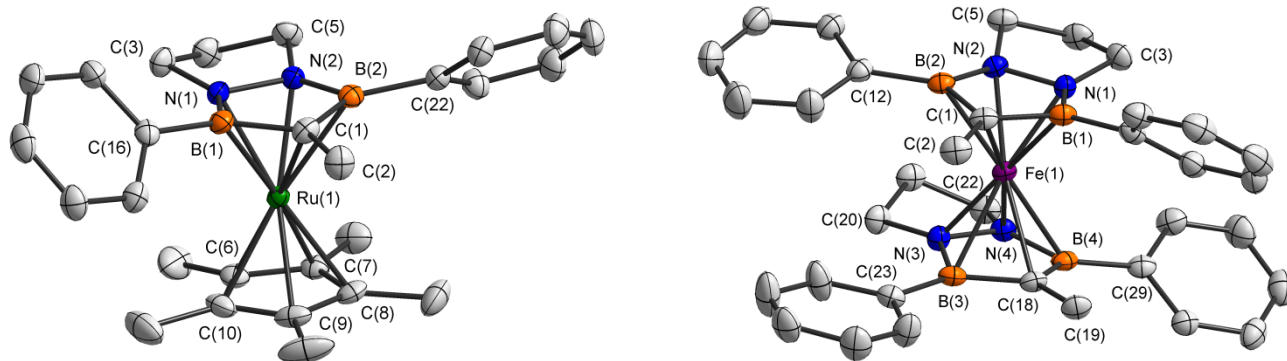


Figure 1. Molecular structure of **3** (left) and **4** (right) with 50 % probability level thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Crystal structure determinations. Data were collected at a temperature of 173(2) K using the ω and ϕ scans on a Nonius Kappa CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation with $\lambda = 0.71073 \text{ \AA}$ (Table 1), and corrected for Lorentz and polarization effects and for absorption using the multi-scan method.¹ The structures were solved by the direct methods² and expanded using Fourier techniques.³ Non-hydrogen atoms were refined anisotropically using SHELXL97.⁴ Hydrogen atoms were included at geometrically calculated positions during the refinement using the riding model.

(1) Otwinowski, Z.; Minor, W. *Methods Enzymol.* 1997, **276**, 307-326.

(2) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* 1993, **26**, 343-350.

(3) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, 1994, University of Nijmegen, The Netherlands.

(4) Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112-122.

Table 1. Selected Data and Structure Refinement Details for **3** and **4**.

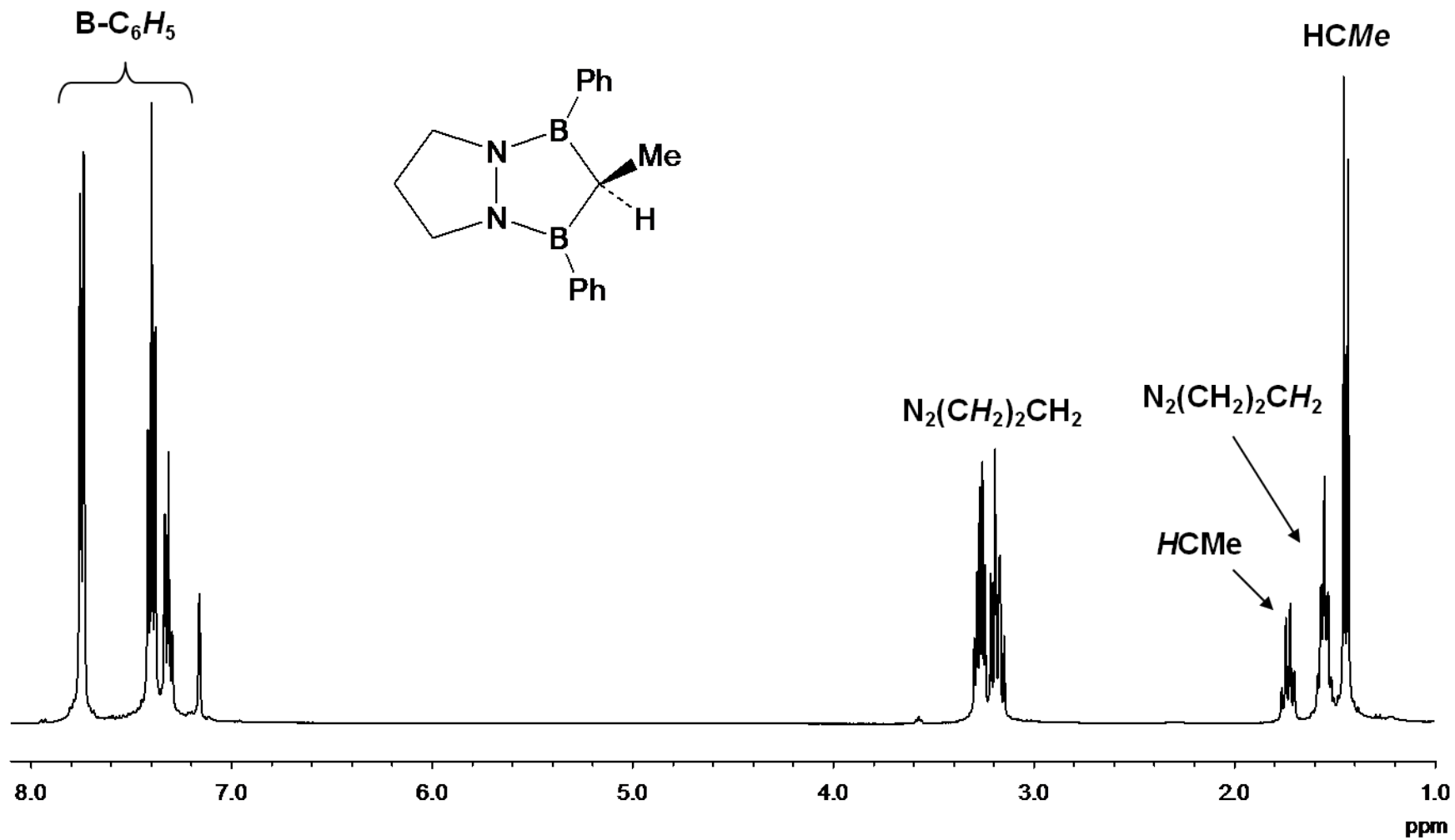
	3	4
Empirical formula	C ₂₇ H ₃₄ B ₂ N ₂ Ru	C ₃₄ H ₃₈ B ₄ FeN ₄
Formula weight	509.25	601.77
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
a (Å)	12.180(3)	11.770(5)
b (Å)	8.6670(11)	15.036(3)
c (Å)	24.155(6)	17.927(7)
β (deg)	101.776(11)	105.487(14)
V (Å ³)	2496.2(9)	3057.4(19)
Z	4	4
d _{calc} (g cm ⁻³)	1.355	1.307
2θ _{max} (deg)	54.96	54.92
μ(Mo Kα)(mm ⁻¹)	0.645	0.525
Independent reflections	5685 (R _{int} = 0.0322)	6954 (R _{int} = 0.0437)
Data/restraints/parameters	5685 / 0 / 294	6954 / 0 / 390
GOF on F ²	1.039	1.031
R ₁ (F) [I > 2σ(I)]	0.0342	0.0477
wR ₂ (F ²) [all data]	0.0884	0.1176

Table 2. Selected Bond Lengths (Å) and Angles (deg) for metallocenes **3** and **4**

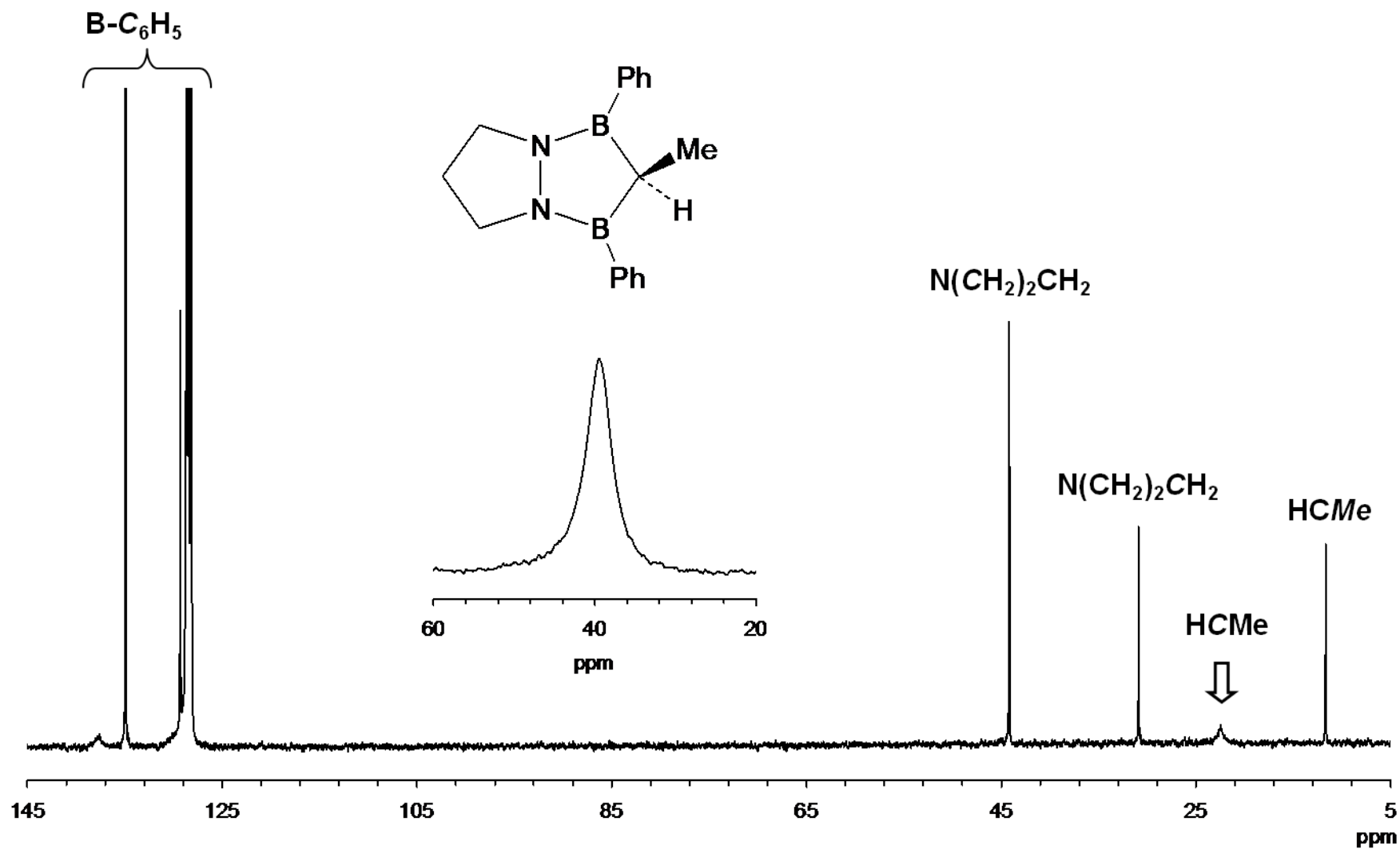
	3 (M = Ru)	4 (M = Fe)
B-C _{intra} ^a	1.511(4), 1.522(4)	1.510(4) – 1.521(4)
N-B	1.479(3), 1.487(3)	1.472(3) – 1.489(4)
N-N	1.431(3)	1.436(3), 1.439(3)
C _{extra} -C _{intra}	1.516(3)	1.513(3), 1.520(3)
B-C _{extra}	1.573(4), 1.58(4)	1.568(4) – 1.572(4)
N-C _{extra}	1.468(3), 1.469(3)	1.469(3) – 1.478(3)
M-C _{intra}	2.296(2)	2.177(2), 2.192(2)
M-B	2.322(3), 2.323(3)	2.198(3) – 2.217(3)
M-N	2.1260(19), 2.1274(19)	1.971(2) – 1.9965(19)
B-C _{intra} -B	109.2(2)	109.5(2), 109.6(2)
B-C _{intra} -C _{extra}	125.1(2), 125.5(2)	122.9(2) – 127.5(2)
N-B-C _{intra}	104.5(2), 104.5(2)	103.8(2) – 104.6(2)
C _{intra} -B-C _{extra}	133.6(2), 133.8(2)	132.6(2) – 133.9(2)
N-B-C _{extra}	121.6(2), 121.9(2)	121.6(2) – 122.8(2)
B-N-N	110.45(17), 110.67(18)	110.00(19) – 110.95(19)
B-N-C _{extra}	138.9(2), 139.2(2)	137.0(2) – 138.9(2)
N-N-C _{extra}	108.94(18), 109.03(18)	108.66(18) – 109.68(18)
Σ _{pentagon angles}	539.3	538.8, 539.4

^a C_{intra} and C_{extra} indicate carbon atoms that are part of the ring (intraannular) and directly connected to the ring (extraannular), respectively.

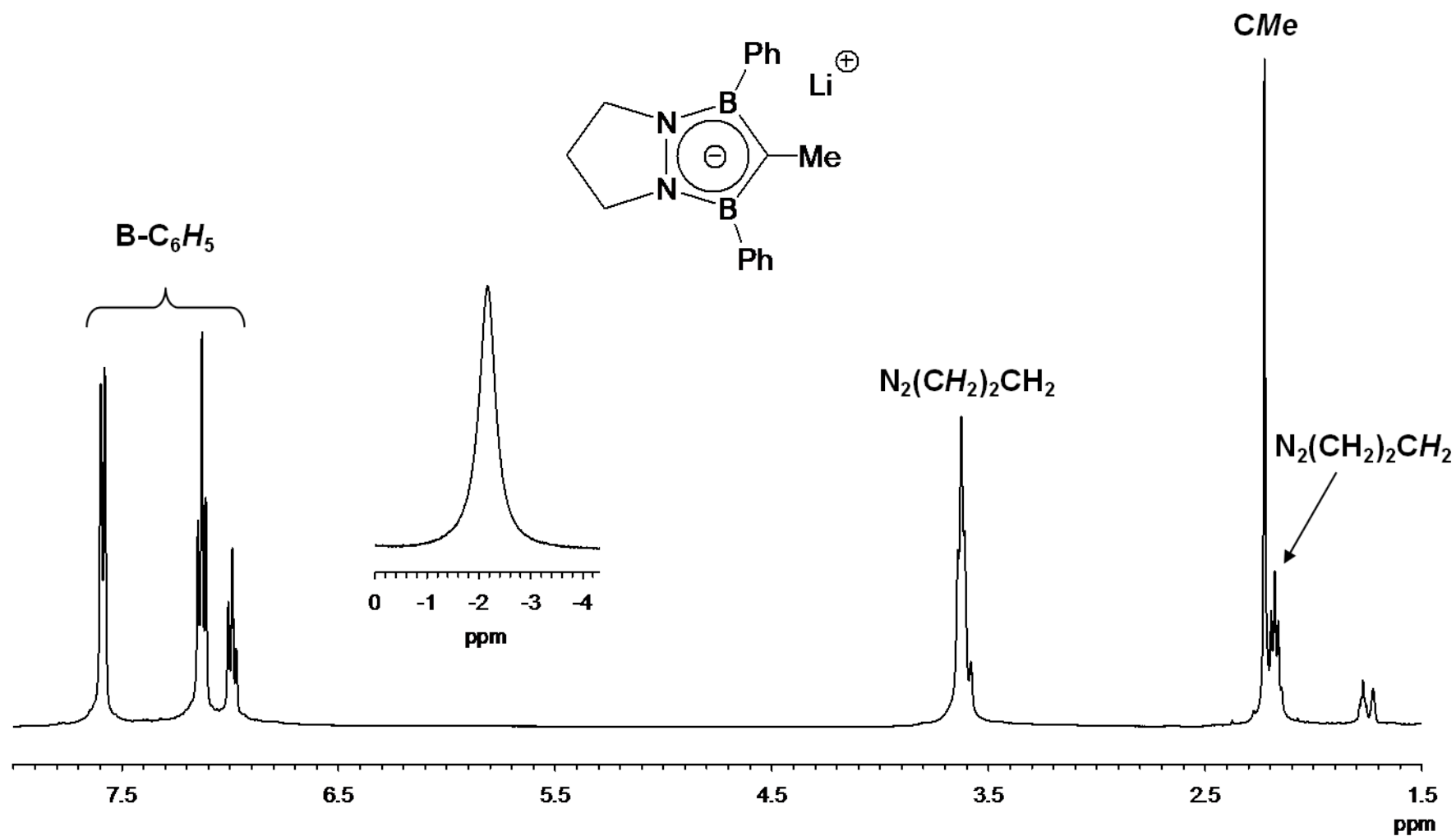
^1H NMR Spectrum of the 1,2-Pyrazo-3,5-diborolidine (**1**) in C_6D_6



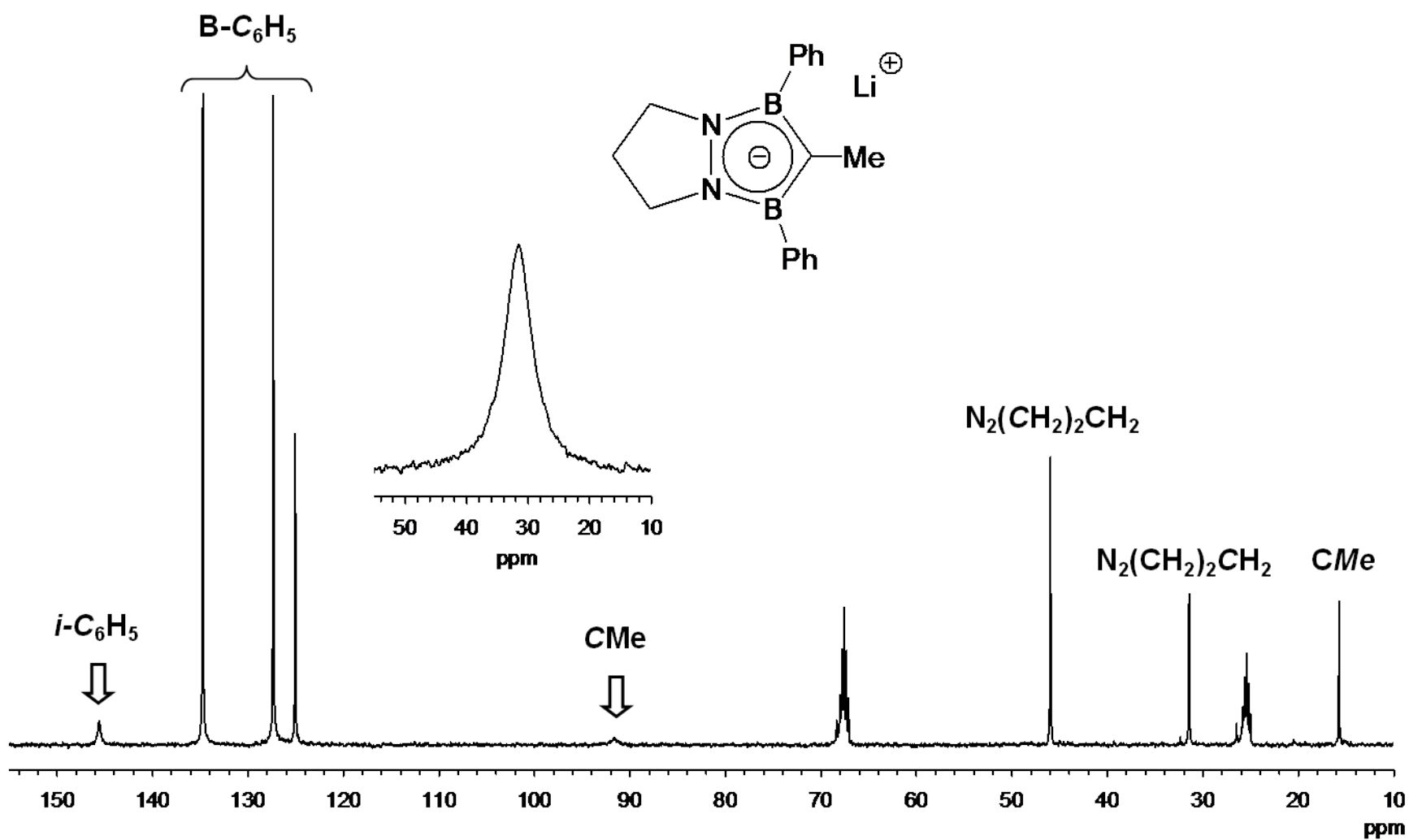
^{13}C and ^{11}B NMR Spectra of the 1,2-Pyrazo-3,5-diborolidine (**1**) in C_6D_6



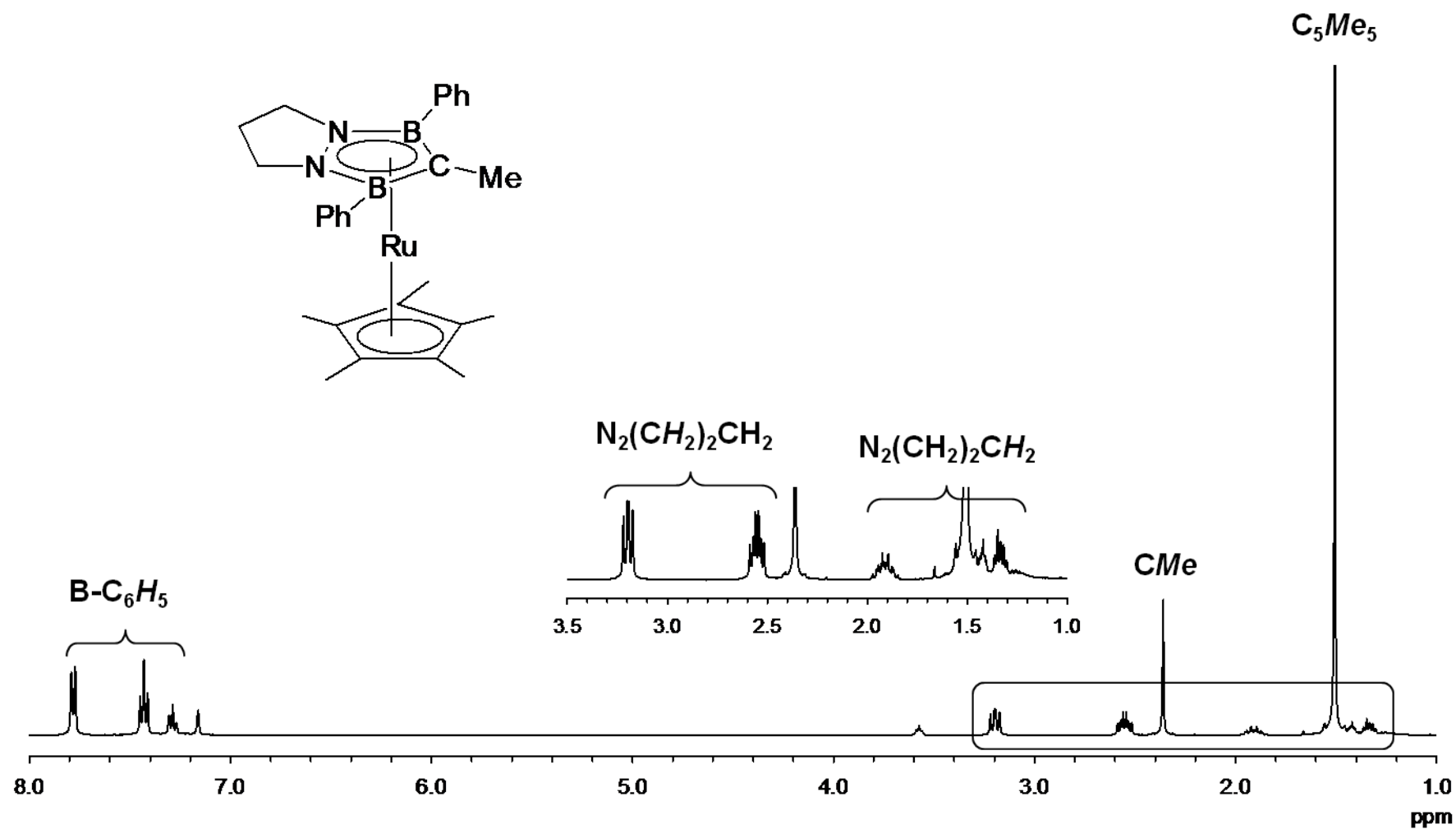
^1H and ^7Li NMR Spectra of the 1,2-Pyrazo-3,5-diborolyllithium (**2**) in THF- d_8



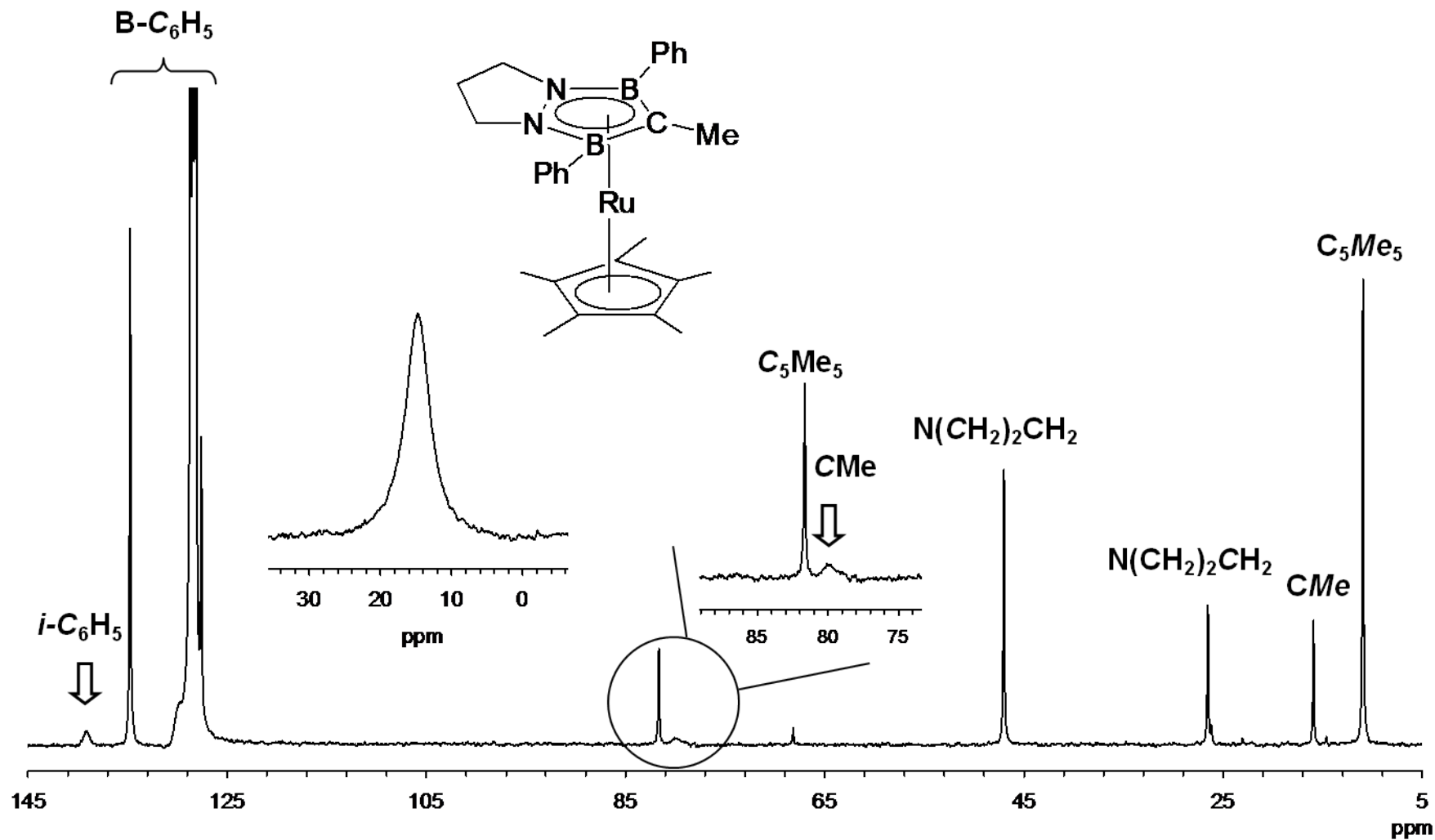
^{13}C and ^{11}B NMR Spectra of the 1,2-Pyrazo-3,5-diborolyllithium (**2**) in THF- d_8



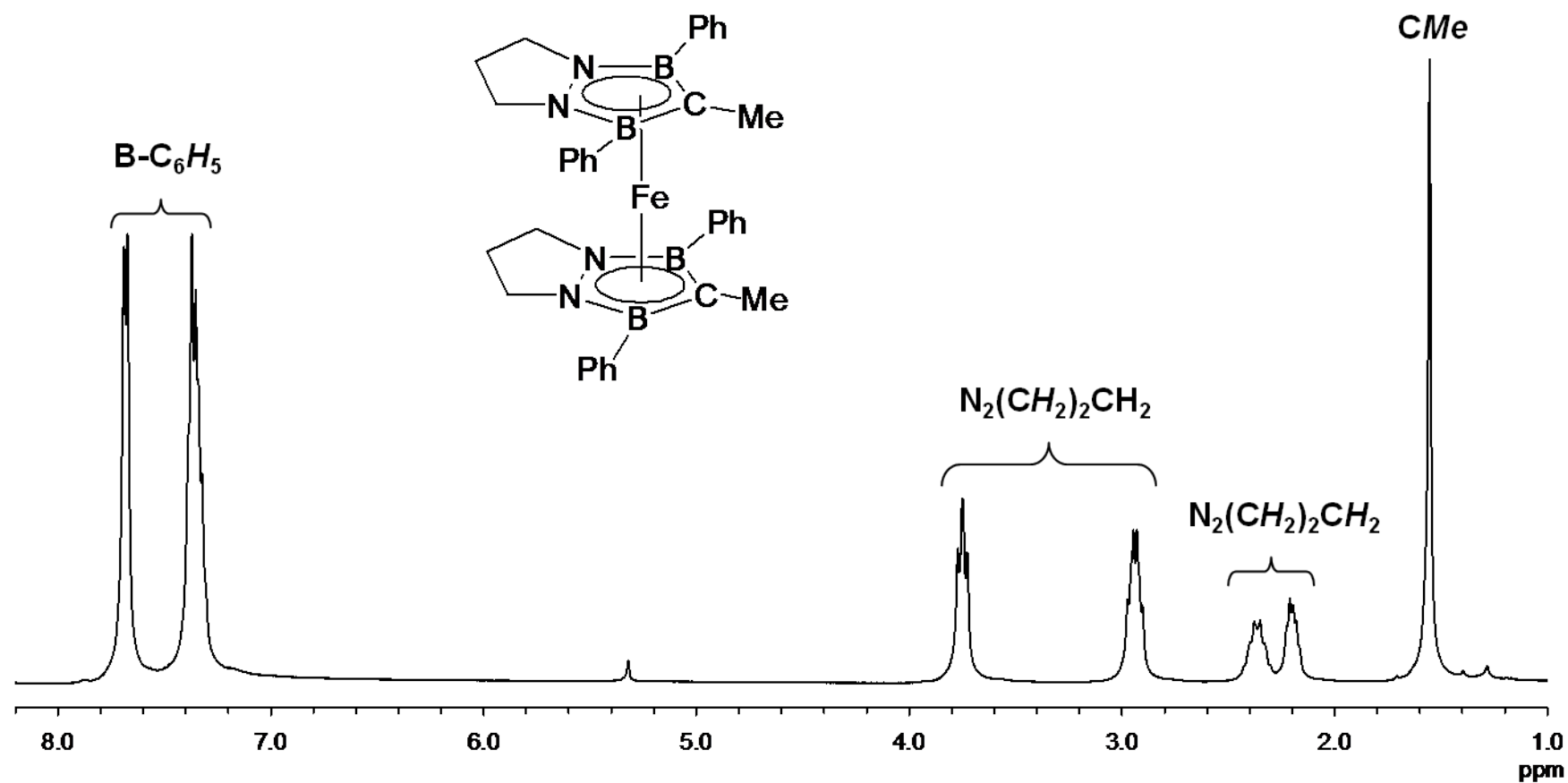
^1H NMR Spectrum of pentamethylcyclopentadienyl(1,2-pyrazo-3,5-diboroly)ruthenocene (**3**) in C_6D_6



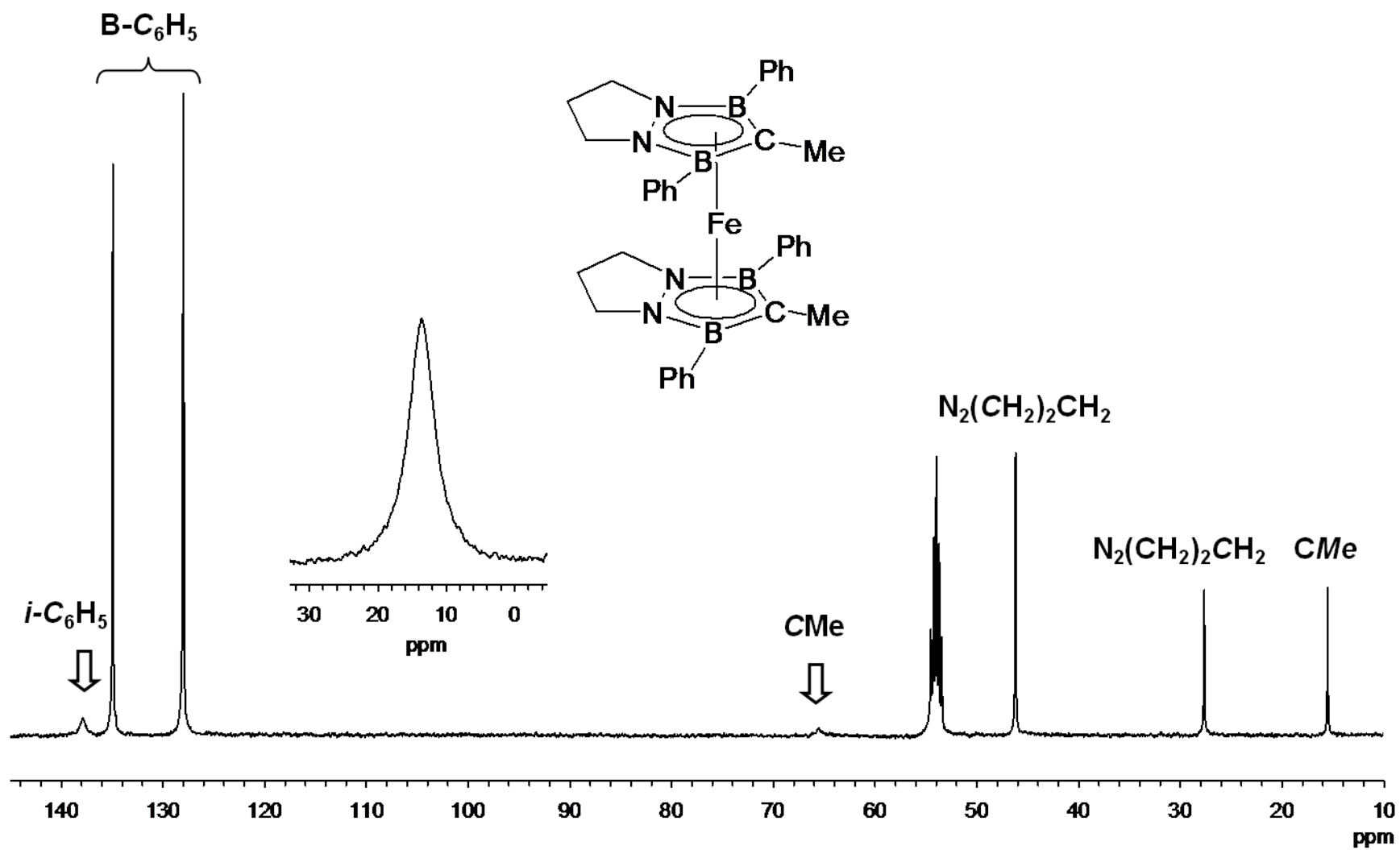
^{13}C and ^{11}B NMR Spectra of pentamethylcyclopentadienyl(1,2-pyrazo-3,5-diboroly)ruthenocene (**3**) in C_6D_6



^1H NMR Spectrum of the Bis(1,2-pyrazo-3,5-diboroly)ferrocene (**4**) in CH_2Cl_2



^{13}C and ^{11}B NMR Spectra of the Bis(1,2-pyrazo-3,5-diboroly)ferrocene (**4**) in CH_2Cl_2

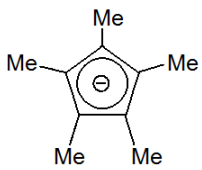
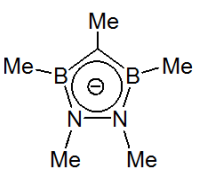
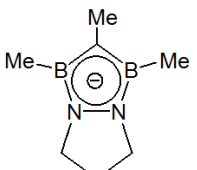
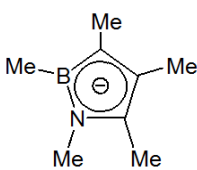


Computational details for 3 and 4

Molecular structures of various Fe and Ru sandwich complexes were optimized using density functional theory. The PBE1PBE hybrid functional¹ was used in together with the def2-TZVP basis sets.² Vertical ionization energies were calculated using the same method-basis set combination and employing the optimized geometries of the neutral complexes. All calculations were performed with the Turbomole 5.10 program package.³

1. (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* 1996, **77**, 3865. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* 1997, **78**, 1396. (c) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* 1996, **105**, 9982. (d) Adamo C.; Barone, V. *J. Chem. Phys.* 1999, **110**, 6158.
2. Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.
3. (a) TURBOMOLE, Program Package for *ab initio* Electronic Structure Calculations, Version 5.10; TURBOMOLE GmbH: Karlsruhe, Germany, 2008. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H; Kölmel, C. *Chem. Phys. Lett.* 1989, **162**, 165.

Table S1. Calculated Vertical Ionization Energies of L₂M (kJ mol⁻¹)

M \ L				
Fe	532	542	531	532
Ru	620	604	596	609