Eur. J. Inorg. Chem. **2008** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2008 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: Reactions of Pendant Boryl Groups in Cp–Metal Complexes: Heterocyclic Ring Annelation in a CpIr System
Author(s): Christoph Herrmann, Gerald Kehr, Roland Fröhlich, Gerhard Erker*
Ref. No.: I200701166

General Information: All syntheses were performed using dried solvents in an inert gas atmosphere (argon) using Schlenk-type glassware or a glove box. Solvents were dried and distilled prior to use. NMR spectra were recorded with *Bruker* AC 200 P (^{11}B: 64.2 MHz), *Bruker* AMX400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz) and a *Varian* UNITYplus 600 (^{1}H: 599.6 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.2 MHz). ^{11}B spectra were referenced to external $Et_2O \cdot BF_3$ (neat) sample, ^{19}F spectra referenced to external $CFCl_3$ (neat) sample. NMR assignments were supported by additional 2D experiments. IR spectra were recorded with a *Varian* 3100 FT-IR (Excalibur Series) spectrometer. Elemental analyses were obtained with a *Foss-Heraeus* CHNO-Rapid. Melting points were determined with a DSC 2010 from (*TA-Instruments*) apparatus. The data was analyzed using the baseline method. Allylcyclopentadienyllithium[1], bis(pentafluorophenyl)borane[2] and chloro(1,5-cyclooctadiene)-iridium dimer[3] were prepared according to literature procedures.

X-ray structure data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation a rotating anode generator was used. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

Preparation of η^5-((allyl)cyclopentadienyl)-η^4-(1,5-cyclooctadienyl)iridium (12): Chloro(1,5-cyclooctadiene)iridium dimer (980 mg, 1.46 mmol) in THF (10 mL) was added to a solution of (allyl)cyclopentadienyllithium (340 mg, 3.03 mmol) in THF (10 mL) at room temperature. After refluxing the solution for 1 h volatiles were removed in vacuo and the residue taken up in pentane (100 mL). Short column chromatography over neutral alumina with pentane yielded (**1**) after removal of the solvent as a colorless oil (969 mg, 82 %).[4] ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ= 5.83 (ddt, $^{3}J_{H,H}$ = 16.8, 10.1, 6.8 Hz, 1 H, 7-H), 4.96 (dm, $^{3}J_{H,H}$ = 16.8 Hz, 1 H, 8-H$_{(Z)}$), 4.94 (dm, $^{3}J_{H,H}$ = 10.1 Hz, 1 H, 8-H′$_{(E)}$), 4.85 (m, 2 H, 2,5-

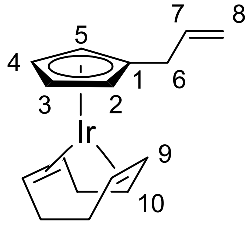
---

[1] M.F. Lappert, C.J. Pickett, P.I. Riley, P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.* **1981**, 805-813; R. Riemschneider, *Z. Naturforsch.* **1963**, *18b*, 641; B. H. Chang, R. H. Grubbs, C. H. Brubaker Jr., *J. Organomet. Chem.* **1985**, *280*, 365-376.

[2] D. J. Parks, W. E. Piers, G. P. A. Jap, *Organometallics* **1998**, *17*, 5492-5503. Reviews: a) W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345-354; b) W. E. Piers, *Top. Catal.* **1999**, *7*, 133-143.

[3] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorganic Syntheses,* **1974**, *15*, 18-20.

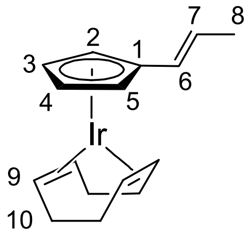
[4] Experimental derived from: J. R. Sowa Jr., R. J. Angelici, *J. Am. Chem. Soc.* **1991**, *113*, 2537-2544.



H), 4.76 (m, 2 H, 3,4-H), 3.74 (m, 4 H, 9-H); 2.77 (d, $^{3}J_{H,H}$ = 6.8 Hz, 2 H, 6-H), 2.21 (m, 4 H, 10-H), 1.96 (m, 4 H, 10-H′) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ= 137.4 (C7), 115.6 (C8), 100.3 (C1), 82.3 (C2,5), 80.7 (C3,4), 47.3 (C9), 34.5 (C10), 31.9 (C6) ppm; GCOSY (400.1 / 400.1 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{1}H= 5.83 / 4.96, 4.94 (7-H / 8-H), 4.85 / 4.76 (2,5-H / 3,4-H), 3.74 / 2.21, 1.96 (9-H / 10-H, 10-H′), 2.77 / 5.83 (6-H / 7-H) ppm; GHSQC (100.6 / 400.1 MHz, C_6D_6, 298 K): δ ^{13}C / δ ^{1}H= 137.4 / 5.83 (C7 / 7-H), 115.6 / 4.96, 4.94 (C8 / 8-$H_{(Z)}$, 8-$H'_{(E)}$), 82.3 / 4.85 (C2,5 / 2,5-H), 80.7 / 4.76 (C3,4 / 3,4-H), 47.3 / 3.74 (C9 / 9-H), 34.5 / 2.21, 1.96 (C10 / 10-H, 10-H′), 31.9 / 2.77 (C6 / 6-H) ppm; GHMBC (100.6 / 400.1 MHz, C_6D_6, 298 K): δ ^{13}C / δ ^{1}H= 137.4 / 2.77 (C7 /6-H), 115.6 / 2.75 (C8 / 6-H), 100.3 / 4.85, 4.76, 2.77 (C1 / 2,5-H, 3,4-H, 6-H), 82.3 / 4.85, 4.76, 2.77 (C2,5 / 2,5-H, 3,4-H, 6-H) ppm; IR (KBr): $\tilde{\nu}$ = 3461 (br), 3076 (w), 2967 (s), 2921 (s), 2872 (s), 2325 (s), 1637 (w), 1429 (w), 1318 (m), 1236 (w), 991 (m), 910 (s), 838 (s), 567 (w), 497 (m). cm^{-1}; elemental analysis: (%) calcd for $C_{16}H_{21}Ir$ (405.6): C 47.38, H 5.22; found: C 47.84, H 5.29.

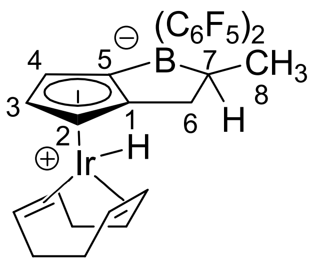
Preparation of η^{5}-((1-Propenyl)cyclopentadienyl)-η^{4}-(1-5-cyclooctadienyl)iridium (13): Chloro(1,5-cyclooctadiene)iridium dimer (972 mg, 1.45 mmol) and (allyl)cyclopentadienyllithium (324 mg, 2.90 mmol) were treated as described for **12**. The colorless oil was heated under vacuum conditions in a Schlenk tube at 100 °C for 1.5 h. A yellow oil was formed, which crystallized after 5 weeks (1.05 g, 90 %).

X-ray crystal structure analysis for **13**: formula $C_{16}H_{21}Ir$, M = 405.53, colorless crystal 0.40 x 0.25 x 0.15 mm, a = 8.384(1), b = 12.611(1), c = 13.447(1) Å, α = 76.69(1), β = 99.93(1), γ = 107.12(1)°, V = 1317.1(2) Å^{3}, ρ_{calc} = 2.045 g cm^{-3}, μ = 10.112 mm^{-1}, empirical absorption correction (0.107 ≤ T ≤ 0.312), Z = 4, triclinic, space group P1bar (No. 2), λ= 0.71073 Å, T = 198 K, ω and φ scans, 13582 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 6198 independent (R_{int} = 0.045) and 5538 observed reflections [$I \geq 2\,\sigma(I)$], 309 refined parameters, R = 0.034, wR^2 = 0.096, max. residual electron density 2.35 (-2.51) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. M.p.: 62.20 °C; ^{1}H NMR (599.6 MHz, C_6D_6, 298 K): δ = 5.79 (dqm, $^{3}J_{H,H}$ = 15.6 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1 H, 6-H), 5.50 (dq, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 1 H, 7-H), 5.09 (m, 2 H, 2,5-H), 4.80 (m, 2 H, 3,4-H), 3.74 (m, 4 H, 9-H), 2.22 (m, 4 H, 10-H), 1.97 (m, 4 H, 10-H′), 1.54 (dd, $^{3}J_{H,H}$ = 6.6 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 3 H,



8-H) ppm;[5] $^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_6, 298 K): δ= 124.7 (C7), 123.2 (C6), 100.3 (C1), 80.8 (C3,4), 80.1 (C2,5), 48.6 (C9), 34.4 (C10), 18.2 (C8) ppm; GCOSY (599.6 / 599.6 MHz, C_6D_6, 298 K): δ ^1H / δ ^1H= 5.79 / 5.50, 1.54 (6-H / 7-H, 8-H), 5.09 / 4.80 (2,5-H / 3,4-H), 3.74 / 2.22, 1.96 (9-H / 10-H, 10-H′), 1.54 / 5.79, 5.50 (8-H / 6-H, 7-H) ppm; GHSQC (150.8 / 599.6 MHz, C_6D_6, 298 K): δ ^{13}C / δ ^1H= 124.7 / 5.50 (C7 / 7-H), 123.2 / 5.79 (C6 / 6-H), 80.8 / 4.80 (C3,4 / 3,4-H), 80.1 / 5.09 (C2,5 / 2,5-H), 48.6 / 3.74 (C9 / 9-H), 34.4 / 2.22, 1.96 (C10 / 10-H, 10-H′), 18.2 / 1.54 (C8 / 8-H) ppm; GHMBC (150.8 / 599.6 MHz, C_6D_6, 298 K): δ ^{13}C / δ ^1H= 124.7 / 1.54 (C7 / 8-H); 123.2 / 1.57 (C6 / 8-H), 100.3 / 5.50, 5.09, 4.80, 1.54 (C1 / 7-H, 2,5-H, 3,4-H, 8-H), 80.8 / 5.09, 4.80 (C3,4 / 2,5-H, 3,4-H), 80.1 / 5.79, 5.09, 4.80 (C2,5 / 6-H, 2,5-H, 3,4-H), 48.6 / 2.22, 1.96 (C9 / 10-H, 10-H′), 34.4 / 3.74, 2.22, 1.96 (C10 / 9-H, 10-H, 10-H′), 18.2 / 5.79, 5.50 (C8 / 6-H, 7-H) ppm; IR (KBr): $\tilde{\nu}$ = 3086 (w), 2965 (s), 2922 (s), 2871 (s), 2825 (s), 2360 (m), 1471 (m), 1438 (m), 1317 (m), 1261 (w), 1234 (w), 1084 (m), 1020 (m), 958 (s), 911 (s), 804 (vs) cm^{-1}; elemental analysis: (%) calcd for $C_{16}H_{21}Ir$ (405.6): C 47.38, H 5.22; found: C 47.12, H 5.34.

Preparation of (16): η^5-((1-Propenyl)cyclopentadienyl)-η^4-(1,5-cyclooctadienyl)iridium (**13**) (81.1 mg, 0.19 mmol) was dissolved in pentane (10 mL). At room temperature a solution of bis(pentafluoro)phenylborane (69.2 mg, 0.19 mmol) in pentane (10 mL) was added. The solution turned a glowing orange color instantly. After 5 minutes a white precipitate formed. After stirring for 2 h the solution was decolorized and a white precipitate has formed. After removing the solvent the remaining powder is washed with pentane (10 mL) and dried in vacuo. A white powder was isolated (117.2 mg, 0.16 mmol, 78.0 %). Crystals suitable for X-ray diffraction could be obtained by generation of **16** in d_2-dichloromethane instead of pentane. X-ray crystal structure analysis for **16**: formula $C_{28}H_{22}BF_{10}Ir$, M = 751.47, colorless crystal 0.25 x 0.15 x 0.10 mm, a = 10.3710(1), b = 13.9206(2), c = 17.6004(2) Å, β = 102.083(1)°, V = 2484.68(5) $Å^3$, ρ_{calc} = 2.009 g cm^{-3}, μ= 5.467 mm^{-1}, empirical absorption correction (0.342 ≤ T ≤ 0.611), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ= 0.71073 Å, T = 198 K, ω and φ scans, 19865 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 $Å^{-1}$, 6081 independent (R_{int} = 0.034) and 5387 observed reflections [$I \geq 2\ \sigma(I)$], 366 refined parameters, R = 0.023, wR^2 = 0.057, max. residual electron density 1.08 (-0.99) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms. M.p.: 138.7 °C; ^1H NMR (599.6 MHz, CD_2Cl_2,



---

[5] Integers for 9-H and 10a/b-H are closer to 5 than 4 protons (additional *cis* / *trans* isomer or 2-propenyl compound as impurity?).

253 K): δ = 5.60 (m, 1 H, 3-H), 5.55 (br, 1 H, 4-H), 5.45 (m, 1 H, 2-H), 4.50, 4.45, 3.95, 3.80 (each m, each 1 H, =CH^{COD}), 2.24 / 2.12, 2.24 (×2), 2.22 / 2.01, 2.21 / 2.04 (m, -CH_2^{COD})[6], 2.23, 2.02 (each m, each 1 H, 6-H), 1.61 (br, 1 H, 7-H), 0.86 (broad, d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 3 H, 8-H), -12.23 (s, 1 H, Ir-H) ppm; ^{13}C{^{1}H} NMR (150.8 MHz, CD$_2$Cl$_2$, 253 K): δ ^{13}C = 126.8 (C1); 92.7 (C3), 84.3 (C4), 76.3 (C2), 69.3, 67.4, 67.0, 66.8 (=CH$^{\mathrm{COD}}$), 33.6 (C6), 33.0, 32.4, 31.9, 31.3 (4 × -CH$_2^{\mathrm{COD}}$), 17.0 (C8), n.o. (C7), n.o. (C5); GCOSY (599.6 / 599.6 MHz, CD$_2$Cl$_2$, 253 K): δ ^{1}H / δ ^{1}H = 5.60 / 5.55, 5.45 (3-H / 4-H, 2-H), 5.55 / 5.60, 5.45 (4-H / 3-H, 2-H), 5.45 / 5,60, 5.55 (2-H / 3-H, 4-H), 4.50 / 3.95, 2.24, 2.01 (=CH^{COD} / =CH^{COD}, 2 × -CH_2^{COD}), 4.45 / 3.80, 2.22, 2.04 (=CH^{COD} / =CH^{COD}, 2 × -CH_2-$^{\mathrm{COD}}$), 3.95 / 4.50, 2.24 (=C$H^{\mathrm{COD\,/}}$ =CH^{COD}, -CH_2^{COD}), 3.80 / 4.45, 2.24, 2.12 (=CH^{COD} / =CH^{COD}, 2 × -CH_2^{COD}), 1.61 / 2.23, 2.02, 0.86 (7-H / 6-H, 6-H, 8-H), 0.86 / 1.61 (8-H / 7-H) ppm; GHSQC (150.8 / 599.6 MHz, CD$_2$Cl$_2$, 253 K): δ ^{13}C / δ ^{1}H = 92.7 / 5.60 (C3 / 3-H), 84.3 / 5.55 (C4 / 4-H), 76.3 / 5.45 (C2 / 2-H), 69.3 / 4.50, 67.4 / 4.45, 66.8 / 3.95, 67.0 / 3.80 (4 × =CH$^{\mathrm{COD}}$ / =CH^{COD}), 33.6 / 2.23, 2.02 (C6 / 6-H), 33.0 / 2.21, 2.04 , 32.4 / 2.22, 2.01, 31.9 / 2.24 (× 2), 31.3 / 2.24, 2.12 (4 × -CH$_2^{\mathrm{COD}}$ / -CH_2^{COD}), 17.0 / 0.86 (C8 / 8-H), n.o. / 1.61 (C7 / 7-H)[7]; GHMBC (150.8 / 599.6 MHz, CD$_2$Cl$_2$, 253 K): δ ^{13}C / δ ^{1}H = 126.8 / 5.60, 5.55, 5.45 (C1 / 3-H, 4-H, 2-H), 92.7 / 5.55, 5.45 (C3 / 4-H, 2-H), 84.3 / 5.45 (C4 / 2-H), 76.3 / 5.60, 5.55 (C2 / 3-H, 4-H), 33.6 / 0.86 (C6 / 8-H) ppm; 1D-TOCSY (599.6 MHz, CD$_2$Cl$_2$, 253 K): δ ^{1}H$_{\mathrm{irr}}$ / δ^{1}H$_{\mathrm{res}}$ = 5.60 / 5.55, 5.45 (3-H / 4-H, 2-H), 4.45 / 4.50, 3.95, 3.80, 2.24, 2.22, 2.12, 2.04, 2.01 (=CH$^{\mathrm{COD}}$ / =CH, -CH$_2^{\mathrm{COD}}$), 0.86 / 2.23, 2.03, 1.61 (8-H / 6-H, 6-H, 7-H) ppm; NOE-DIFF (599.6 MHz, CD$_2$Cl$_2$, 253 K): δ ^{1}H$_{\mathrm{irr}}$ / δ^{1}H$_{\mathrm{res}}$ = 5.60 / 5.45, 4.50, 4.45 (3-H / 2-H, =CH$^{\mathrm{COD}}$), 5.45 / 5.60, 2.23 (2-H / 3-H, 6-H), 4.50 / 5.60, 3.95, 2.23 (=CH$^{\mathrm{COD}}$ / 3-H, =CH$^{\mathrm{COD}}$, -CH$_2^{\mathrm{COD}}$), 4.45 / 5.60, 5.55, 3.80, 2.23 (=CH$^{\mathrm{COD}}$ / 3-H, 4-H, =CH$^{\mathrm{COD}}$, -CH$_2^{\mathrm{COD}}$), 3.95 / 4.50, 2.24, 1.61, -12.23 (=CH$^{\mathrm{COD}}$ / =CH$^{\mathrm{COD}}$, -CH$_2^{\mathrm{COD}}$, 7-H, Ir-H), 3.80 / 4.45, 2.24, -12.23 (=CH$^{\mathrm{COD}}$ / =CH$^{\mathrm{COD}}$, -CH$_2^{\mathrm{COD}}$, Ir-H), 0.86 / 1.61, 2.02 (8-H / 7-H, 6-H) ppm; ^{19}F NMR (564.2 MHz, CD$_2$Cl$_2$, 243 K) δ = -129.7, -131.0 (each br, each 1 F, *o*-C$_6F_5^{\mathrm{A}}$); -131.5, -135.8 (each m, each 1 F, *o*-C$_6F_5^{\mathrm{B}}$), -162.4 (t, $^3J_{\mathrm{FF}}$ = 20.6 Hz, 1 F, *p*-C$_6F_5^{\mathrm{B}}$), -162.5 (t, $^3J_{\mathrm{FF}}$ = 21.5 Hz, 1 F, *p*-C$_6F_5^{\mathrm{A}}$), -165.2, -165.4 (each m, each 1 F, *m*-C$_6F_5^{\mathrm{B}}$), -165.9, -166.2 (each br, each 1 F, *m*-C$_6F_5^{\mathrm{A}}$) ppm; ^{19}F NMR (564.2 MHz, CD$_2$Cl$_2$, 298 K) δ = (each broad) -130.2 (2 F, *o*-C$_6F_5^{\mathrm{A}}$), -131.3, -135.4 (each 1 F, *o*-C$_6F_5^{\mathrm{B}}$), -162.9 (2 F, *p*-C$_6F_5^{\mathrm{A/B}}$), -165.9 (2 F, *m*-C$_6F_5^{\mathrm{B}}$), -166.5 (2 F, *p*-C$_6F_5^{\mathrm{A}}$) ppm; ^{19}F/^{19}F-GCOSY

---

[6] Chemical shifts were determined by 1DTOCSY, GCOSY, GHSQC and GHMBC experiments.

[7] The C7 / 7-H crosspeak was not observed due to the low concentration of the sample and the bound boron atom leading to a broadening of the supposed signal.

(564.2 / 564.2 MHz, CD_2Cl_2, 243 K): δ ^{19}F / δ ^{19}F = -129.7 / -165.9 (o-$C_6F_5^A$ / m-$C_6F_5^A$), -131.0 / -166.2 (o-$C_6F_5^A$ / m-$C_6F_5^A$), -131.5 / -165.4 (o-$C_6F_5^B$ / m-$C_6F_5^B$), -135.8 / -165.2 (o-$C_6F_5^B$ / m-$C_6F_5^B$), -162.4 / -165.2, -165.4 (p-$C_6F_5^B$ / m-$C_6F_5^B$), -162.5 / -165.2, -166.2 (p-$C_6F_5^A$ / m-$C_6F_5^A$) ppm; ^{11}B{^{1}H} NMR (64.2 MHz, CD_2Cl_2, 300 K) δ = -13.0 ppm ($\nu_{1/2}$ = 40 Hz); IR (KBr): $\tilde{\nu}$ = 3039 (w), 2961 (m), 2921 (s), 2901 (sh), 2858 (m), 2829 (w), 2371 (w), 2345 (w), 2157 (m), 1643 (s), 1512 (vs), 1463 (vs), 1269 (s), 1088 (s), 965 (s), 771 (s), 748 (m), 701 (m), 681 (m), 641 (m), 603 (w) cm^{-1}; elemental analysis: (%) calcd for $C_{28}H_{22}BF_{10}Ir$ (751.45): C 44.75, H 2.95; found: C 44.88, H 2.89.

Calculation of the Gibbs Activation Energy ($\Delta G^{\neq}$)

The Eyring equation can give an estimate of the energy barrier of the observed process at the coalescence temperature T_c (K) (advanced equation):

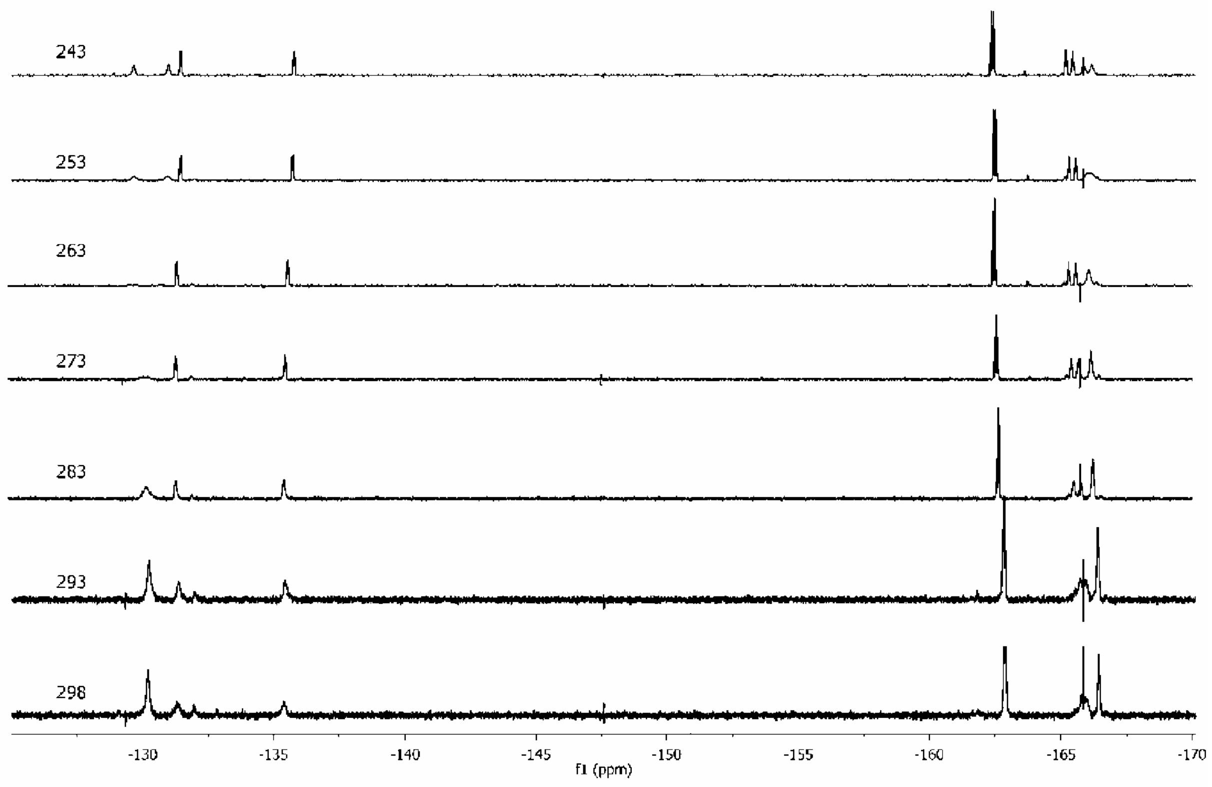
$$\Delta G^{\neq} = R\,T_c\left(22.96 + \ln {T_c}/{\Delta\nu}\right)\ [J\ mol^{-1}]$$

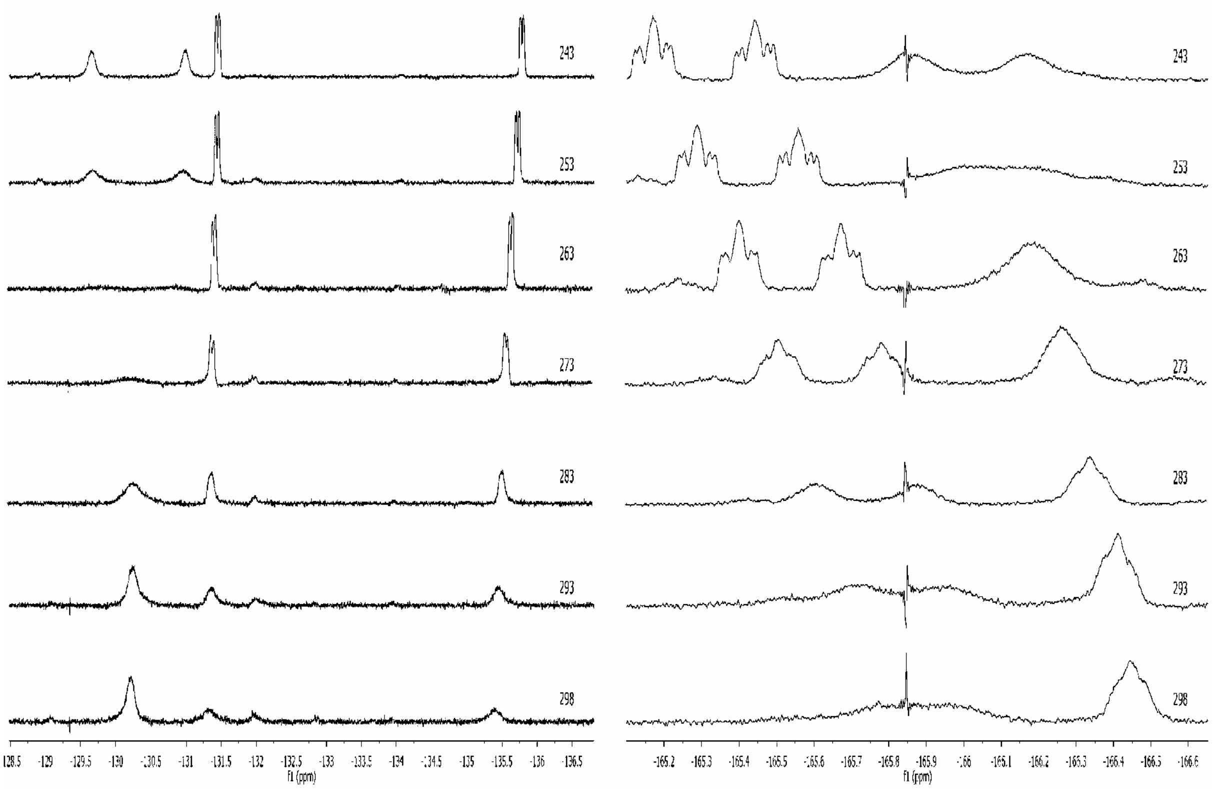
$\Delta G^{\neq}$ = Gibbs Activation Energy
R = ideal gas constant
T_c = temperature of coalescene (in K)
$\Delta\nu$ = $|\nu_{\alpha}-\nu_{\beta}|$ (in Hz)

For the determination of $\Delta G^{\neq}$ the following parameters were determined from ^{19}F DNMR:

ortho-$C_6F_5^{A}$: $\Delta\nu$ (243 K) = 753 Hz; T_c = 268 K. $\Delta G^{\neq}$ = 48858 J / mol = 11.7 kcal/mol
δ ^{19}F (243 K) = -129.7, -131.0.
meta-$C_6F_5^{A}$: $\Delta\nu$ (243 K) = 181 Hz; T_c = 258 K. $\Delta G^{\neq}$ = 50012 J / mol = 12.0 kcal/mol
δ ^{19}F (243 K) = -165.9, -166.2.
meta-$C_6F_5^{B}$: $\Delta\nu$ (243 K) = 155 Hz; T_c = 298 K. $\Delta G^{\neq}$ = 58507 J / mol = 14.0 kcal/mol
δ ^{19}F (243 K) = -165.2, -165.4.

For the free rotaion of -$C_6F_5^{A}$ one can average a $\Delta G^{\neq}$ of 11.9 (±0.2) kcal/mol.





Temperature dependent ^{19}F NMR of **16** (left: ortho-, right: meta-domain).