Supporting information for the article

Synthesis of 13-vertex Dimetallacarboranes by Electrophilic Insertion into 12-vertex Ruthenacarboranes

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General Remarks. All reactions were carried out under argon in anhydrous solvents which were purified and dried using standard procedures. The isolation of products was conducted in air. The starting materials $[Co(C_6Me_6)_2]PF_6$,[1] $[(C_4Me_4)Co(MeCN)_3]PF_6$ and $[(C_4Me_4)Co(C_6H_6)]PF_6$,[2] $[CpRu(MeCN)_3]PF_6$,[3] $[Cp^*Ru(MeCN)_3]PF_6$,[4] $[Cp^*RuCl]_4$,[5] $[CpNi(SMe_2)_2]BF_4$,[6] $Tl_2[7,8\text{-}C_2B_9H_{11}]$ and $Tl_2[7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$,[7] complexes **1**,[8] and **6** (ref.[9]) were prepared as described in the literature. The compound $Tl_2[7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_9]$ was prepared similar to preparation of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ from the corresponding $1,2\text{-}CH_2OCH_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ carborane. Visible light irradiation was performed by a high pressure mercury vapor lamp with phosphor coated bulb (400 W, Philips HPL Comfort). The ^1H and $^{11}B\{^1H\}$ NMR spectra were recorded with a Bruker Avance 400 spectrometer operating at 400.13 and 128.38 MHz, respectively. Chemical shifts are given in ppm relative to residual signals of the solvents (^1H) or external $BF_3{\cdot}OEt_2$ (^{11}B). Electrochemistry and spectroelectrochemistry: anhydrous 99.9% dichloromethane was an Aldrich product, Fluka $[NBu_4][PF_6]$ (electrochemical grade) was used as supporting electrolyte (0.2 M). Cyclic voltammetry was performed in a three-electrode cell containing a platinum working electrode surrounded by a platinum-spiral counter electrode, and an aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. Controlled potential coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. A BAS 100W electrochemical analyzer was used as polarizing unit. All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at E°'=+0.39 V. The UV-vis spectroelectrochemical measurements were carried out using a PerkinElmer Lambda 900 UVvis spectrophotometer and an OTTLE (optically transparent thin-layer electrode) cell[10] equipped with a Pt-minigrid working electrod, Pt minigrid auxiliary electrode, Ag wire pseudoreference and CaF2 windows. The electrode potential was controlled during electrolysis by an Amel potentiostat 2059 equipped with an Amel function generator 568. Nitrogen-saturated CH_2Cl_2 solutions of the compound under study were used with $[NBu_4][PF_6]$ (0.2 M) as supporting electrolyte.

Tl[3-Cp*-1,2-CH_2OCH_2-3,1,2-$RuC_2B_9H_9$] (3). A mixture of $[Cp^*RuCl]_4$ (109 mg, 0.1 mmol) and Tl_2[7,8-CH_2OCH_2-7,8-$C_2B_9H_9$] (292 mg, 0.5 mmol) was stirred for 48 h in 8 ml of MeCN and then evaporated in vacuo. The residue was dissolved in THF, filtered and the pale yellow solid was precipitated by excess of Et_2O. Yield 178 mg (72%). ^{1}H NMR ($(CD_3)_2CO$): δ = 4.31 (s, 4H, CH_2), 1.89 (s, 15H, Cp*); $^{11}B\{^1H\}$ NMR: δ = 0.8, −6.6, −8.0, −16.3, −23.8 (1:2:1:3:2). Anal. Calcd. for $C_{14}H_{28}B_9ORuTl$: C, 27.34; H, 4.59; B, 15.82. Found: C, 27.50; H, 4.72; B, 15.61.

CpRu($C_2B_9H_{11}$)RuCp* (2a). A mixture of Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) and $[CpRu(MeCN)_3]PF_6$ (65 mg, 0.15 mmol) was refluxed in 5 ml of CH_3NO_2 for 4 h, while the color changed from yellow to red. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate orange-red crystals. Yield 38 mg (47%). ^{1}H NMR ($CDCl_3$): δ = 5.22 (s, 5H, Cp), 1.60 (s, 15H, Cp*), −0.69 (bs, 2H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 95.1, 38.3, 31.9, 17.9, 16.2, −5.3 (1:1:1:2:2:2). Anal. Calcd. for $C_{17}H_{31}B_9Ru_2$: C 38.17, H 5.84, B 18.19. Found: C 38.16, H 5.89, B 18.11.

Cp*Ru($C_2B_9H_{11}$)RuCp* (2b). (a) A mixture of Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) and $[Cp^*RuCl]_4$ (41 mg, 0.037 mmol) was stirred for 4 h in 4 ml of THF, while the color changed from orange to dark-red. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate orange-red crystals. Yield 67 mg (74%). ^{1}H NMR ($CDCl_3$): δ = 1.59 (s, 30H, Cp*), −1.27 (bs, 2H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 97.0, 36.4, 17.8, −5.6 (1:2:4:2). Anal. Calcd. for $C_{22}H_{41}B_9Ru_2$: C 43.68, H 6.83, B 16.80. Found: C 43.65, H 6.78, B 16.98.

(b) The direct reaction of Tl_2[7,8-$C_2B_9H_{11}$] (81 mg, 0.15 mmol) with $[Cp^*RuCl]_4$ (82 mg, 0.075 mmol) in 5 ml THF for 48 h, followed by the isolation as described above give 64 mg (70%) of **2b**.

CpRu($C_2B_9H_{11}$)RuCp (2c). A mixture of Tl_2[7,8-$C_2B_9H_9$] (81 mg, 0.15 mmol) and $[CpRu(MeCN)_3]PF_6$ (130 mg, 0.3 mmol) was stirred for 18 h in 6 ml of THF. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate orange-red crystals. Yield 93 mg (67%). ^{1}H NMR ($CDCl_3$): δ = 5.26 (s, 10H, Cp), −1.24 (bs, 2H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 93.9, 33.7, 16.4, −4.9 (1:2:4:2). Anal. Calcd. for $C_{12}H_{19}B_9Ru_2$: C 31.17, H 4.11, B 21.04. Found: C 31.40, H 4.32, B 20.81.

Cp*Ru(Me$_2$C$_2$B$_9$H$_9$)RuCp* (2d). A mixture of Tl$_2$[7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$] (114 mg, 0.2 mmol) and [Cp*RuCl]$_4$ (97 mg, 0.09 mmol) was stirred for 18 h in 4 ml of THF. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The orange fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate orange crystals. Yield 60 mg (53%). NMR ($CDCl_3$): δ = 1.60 (s, 30H, Cp*), 0.62 (s, 6H, CMe_{cage}); $^{11}B\{^1H\}$ NMR: δ = 101.0, 35.5, 22.2, −5.2 (1:2:4:2). Anal. Calcd. for $C_{24}H_{45}B_9Ru_2$: C 45.53, H 7.16, B 15.37. Found: C 45.70, H 7.25, B 15.12.

3-Cp*-1,2-CH$_2$OCH$_2$-7-C$_4$H$_8$O-3,1,2-RuC$_2$B$_9$H$_8$ (4). A mixture of Tl[3-Cp*-1,2-CH_2OCH_2-3,1,2-$RuC_2B_9H_9$] (**3**) (104 mg, 0.2 mmol) and [Cp*RuCl]$_4$ (54 mg, 0.05 mmol) was stirred for 14 h in 5 ml of THF. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a Al_2O_3 column (8 cm). The orange fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate pale orange powder of **4**. Yield 56 mg (58%). ^1H NMR ($(CD_3)_2CO$): δ = 4.26 (s, 4H, карб. CH_2OCH_2), 4.13 (d (J = 6), 2H, α-CH_2 (C_4H_8O)), 4.02 (d (J = 6), 2H, α-CH_2 (C_4H_8O)), 2.24 (m, 4H, β-CH_2 (C_4H_8O)), 1.82 (c, 15H, Cp*); $^{11}B\{^1H\}$ NMR: δ = 22.33 (B–OC_4H_8), −8.51, −10.75, −17.24, −19.11, −24.25 (1:2:1:2:1:2). Anal. Calcd. for $C_{18}H_{35}B_9O_2Ru$: C 44.87, H 7.32, B 20.19. Found: C 45.12, H 7.44, B 19.96.

(C$_4$Me$_4$)Co(C$_2$B$_9$H$_{11}$)RuCp* (5). A mixture of Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) and [$(C_4Me_4)Co(C_6H_6)$]PF_6 (59 mg, 0.15 mmol) in 4 ml of THF and 12 ml CH_2Cl_2 was irradiated with stirring for 4 h. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate orange-red crystals. Yield 41 mg (51%). ^1H NMR ($CDCl_3$): δ = 1.64 (s, 15H, Cp*), 1.25 (s, 12H, (C_4Me_4)Co), −0.76 (bs, 2H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 103.9, 43.3, 39.8, 29.0, 23.1, 1.9 (1:1:1:2:2:2). Anal. Calcd. for $C_{20}H_{38}B_9CoRu$: C 44.73, H 7.15, B 18.16. Found: C 44.92, H 7.46, B 18.10.

[(C$_5$R$_5$)Ru(Me$_2$SC$_2$B$_9$H$_{10}$)RuCp*]PF$_6$ (7a,b). The solution of **6** (43 mg, 0.1 mmol) and [$(C_5R_5)Ru(MeCN)_3$]PF_6 (R = H, Me) (0.1 mmol) in $MeNO_2$ (2 mL) was refluxed for 4 h. Then the solvent was evaporated, the residue was dissolved in acetone and chromatographed on short Al_2O_3 column (10 cm) with acetone as the eluent. The orange band was collected, evaporated and the residue was reprecipitated from CH_2Cl_2 with ether to give **7a**,**b** as orange-red crystals (yield is ca. 60%).

For **7a**: ^1H NMR (CD_2Cl_2): δ = 5.50 (s, 5H, Cp), 2.63 (s, 3H, SMe_2), 2.12 (s, 3H, SMe_2), 1.71 (s, 15H, Cp*), −0.03 (bs, 1H, CH_{cage}), −0.84 (bs, 1H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 96.4, 31.5, 30.9, 18.6, 16.8, 12.4, 12.2, –2.7, –10.52 (1:1:1:1:1:1:1:1:1). Anal. Calcd. for $C_{19}H_{36}B_9F_6PRu_2S$: C 30.80, H 4.90. Found: C 31.23, H 5.08.

For **7b**: ^{1}H NMR (CD_2Cl_2): δ = 2.63 (s, 3H, SMe_2), 2.13 (s, 3H, SMe_2), 1.70 (s, 15H, Cp*), 1.64 (s, 15H, Cp*), −0.72 (bs, 1H, CH_{cage}), −1.41 (bs, 1H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 97.8, 35.1, 29.9, 18.7, 13.1, 12.4, –2.9, –10.9 (1:1:1:2:1:1:1:1). Anal. Calcd. for $C_{24}H_{46}B_9F_6PRu_2S$: C 35.34, H 5.72. Found: C 35.89, H 5.96.

$[(C_4Me_4)Co(Me_2SC_2B_9H_{10})RuCp^*]PF_6$ (8). The solution of **6** (43 mg, 0.1 mmol) and $[(C_4Me_4)Co(MeCN)_3]PF_6$ (R = H, Me) (44 mg, 0.1 mmol) in $MeNO_2$ (2 mL) was refluxed for 4 h. Then the solvent was evaporated, the residue was dissolved in acetone and chromatographed on short Al_2O_3 column (10 cm) with acetone as the eluent. The orange band was collected, evaporated and the residue was reprecipitated from CH_2Cl_2 with ether to give **8** as red crystals (28 mg, 38%). ^{1}H NMR ($(CD_3)_2CO$): δ = 2.76 (s, 3H, SMe_2), 2.20 (s, 3H, SMe_2), 1.80 (s, 12H, C_4Me_4), 1.77 (s, 15H, Cp*), −0.14 (bs, 1H, CH_{cage}), −0.62 (bs, 1H, CH_{cage}); $^{11}B\{^1H\}$ NMR: δ = 106.6, 41.3, 31.4, 24.7, 21.6, 16.1, 14.9, 4.3, –4.8 (1:1:1:1:1:1:1:1:1). Anal. Calcd. for $C_{22}H_{43}B_9CoF_6PRuS$: C 35.62, H 5.84, B 13.11. Found: C 35.44, H 5.63, B 13.26.

$CpNi(C_2B_9H_{11})RuCp^*$ (9a). A mixture of Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) and $[CpNi(SMe_2)_2]BF_4$ (50 mg, 0.15 mmol) was stirred for 4 h in 5 ml of THF. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate dark-red crystals. Yield 42 mg (57%). ^{1}H NMR ($CDCl_3$): δ = 5.76 (5H, CpNi), 3.88 (bs, 2H, CH_{cage}), 1.72 (s, 15H, Cp*); $^{11}B\{^1H\}$ NMR: δ = 39.72, 21.95, 11.29, 0.03, −5.83 (1:2:3:1:2). Anal. Calcd. for $C_{17}H_{31}B_9NiRu$: C 41.46, H 6.34, B 19.76. Found: C 41.44, H 6.27, B 19.57.

$Cp^*Ni(C_2B_9H_{11})RuCp^*$ (9b). To the cooled (–78 °C) solution of $NiBr_2$·DME (46 mg, 0.15 mmol) in THF (3 ml) the suspension of Cp*Li in THF (1 ml, 0.15 mmol) was added and the resulting mixture was stirred for 20 min to produce $[Cp^*NiBr]_2$. Then complex Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) was added and the mixture was stirred for additional 1 h. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate dark-red crystals. Yield 24 mg (29%). ^{1}H NMR ($CDCl_3$): δ = 3.28 (bs, 2H, CH_{cage}), 1.75 (15H, Cp*Ni), 1.70 (s, 15H, Cp*); $^{11}B\{^1H\}$ NMR: δ = 35.11, 21.99, 17.02, 9.79, 4.07, −7.30 (1:2:1:2:1:2). Anal. Calcd. for $C_{22}H_{41}B_9NiRu$: C 47.00, H 7.30, B 17.31. Found: C 47.24, H 7.33, B 17.09.

$(C_6Me_6)Co(C_2B_9H_{11})RuCp^*$ (10). A mixture of Tl[3-Cp*-3,1,2-$RuC_2B_9H_{11}$] (**1**) (86 mg, 0.15 mmol) and $[Co(C_6Me_6)_2]PF_6$ (79 mg, 0.15 mmol) was stirred for 4 h in 5 ml of THF. The resulting solution was evaporated, the residue was dissolved in CH_2Cl_2 and eluted through a short layer of Al_2O_3 (3 cm). The red fraction was reduced in vacuo to ca. 2 ml and excess of petroleum ether was added to precipitate dark-red crystals. Yield 50 mg (56%). ^{1}H NMR ($CDCl_3$): δ = 2.84 (bs, 2H, CH_{cage}), 2.15 (18H, (C_6Me_6Co), 1.67 (s, 15H, Cp*); $^{11}B\{^1H\}$ NMR: δ = 30.54, 13.35, 8.57, −0.81, −9.92 (1:3:2:1:2). Anal. Calcd. for $C_{24}H_{42}B_9CoRu$: C 49.03, H 7.20, B 16.55. Found: C 49.24, H 7.48, B 16.30.

Reduction of 2b. To the bright red suspension of **2b** (60 mg, 0.1 mmol) in 3 ml of THF a solution of $NaC_{10}H_8$ in THF (0.2 ml, 0.5M, 0.1 mmol) was added. The dissolution occurs immediately and the reaction mixture turns dark violet. The ^{11}B NMR spectrum of the sample confirms the formation of paramagnetic species assigned as [**2b**]$^-$. After 10 minutes the additional 0.2 ml of $NaC_{10}H_8$ solution was added and the reaction mixture became bright red. The addition of AcOH (0.1 ml) leads to the vigorous gas evolution and formation of **2b**. In order to record ^{1}H NMR spectra the reduction was performed in THF-d_8 by the Na/K alloy. ^{1}H NMR of [**2b**]$^{2-}$: δ = 1.87 (s, 30H, Cp*); $^{11}B\{^1H\}$ NMR: δ = –8.52, –16.57, –19.62 (2:4:2).

X-ray diffraction study. X-ray diffraction data were collected on a APEX II CCD diffractometer using molybdenum radiation [λ(MoKα) = 0.71072 Å, ω-scans] for **5** and **9A**. The substantial redundancy in data allowed empirical absorption correction to be applied with SADABS by multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positional and anisotropic displacement parameters of the disordered Cp ring and boron atoms in one of the independent molecules in **9a** were refined with the constraints on the bond length (DFIX) and anisotropic displacement parameters (EADP). C-H hydrogen atoms in Cp and cyclobutadiene ligands were placed in calculated positions and refined within the riding model, while C-H and B-H hydrogen atoms of carborane polyhedron were located from the Fourier density synthesis. All calculations were performed with the SHELXTL software package.[11]

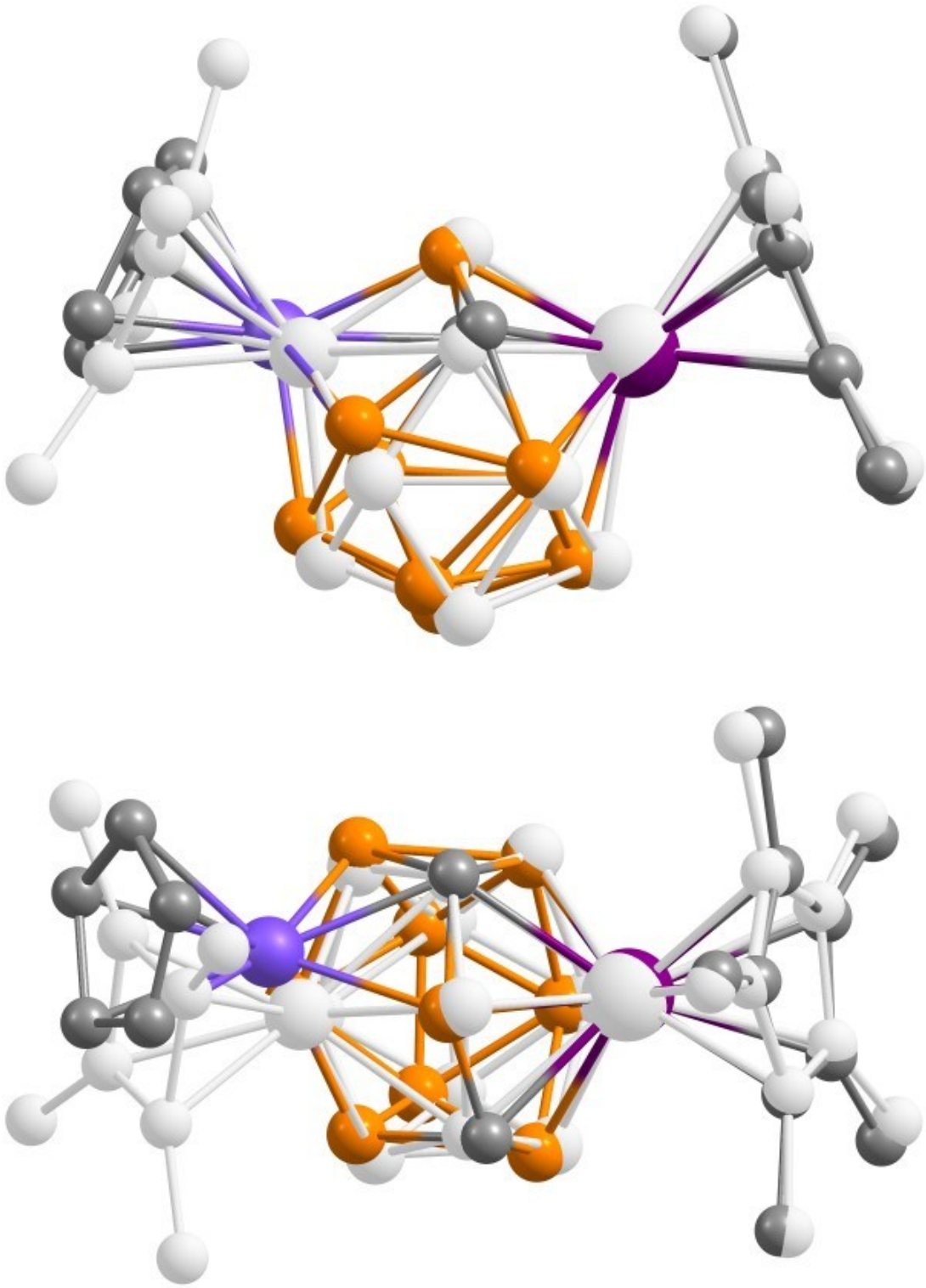
Crystal data and structure refinement parameters are listed in the table below. Crystallographic data for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre: CCDC- 1570484 (for **5**) and CCDC- 1570483 (for **9a**). These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement parameters for **5** and **9a**.

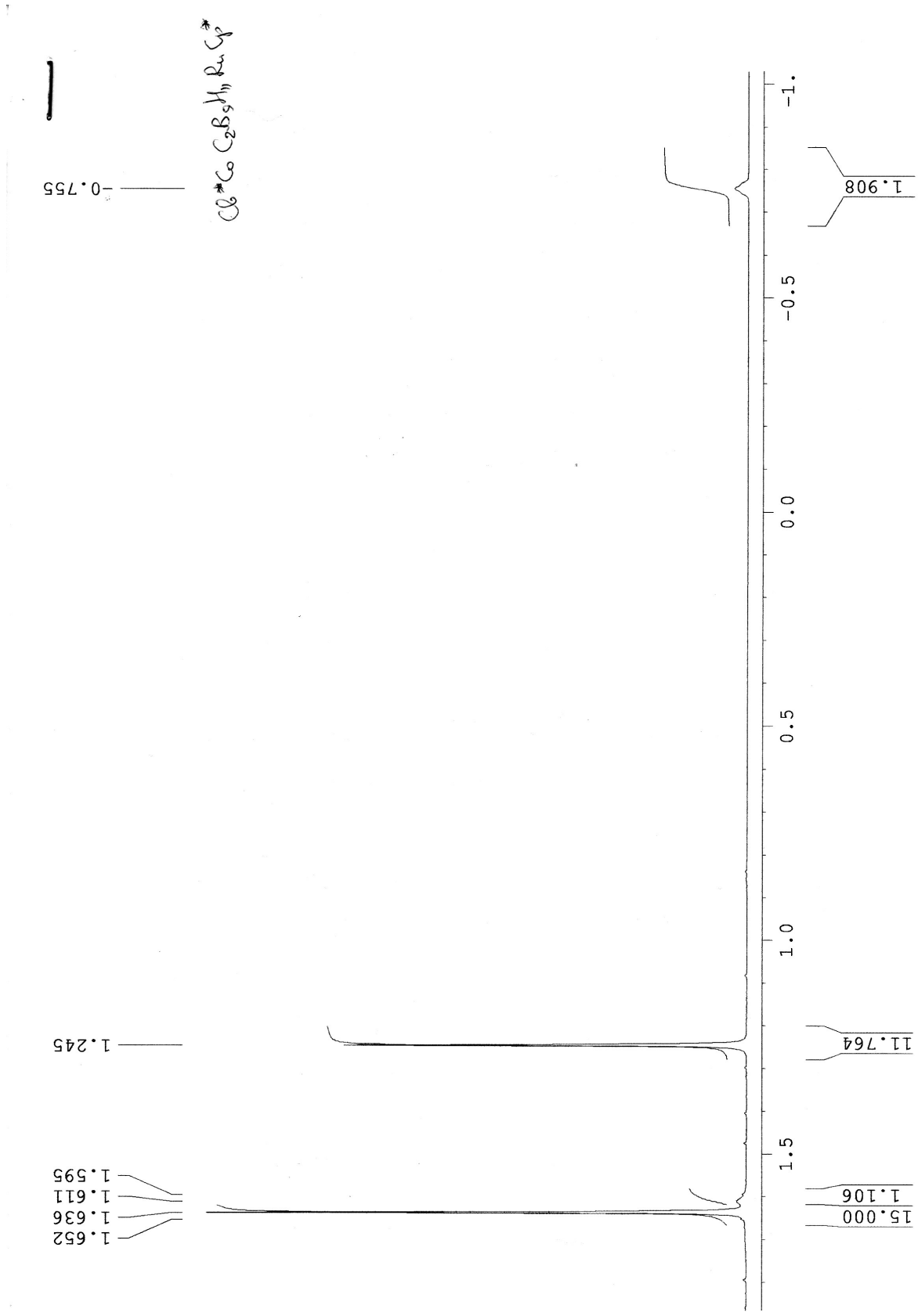
	5	**9a**
Brutto formula	$C_{20}H_{38}B_9CoRu$	$C_{17}H_{31}B_9NiRu$
Formula weight	535.79	492.49
T, K	120	120
Space group	$P2_1/c$	$Pca2_1$
Z(Z')	4	8(2)
a/Å	8.2693(9)	14.285(4)
b/Å	14.9393(16)	10.242(3)
c/Å	20.259(2)	28.482(7)
β/°	100.603(2)	90.000
Volume/Å^3	2460.0(5)	4167.4(18)
ρ_{calc}g/cm^3	1.447	1.570
μ/cm^{-1}	1.295	16.29
F(000)	1096	2000
$2\theta_{max}$, °	60.00	58
Reflections collected (R_{int})	20373(0.1578)	44789 (0.0381)
Independent reflections	7146	11044
Reflections with I>2σ(I)	3194	9293
Parameters	293	514
R_1 [I>2σ (I)]	0.0545	0.0419
wR_2	0.1284	0.0938
GOF	0.952	1.142
Residual electron density, e·Å^{-3} (ρ_{min}/ρ_{max})	-0.877/ 1.325	-0.766/2.760

Computational details. Geometry optimizations were performed using PBE exchange-correlation functional,[12] the scalar-relativistic Hamiltonian,[13] atomic basis sets of generally-contracted Gaussian functions,[14] and a density-fitting technique[15] as implemented in a recent version of PRIRODA code.[16] The all-electron double-ζ basis set L1 augmented by one polarization function was used.[17] Preliminary search for transition states was performed at the B3LYP/TZ2P level by QST3 procedure available in Gaussian 98 program.[18] This was followed by transition state optimization carried out by PRIRODA. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. ZPE corrections were added to total energy. The path of the reaction was traced from the transition state to the product and back to the reactant using the Intrinsic Reaction Coordinate method (IRC).[19] The visualization of calculation results was performed by ChemCraft (version 1.6) software (www.chemcraftprog.com). Cartesian coordinates for the optimized structure are available as Supporting information in form of the combined xyz file.

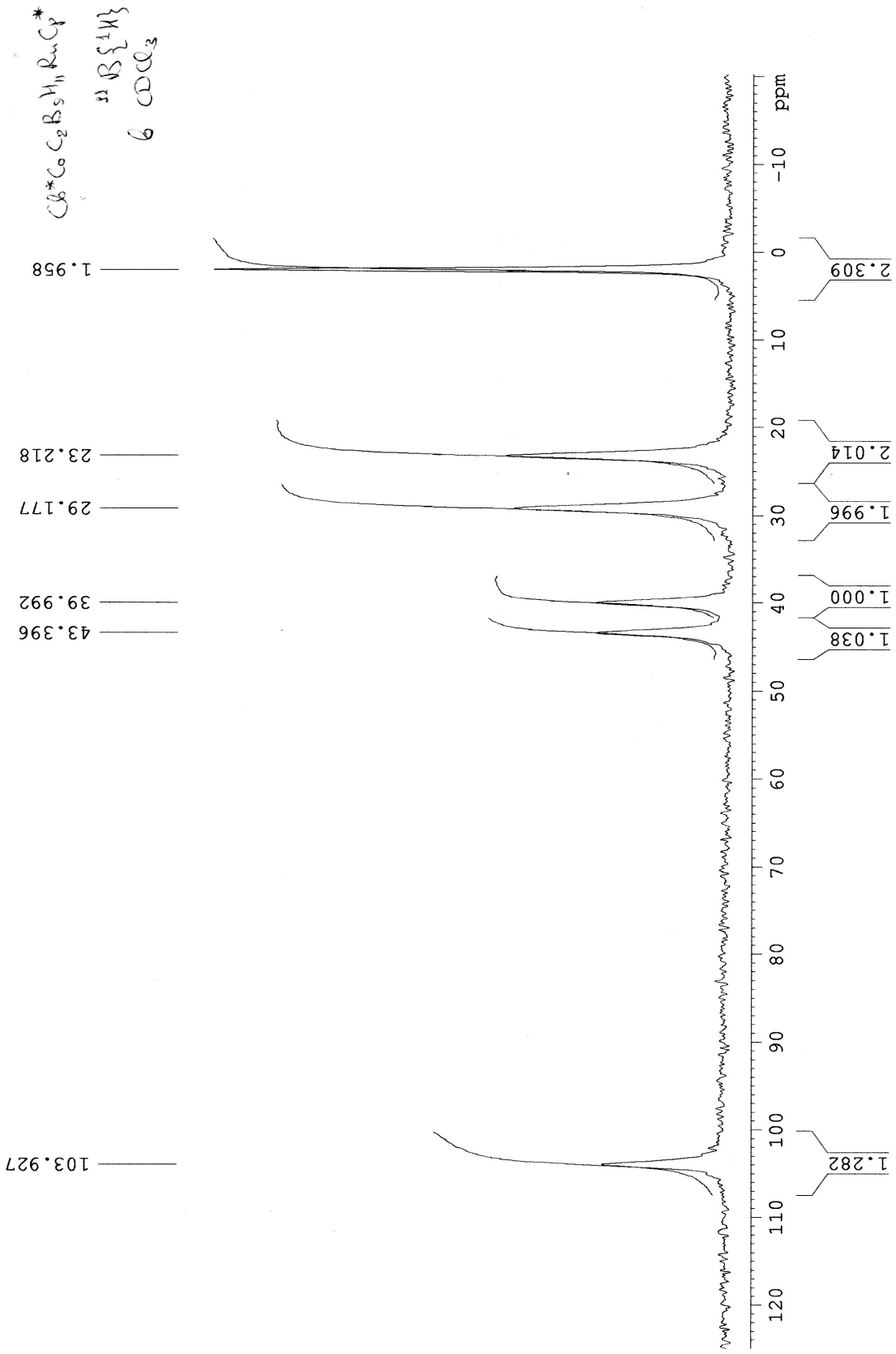
Figure 1S. Overlay of the X-ray structures of the C_s-symmetrical metallacarborane $(C_4Me_4)Co(C_2B_9H_{11})RuCp^*$ (**5**; shown in white) and the distorted metallacarborane $CpNi(C_2B_9H_{11})RuCp^*$ (**9a**; coloured).



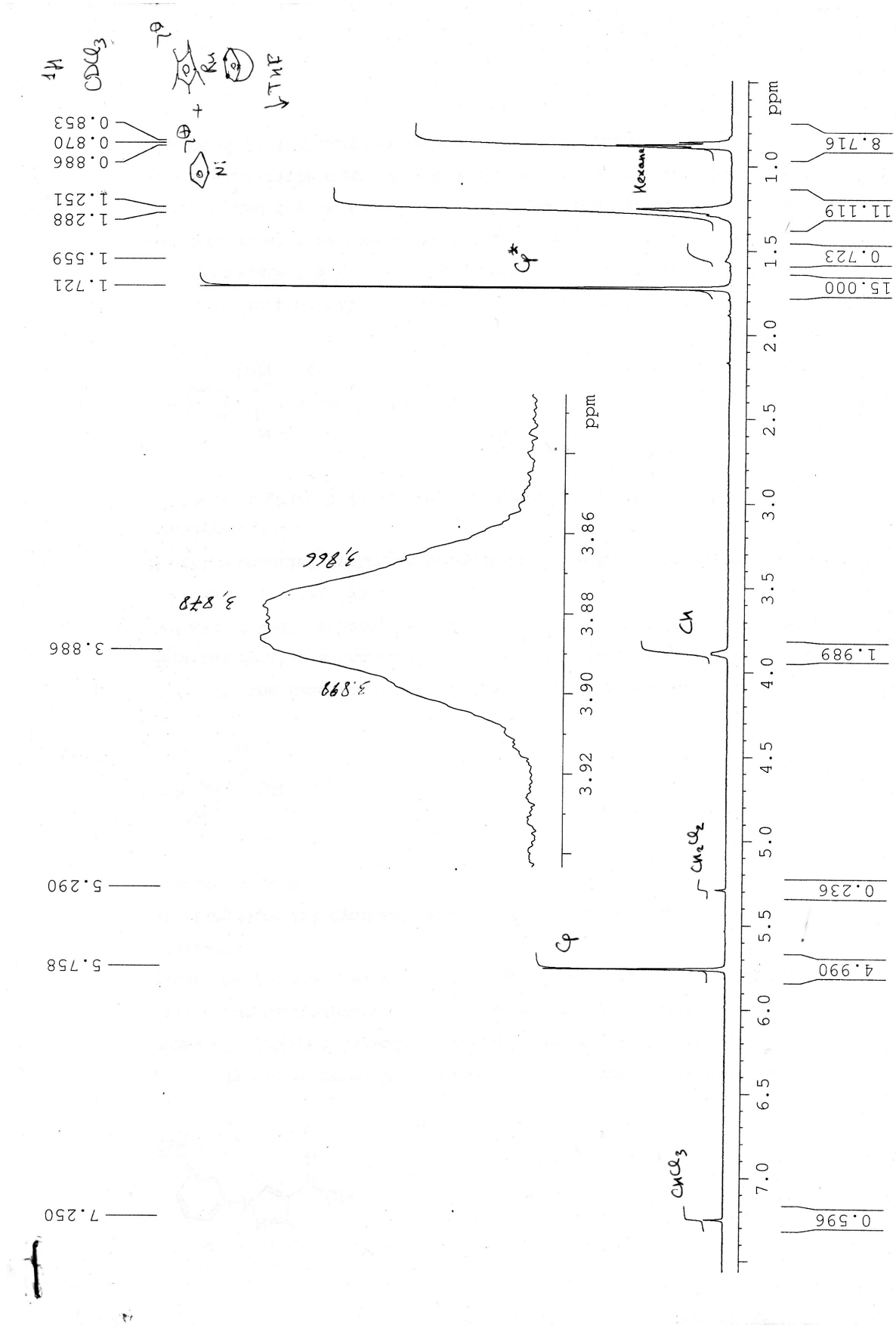
^{1}H NMR spectrum of $(C_4Me_4)Co(C_2B_9H_{11})RuCp^*$ (5) in $CDCl_3$



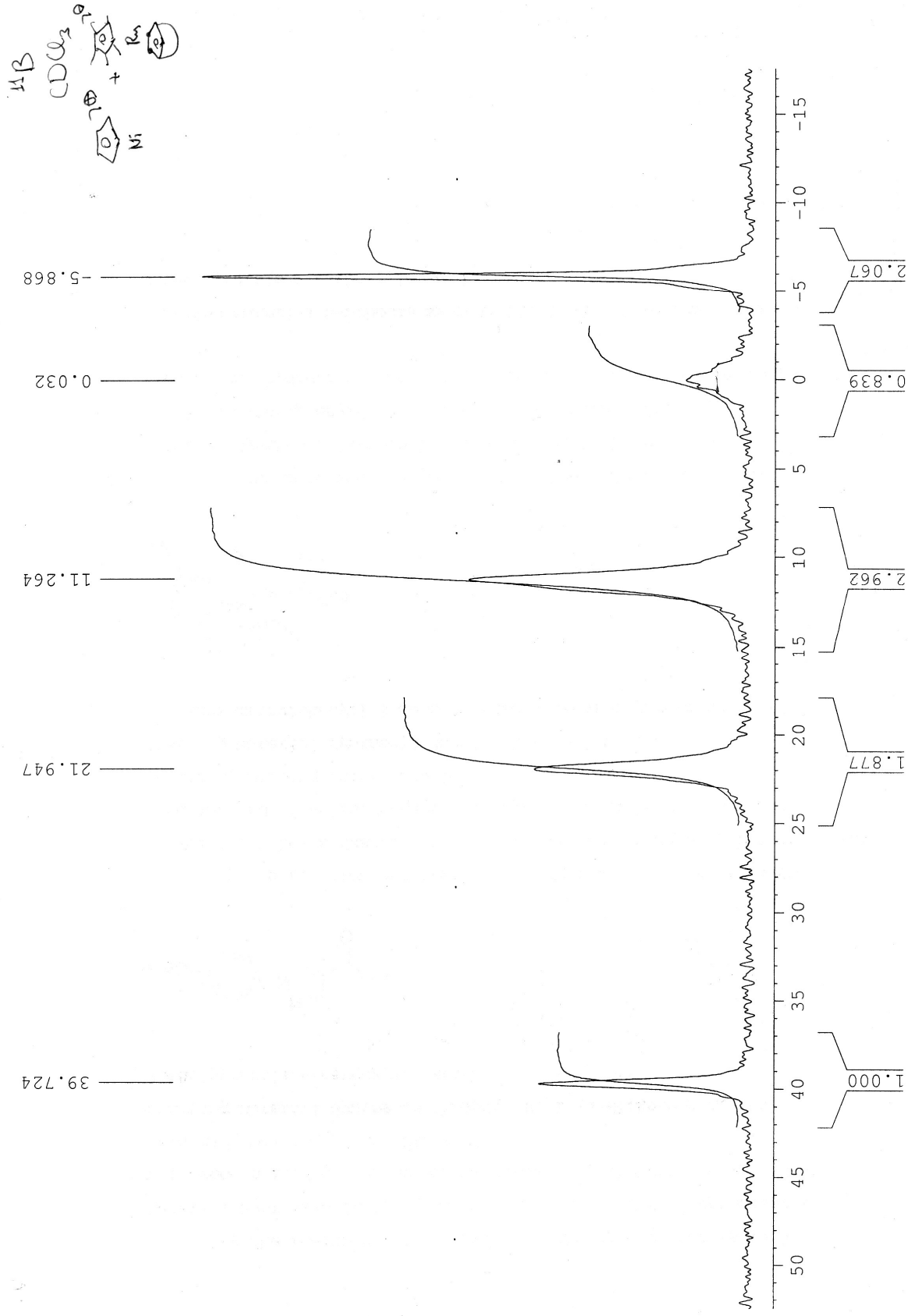
^{11}B NMR spectrum of $(C_4Me_4)Co(C_2B_9H_{11})RuCp^*$ (5) in $CDCl_3$



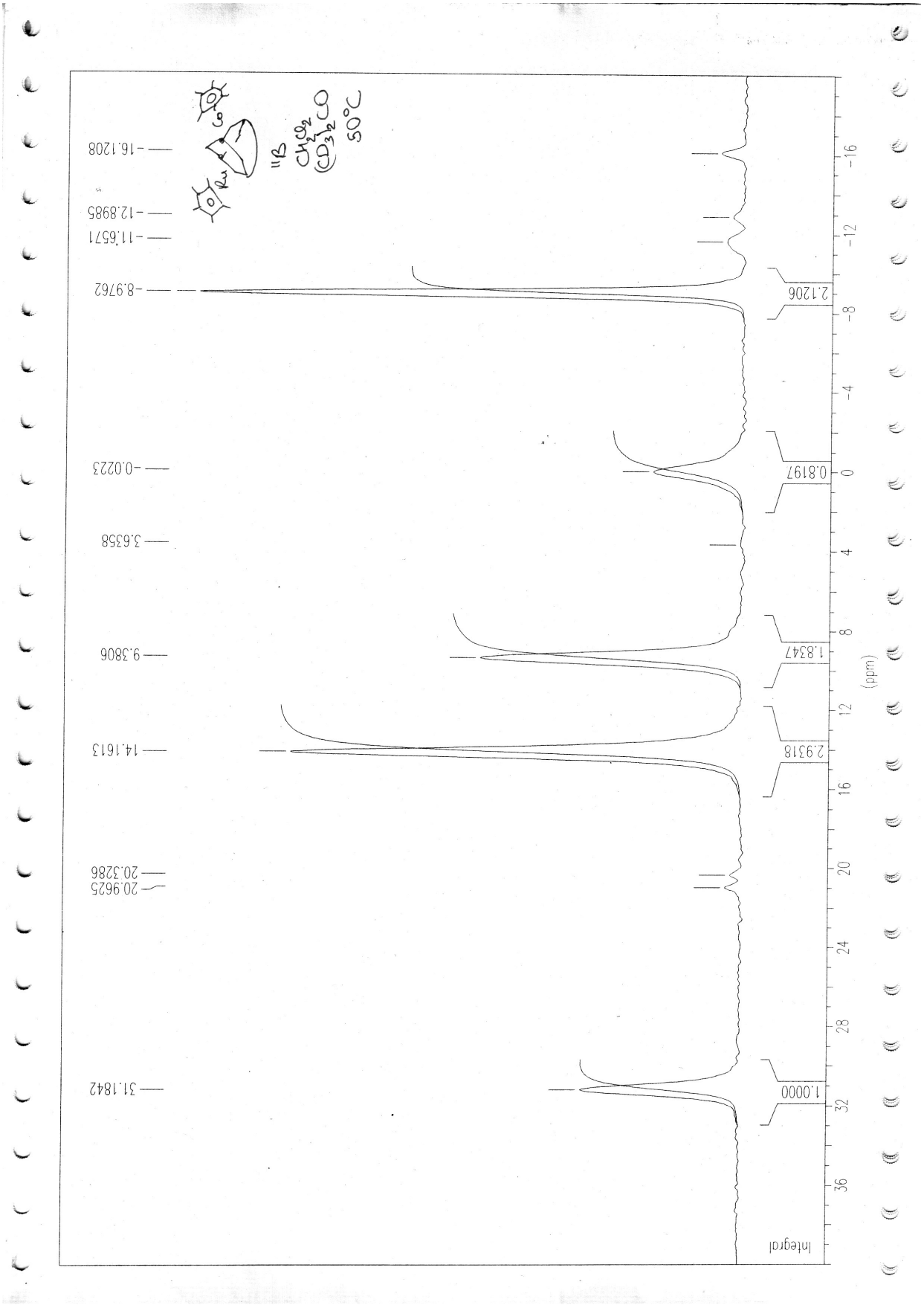
^{1}H NMR spectrum of $CpNi(C_2B_9H_{11})RuCp^*$ (9a) in $CDCl_3$



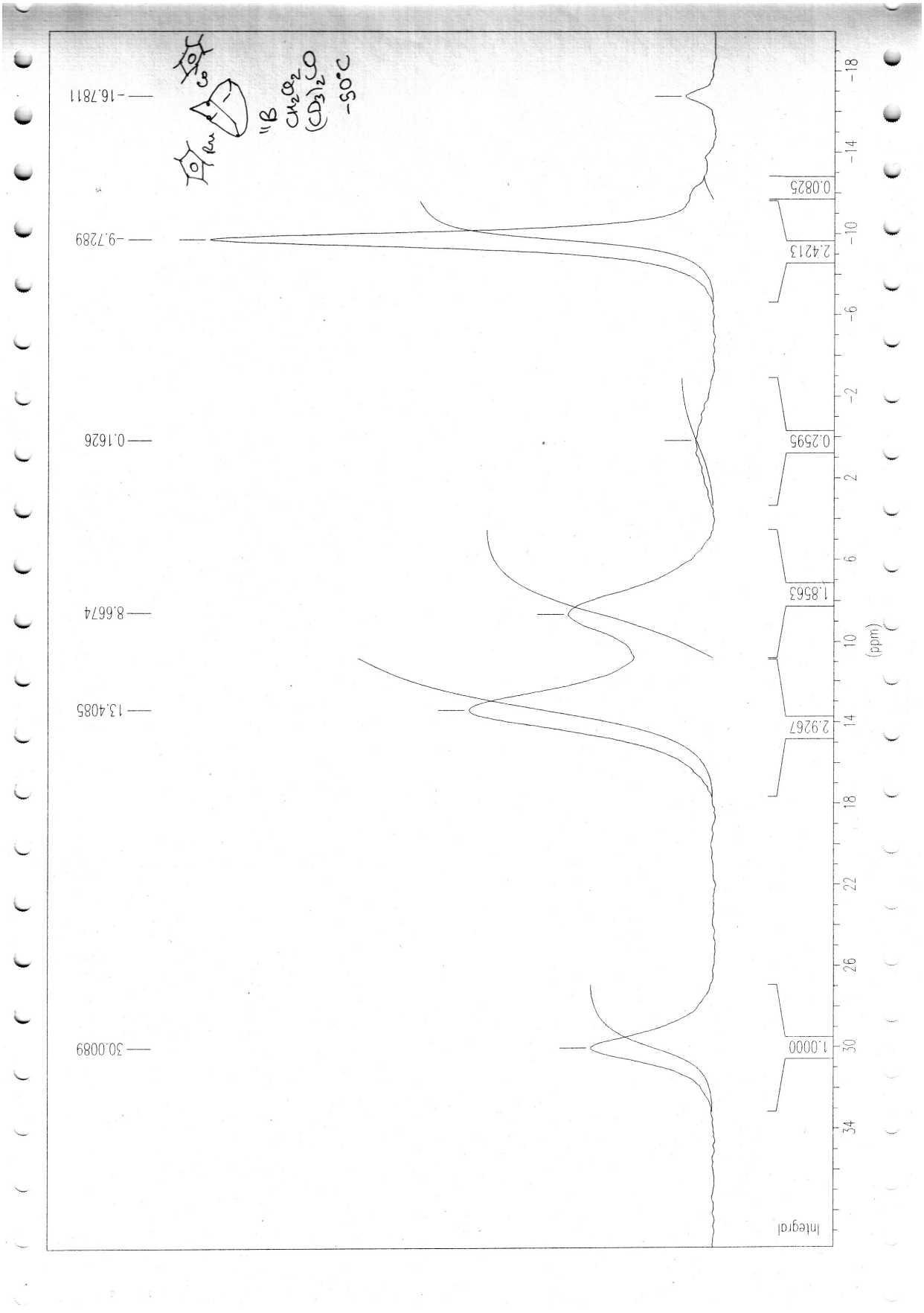
^{11}B NMR spectrum of $CpNi(C_2B_9H_{11})RuCp^*$ (9a) in $CDCl_3$



^{11}B NMR spectrum of $(C_6Me_6)Co(C_2B_9H_{11})RuCp^*$ (10) in $CH_2Cl_2/(CD_3)_2CO$ at 50 °C



^{11}B NMR spectrum of $(C_6Me_6)Co(C_2B_9H_{11})RuCp^*$ (10) in $CH_2Cl_2/(CD_3)_2CO$ at −50 °C



References

[1] Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307.

[2] (a) Butovskii, M. V.; Englert, U.; Fil'chikov, A. A.; Herberich, G. E.; Koelle, U.; Kudinov, A. R. *Eur. J. Inorg. Chem.* **2002**, 2656. (b) Mutseneck, E. V.; Loginov, D. A.; Perekalin, D. S.; Starikova, Z. A.; Golovanov, D. G.; Petrovskii, P. V.; Zanello, P.; Corsini, M.; Laschi, F.; Kudinov, A. R. *Organometallics*, **2004**, *23*, 5944.

[3] (a) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (b) Kündig, E. P.; Monnier, F. R. *Adv. Synth. Catal*. **2004**, *346*, 901.

[4] Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501.

[5] Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Amer. Chem. Soc.* **1989**, *111*, 1698.

[6] Kuhn, N.; Winter, M. *Chem. Ztg*. **1983**, *107*, 73.

[7] Smith, H. D. Jr., Hawthorne, M. F. *Inorg. Chem*. **1974**, *13*, 2312.

[8] Kudinov, A. R.; Perekalin, D. S.; Rynin, S. S.; Lyssenko, K. A.; Grintselev-Knyazev, G. V.; Petrovskii, P. V. *Angew. Chem. Int. Ed.* **2002**, *41*, 4112.

[9] Kudinov, A. R.; Petrovskii, P. V.; Meshcheryakov, V. I.; Rybinskaya, M. I. *Russ. Chem. Bull.* **1999**, *48*, 1356.

[10] Krejčik, M.; Daněk, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179.

[11] Sheldrick, M. *Acta. Cryst.* **2008**, *A64*, 112.

[12] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[13] Dyall, K. G. *J. Chem. Phys.* **1994**, *100*, 2118.

[14] Laikov, D. N. *Chem. Phys. Lett.* **2005**, *416*, 116.

[15] Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151.

[16] Laikov, D. N.; Ustynyuk, Yu. A. *Russ. Chem. Bull.* **2005**, *54*, 820.

[17] Misochko, E. Ya.; Akimov, A. V.; Belov, V. A.; Tyurin, D. A.; Laikov, D. N. *J. Chem. Phys.* **2007**, *127*, 084301.

[18] Frisch, M. J.; Pople, J. A. et al. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[19] Fukui, K. *Acc. Chem. Res.* **1980**, *14*, 363.