Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Substitution Lability of the Perfluorinated Cp* Ligand in Rh(I) Complexes

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General Conditions

All reactions and workups (except the recrystallization of $[NEt_4][C_5(CF_3)_5]$ and $[NEt_4][C_5(CF_3)_4H]$) were performed under an argon atmosphere provided by *Linde*. Used glass equipment was dried by a heat gun under high vacuum (10^{-3} mbar) and flushed with argon three times. Syringes and needles were flushed three times with argon prior to use, while solids were added in argon stream. Low temperature reactions were carried out in a cooled ethanol-bath. Room temperature (rt) refers to 25 °C.

Solvents and Reagents

All reagents were provided by commercial suppliers and used without further purification, unless otherwise stated. Anhydrous CH_2Cl_2, MeCN, *n*-pentane were obtained through a FMBRAUN MB SPS-800 solvent system and stored over activated 3 Å molecular sieves. Deuterated solvents (CD_2Cl_2, $CDCl_3$, D_3-MeCN) were used as purchased and stored over activated 3 Å molecular sieves. Sulfolane and 18-crown-6 were heated at 60 °C for 24 h over activated 3 Å molecular sieves prior to use.

Pressure Reactions

The synthesis of $[NEt_4][C_5(CF_3)_5]$ involves high temperatures and volatile substances in a closed system. Therefore, it is assumed that a high pressure arises upon heating, requiring special caution while performing the reaction. The reaction vessel should not be opened or moved until the reaction is completed and reached rt.

Nuclear magnetic resonance (NMR)-spectroscopy

All NMR-spectra were measured on a *JEOL ECX 400* (400 MHz), *JEOL ECP 500* (500 MHz), *Varian INOVA 600* (600 MHz) or *Bruker Avance 700* (700 MHz), using deuterated solvents by the company *Eurisotop*. All spectra were measured at 298 K. Chemical shifts were reported in ppm and referenced according to the signal of the respective deuterated solvent. ^{19}F spectra are device-internal calibrated relative to the resonance signal of tetramethylsilane. Signal multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet or as combinations of the abbreviations to describe complex multiplicities. Coupling constants *J* are given in Hertz (Hz). All spectra were analyzed using *MestReNova* 14.0.0.[1] $^{13}C\{^1H\}$ NMR signals of $[C_5(CF_3)_5]^-$ are not visible due to pronounced coupling patterns.

Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were measured using a *Nicolet iS50* FT-IR-spectrometer or a *FT Bruker ALPHA* IR-spectrometer. Samples were measured by ATR (attenuated total reflection) technique. The wavenumbers are given in [cm^{-1}]. Following abbreviations were used to describe the signals: vs = very strong, s = strong, m = medium, w = weak, br = broad.

High Resolution Mass Spectroscopy (HRMS)

HRMS was performed on an *AGILENT 6210 ESI-TOF* spectrometer by electrospray ionization (ESI) or electron impact ionization (EI).

Elemental Analysis

Elemental analysis was performed using a VARIO EL (Fa. ELEMENTAR) analysator.

X-Ray Diffraction (XRD)

X-Ray data were collected on a BRUKER D8 Venture system. Data were collected at 100(2) K using graphite-monochromated Mo K_α radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard "ψ-ω scan techniques" and were scaled and reduced using Saint+software. The structures were solved by using Olex2[2] and XT[3] structure solution program using Intrinsic Phasing and refined with the XL refinement package[4-5] using Least Squares minimization. Drawings were generated with Mercury[6] and POV-Ray.[7] Crystallographic tables were generated with publcif.[8] Deposition number CCDC contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Density Functional Theory (DFT) Calculations

DFT calculations were performed with Gaussian 16.[9] Structure optimizations were done using B3LYP-D3/def2tzvp. Solutions were processed using Avogadro and Chemcraft 1.8.[10–11]

NMR Spectra

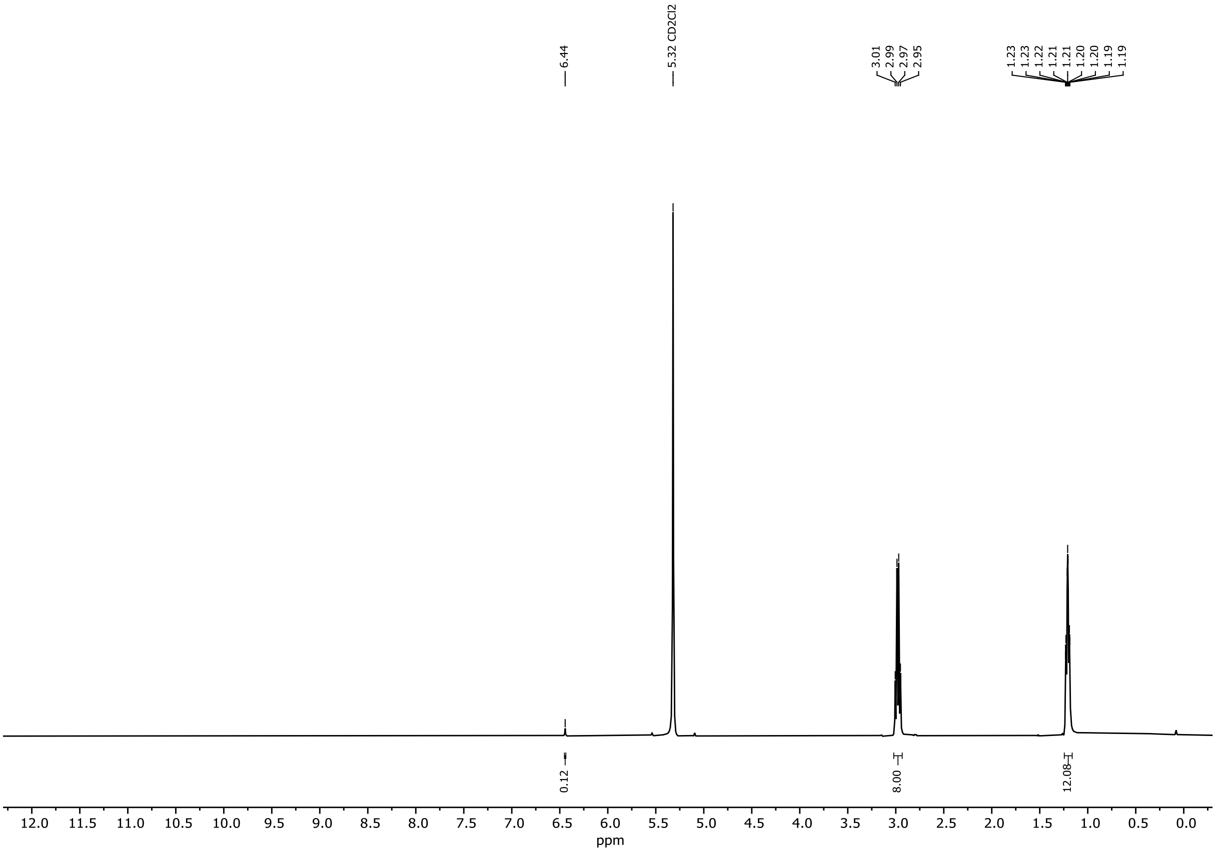

Figure 1: ^1H NMR (401 MHz, CD_2Cl_2, rt) spectrum of $[NEt_4][C_5(CF_3)_5]$ with quantities of $[NEt_4][C_5(CF_3)_4H]$.

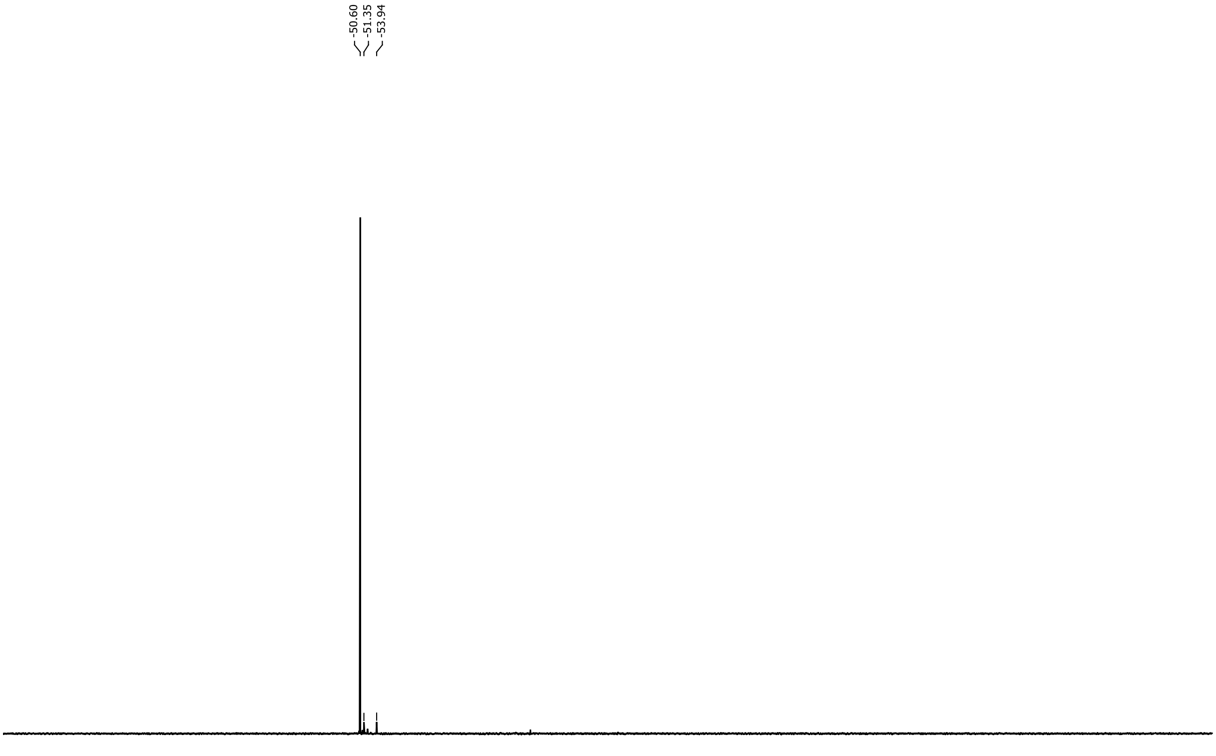

Figure 2: ^{19}F NMR (377 MHz, CD_2Cl_2, rt) spectrum of $[NEt_4][C_5(CF_3)_5]$ with quantities of $[NEt_4][C_5(CF_3)_4H]$.

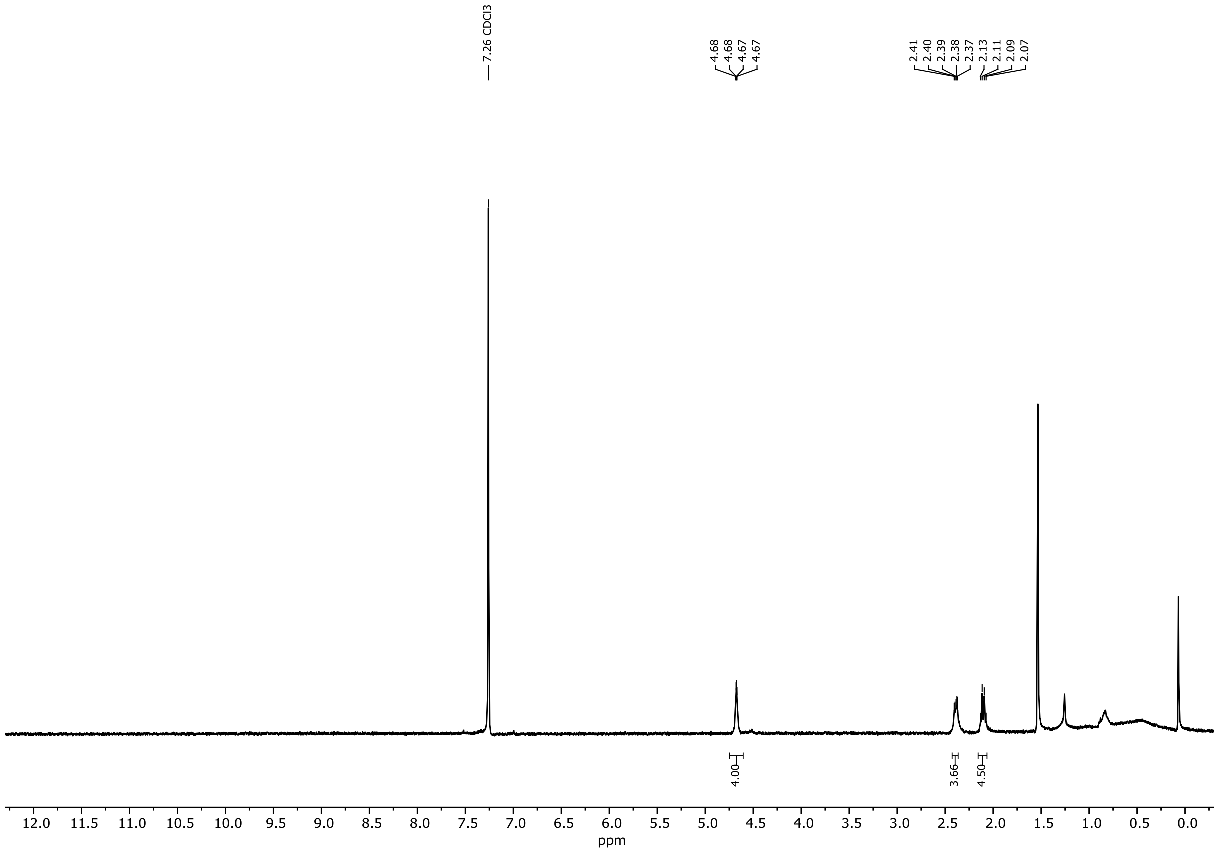

Figure 3: ^{1}H NMR (401 MHz, $CDCl_3$, rt) spectrum of $[Rh(COD)(C_5(CF_3)_5)]$.

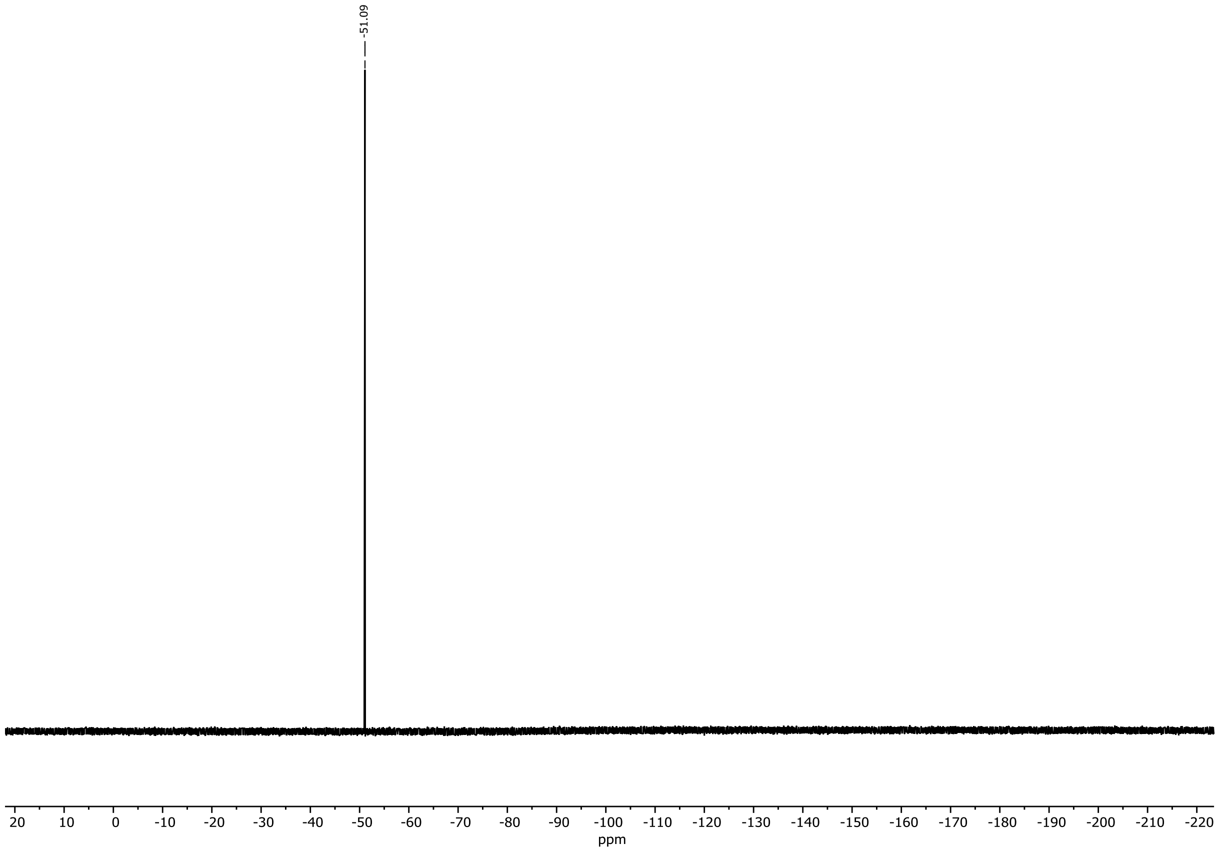

Figure 4: ^{19}F NMR (377 MHz, $CDCl_3$, rt) spectrum of $[Rh(COD)(C_5(CF_3)_5)]$.

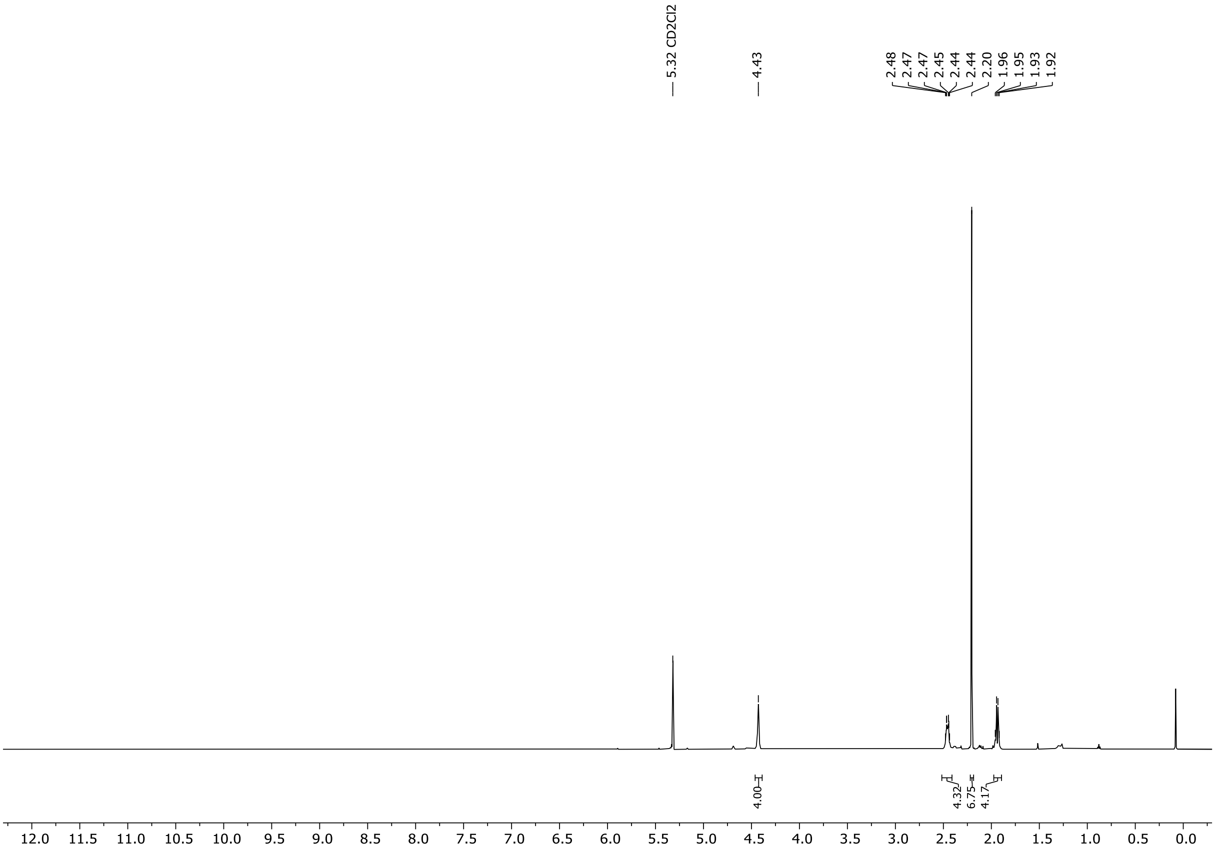

Figure 5: ^{1}H NMR (600 MHz, CD_2Cl_2, rt) spectrum of [Rh(COD)(MeCN)$_2$][$C_5(CF_3)_5$].

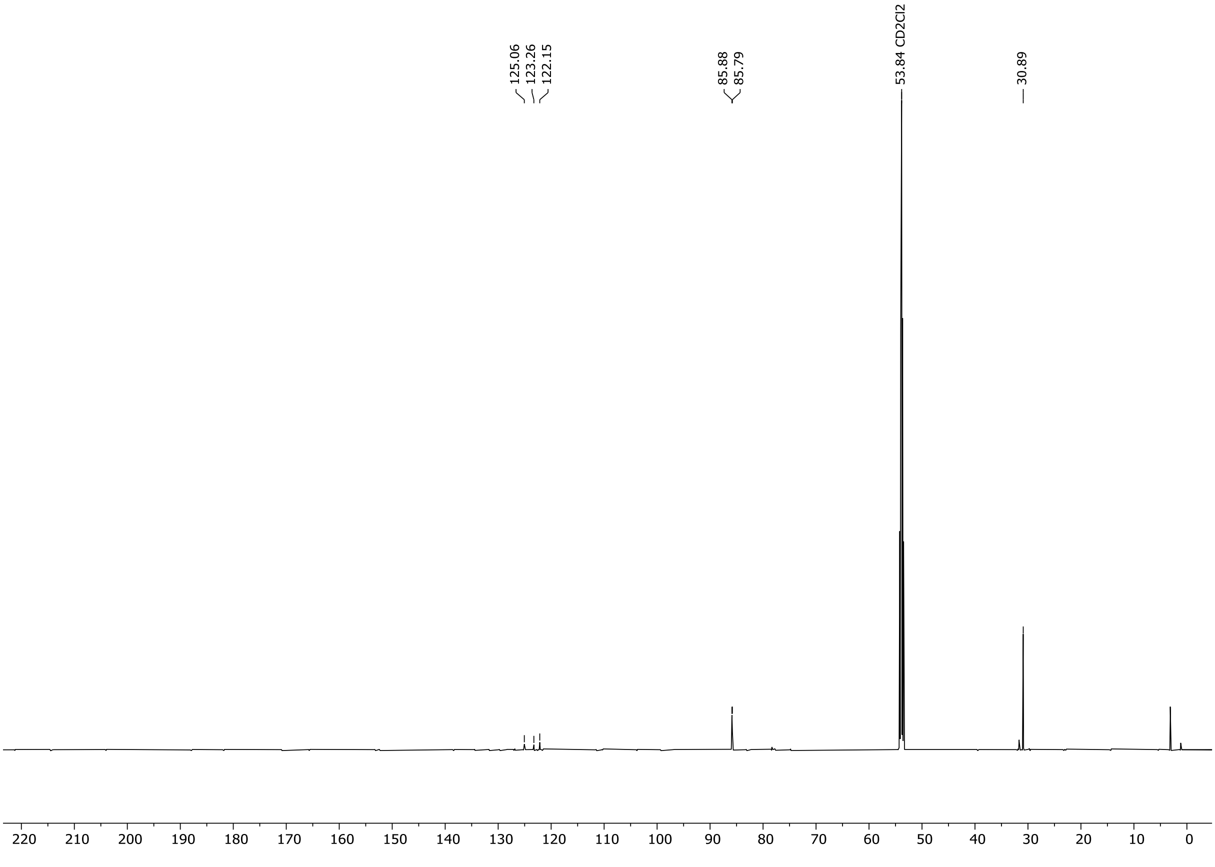

Figure 6: $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, rt) spectrum of [Rh(COD)(MeCN)$_2$][$C_5(CF_3)_5$].

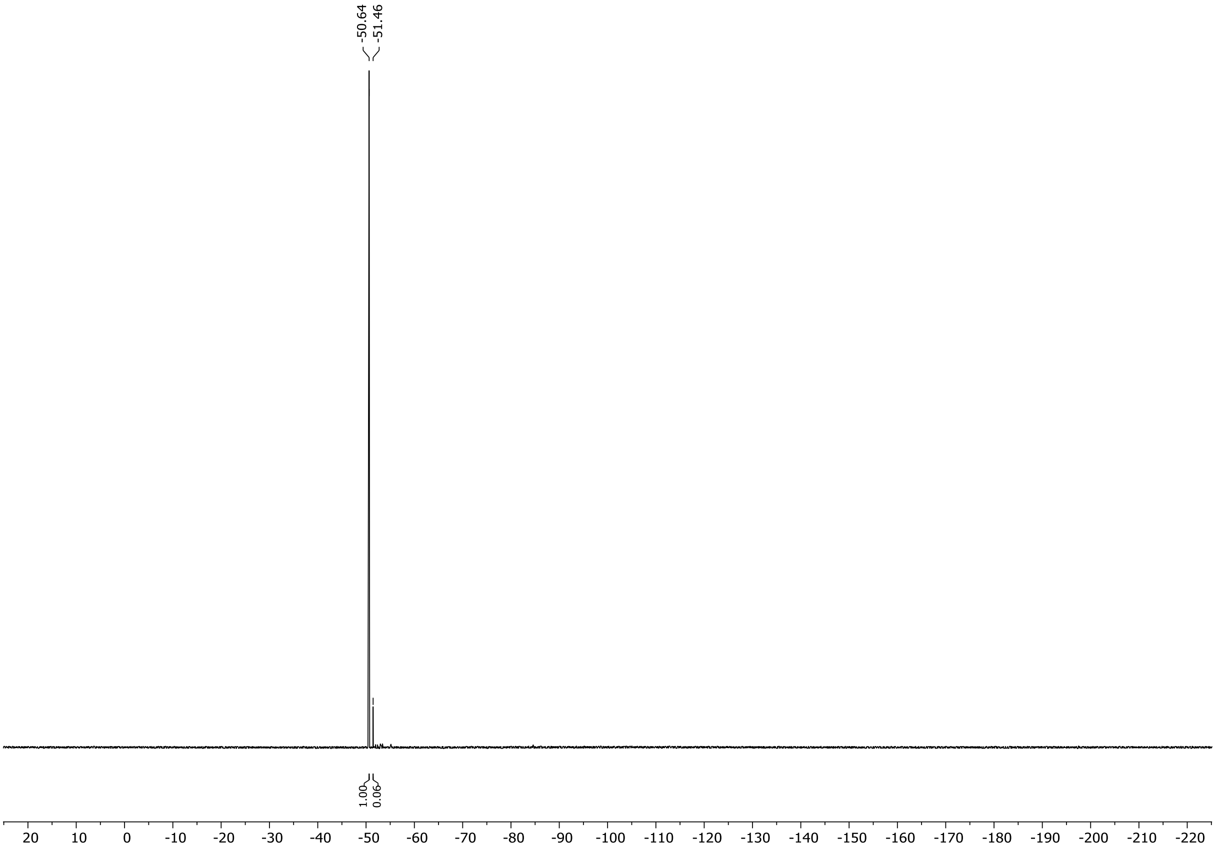

Figure 7: ^{19}F NMR (377 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(MeCN)_2][C_5(CF_3)_5]$ with minor quantities of $[Rh(COD)(C_5(CF_3)_5)]$.

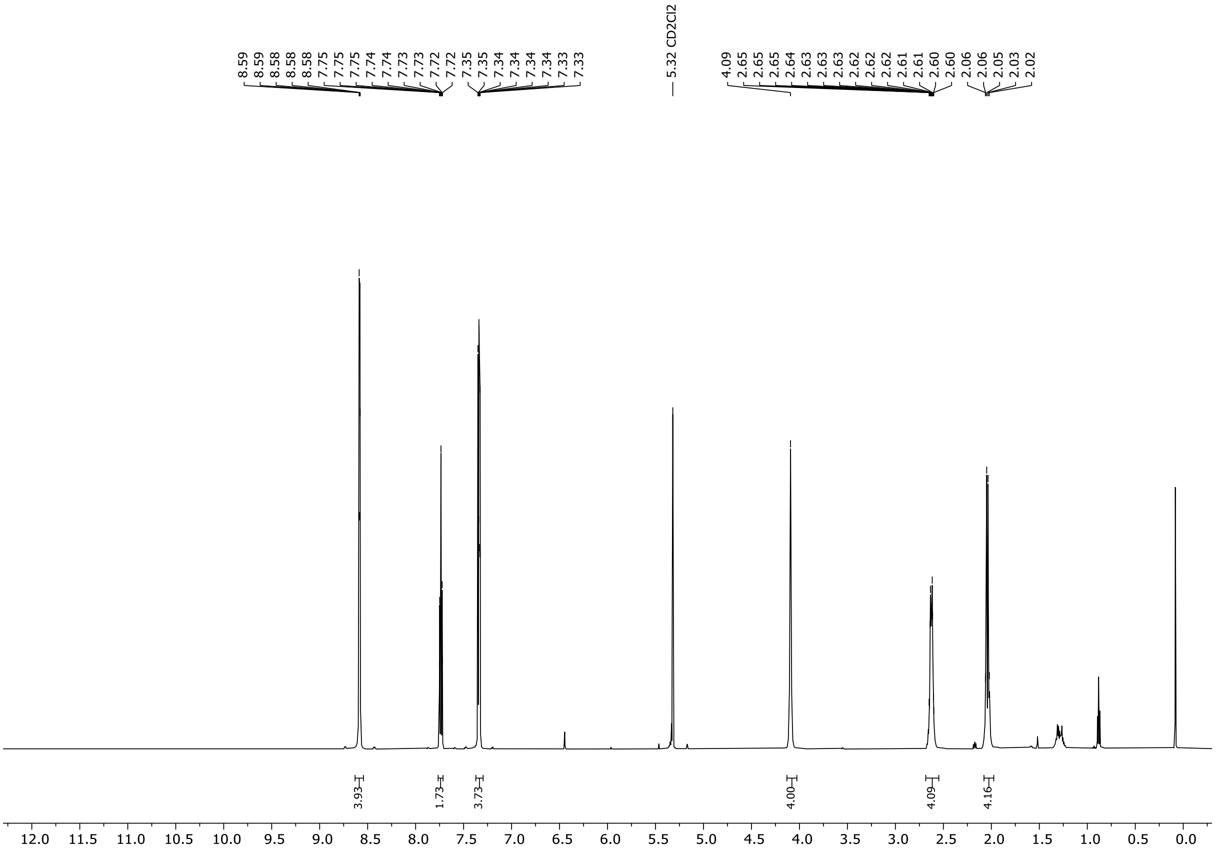

Figure 8: ^{1}H NMR (600 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(C_5H_5N)_2][C_5(CF_3)_5]$.

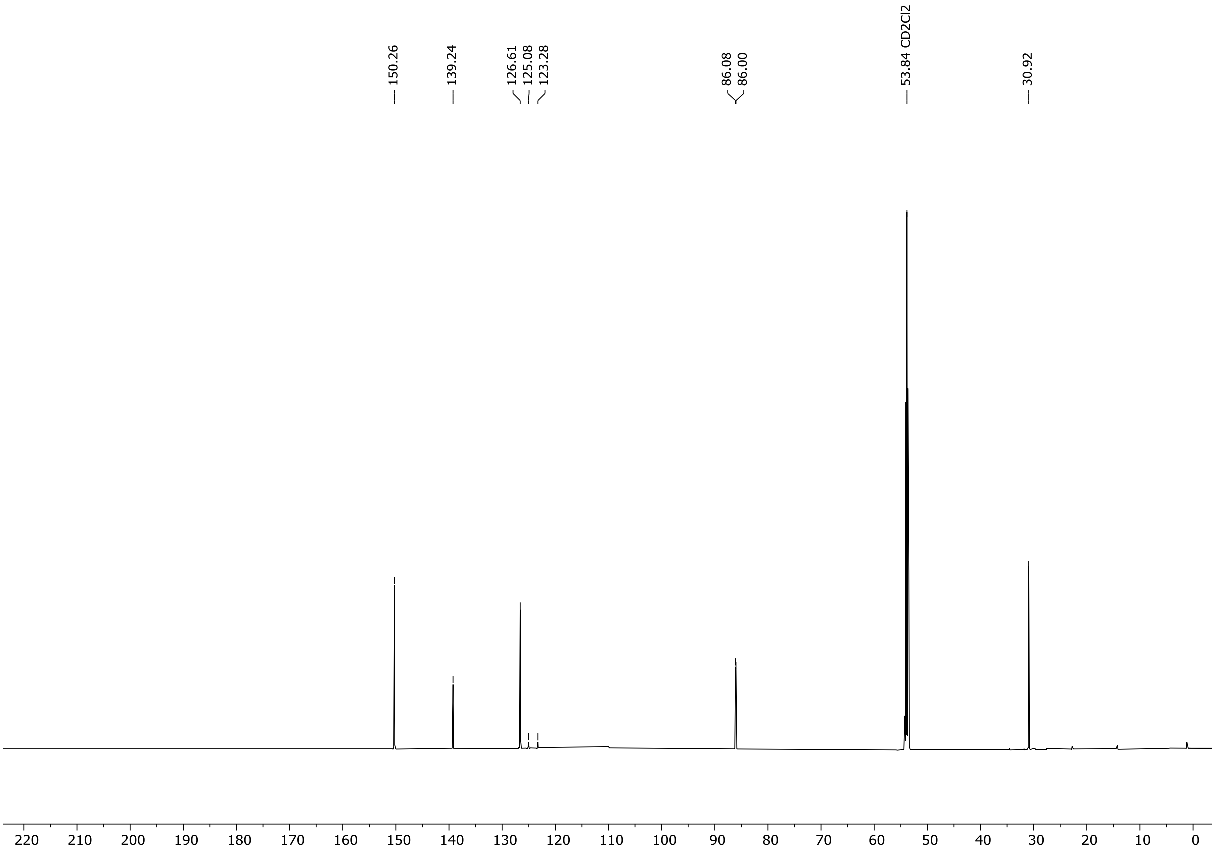

Figure 9: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(C_5H_5N)_2][C_5(CF_3)_5]$.

Figure 10: ^{19}F NMR (565 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(C_5H_5N)_2][C_5(CF_3)_5]$.

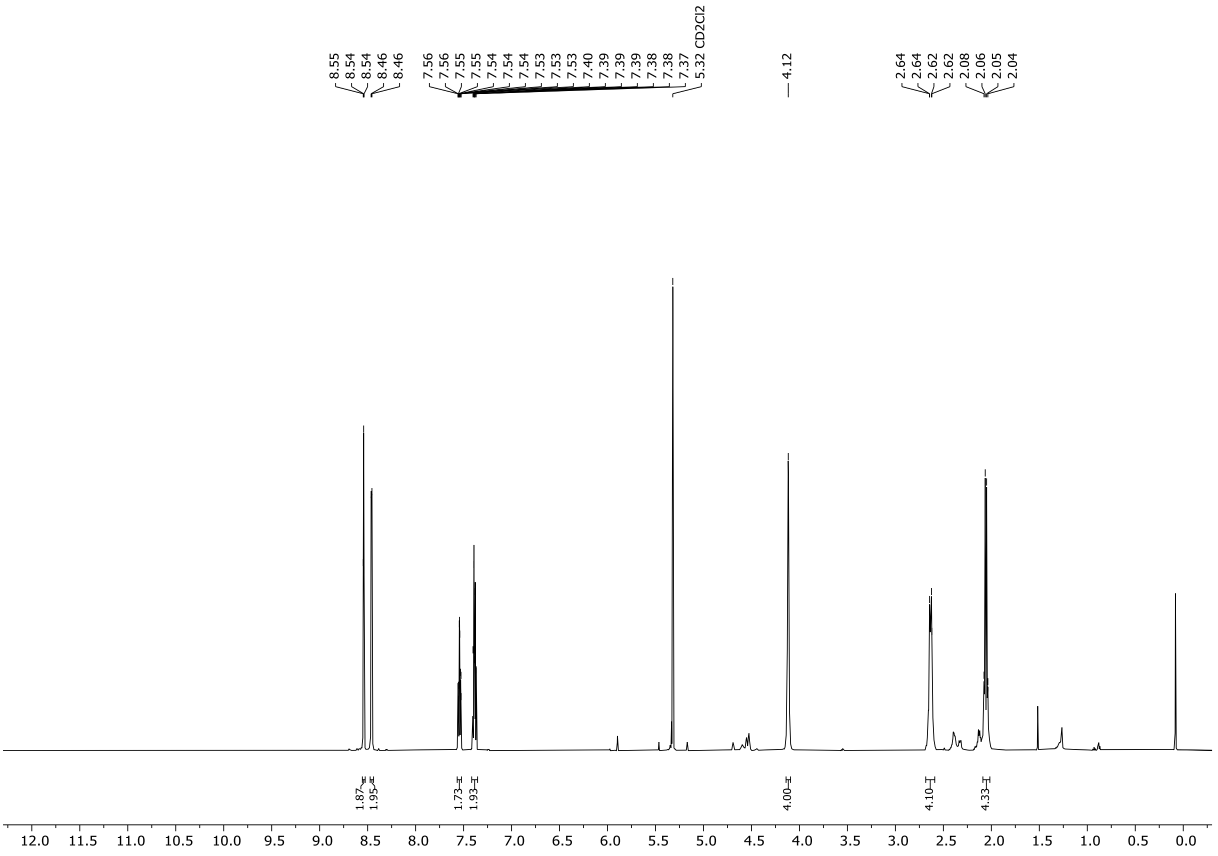

Figure 11: ^{1}H NMR (600 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

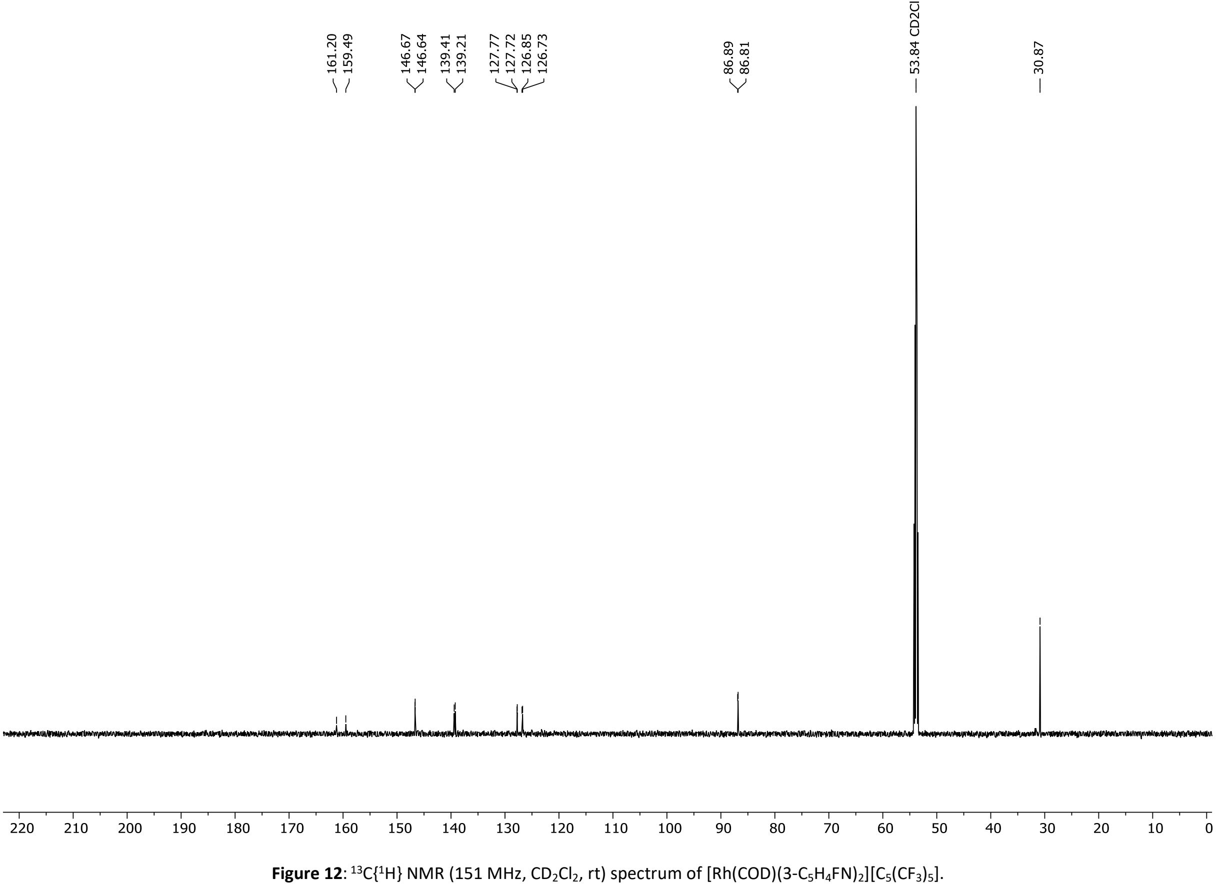

Figure 12: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

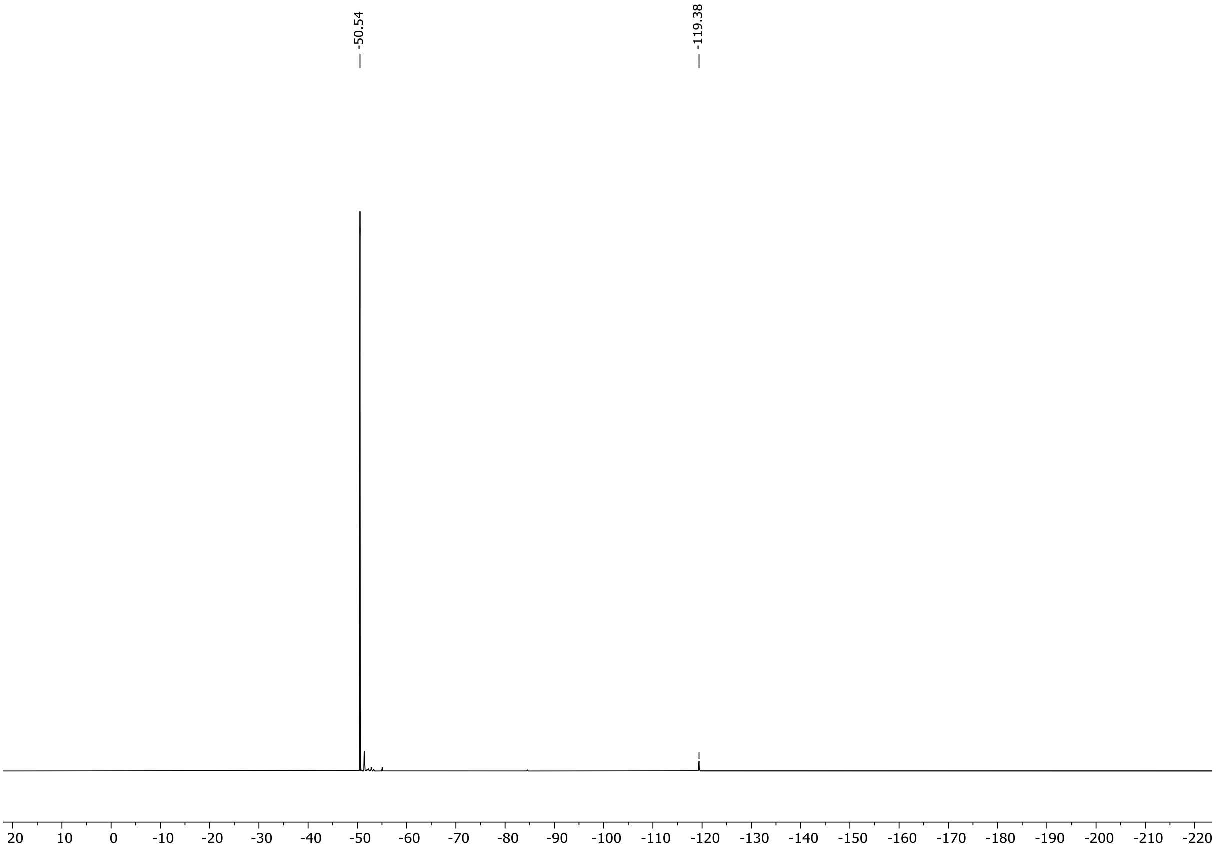

Figure 13: ^{19}F NMR (565 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

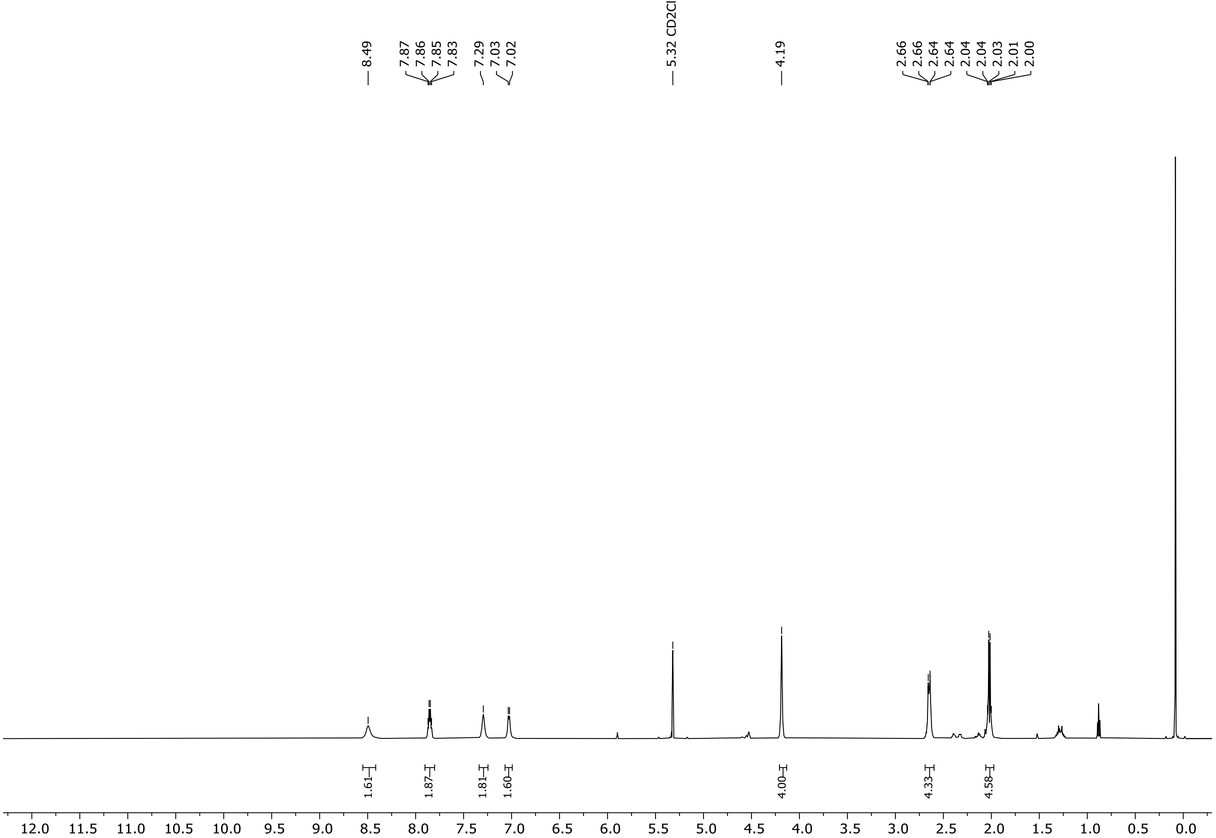

Figure 14: ^{1}H NMR (600 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(2\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

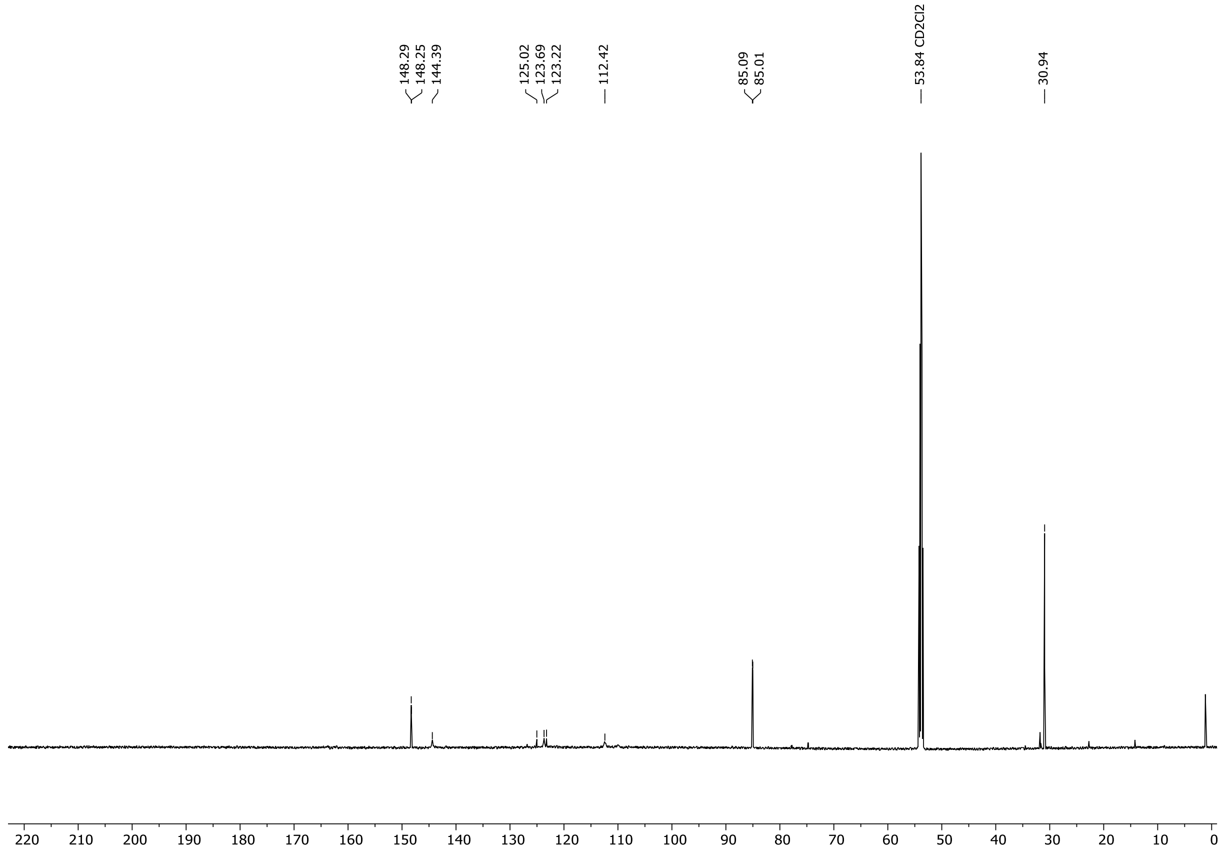

Figure 15: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(2\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

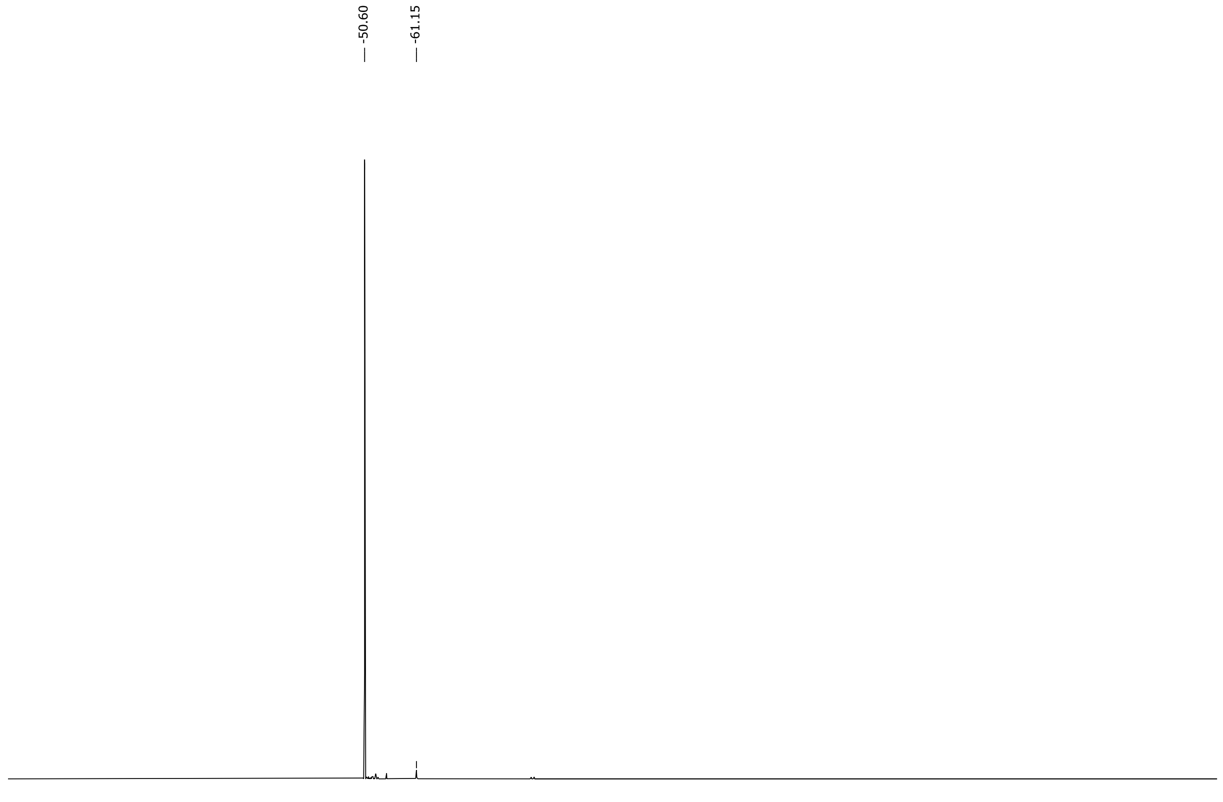

Figure 16: ^{19}F NMR (565 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(2\text{-}C_5H_4FN)_2][C_5(CF_3)_5]$.

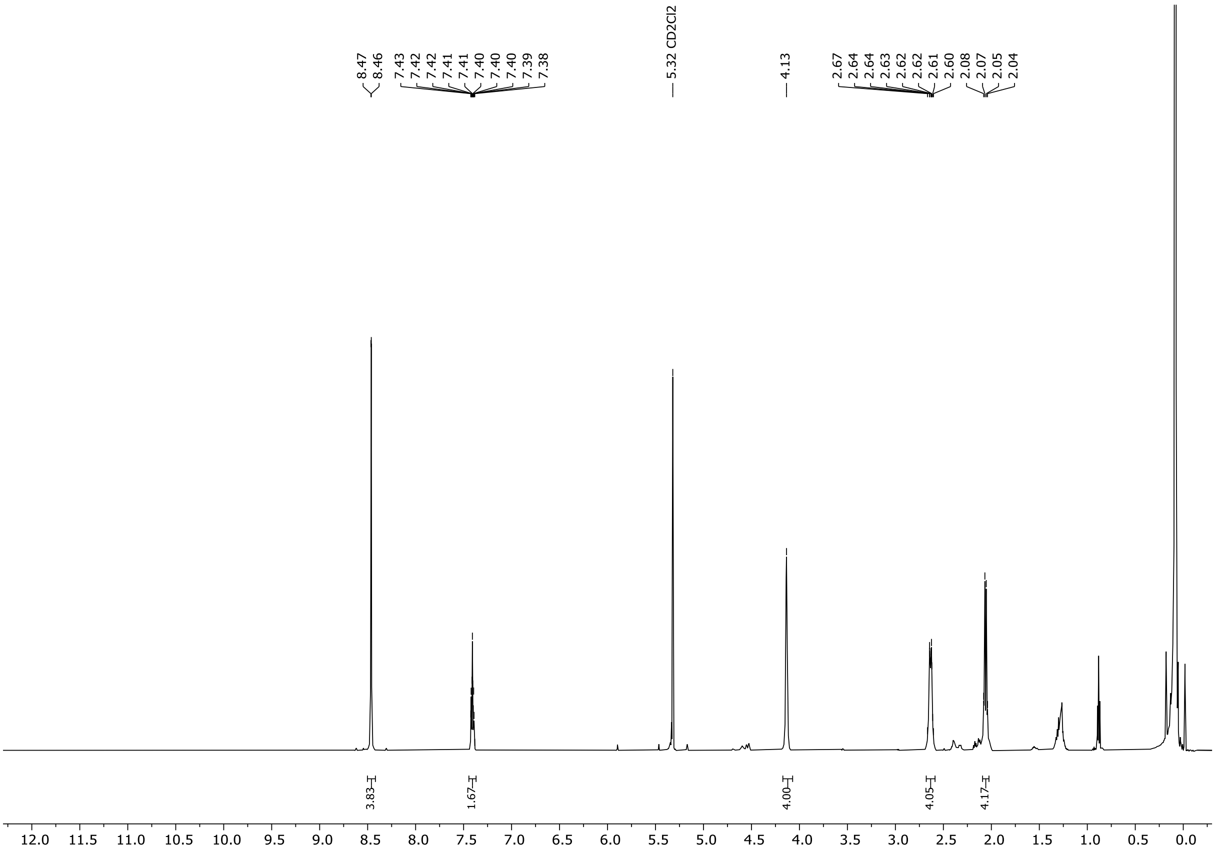

Figure 17: ^{1}H NMR (600 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3,5\text{-}C_5H_3F_2N)_2][C_5(CF_3)_5]$.

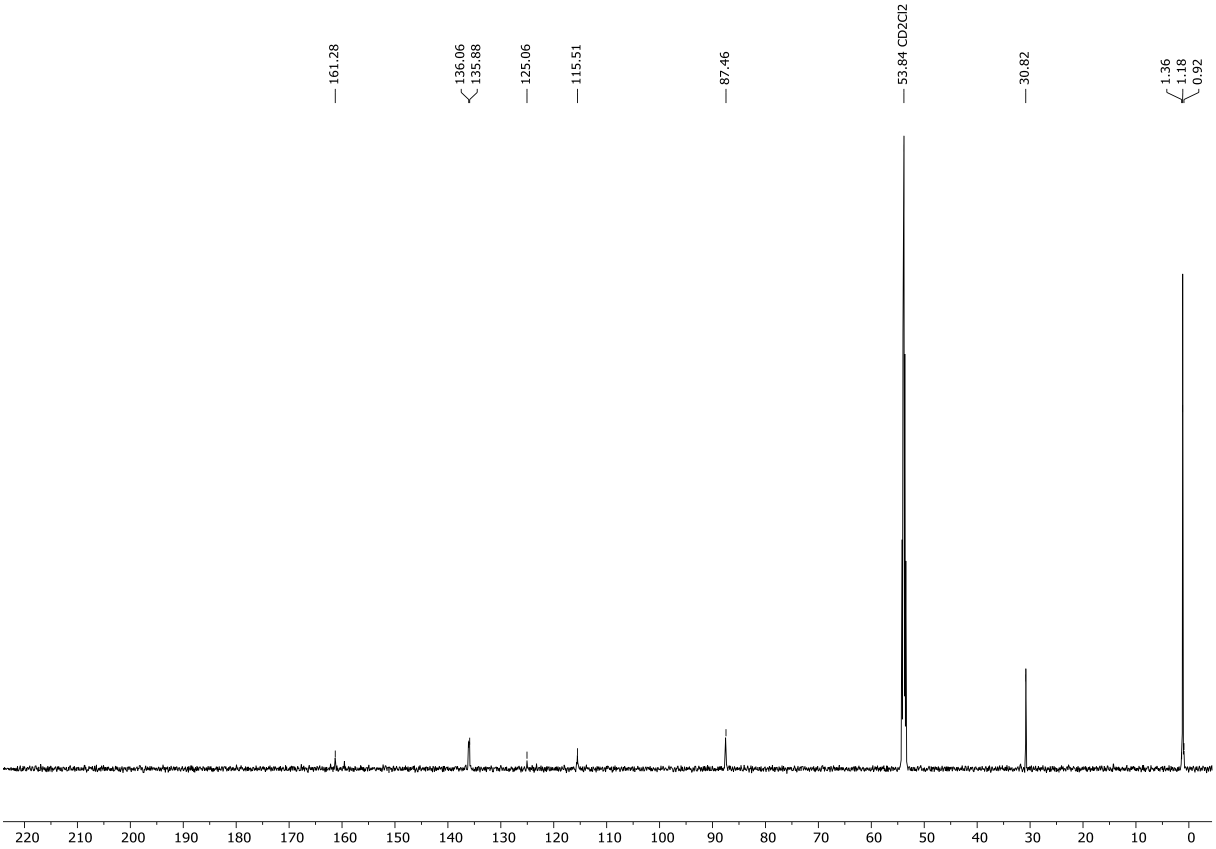

Figure 18: $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3,5\text{-}C_5H_3F_2N)_2][C_5(CF_3)_5]$.

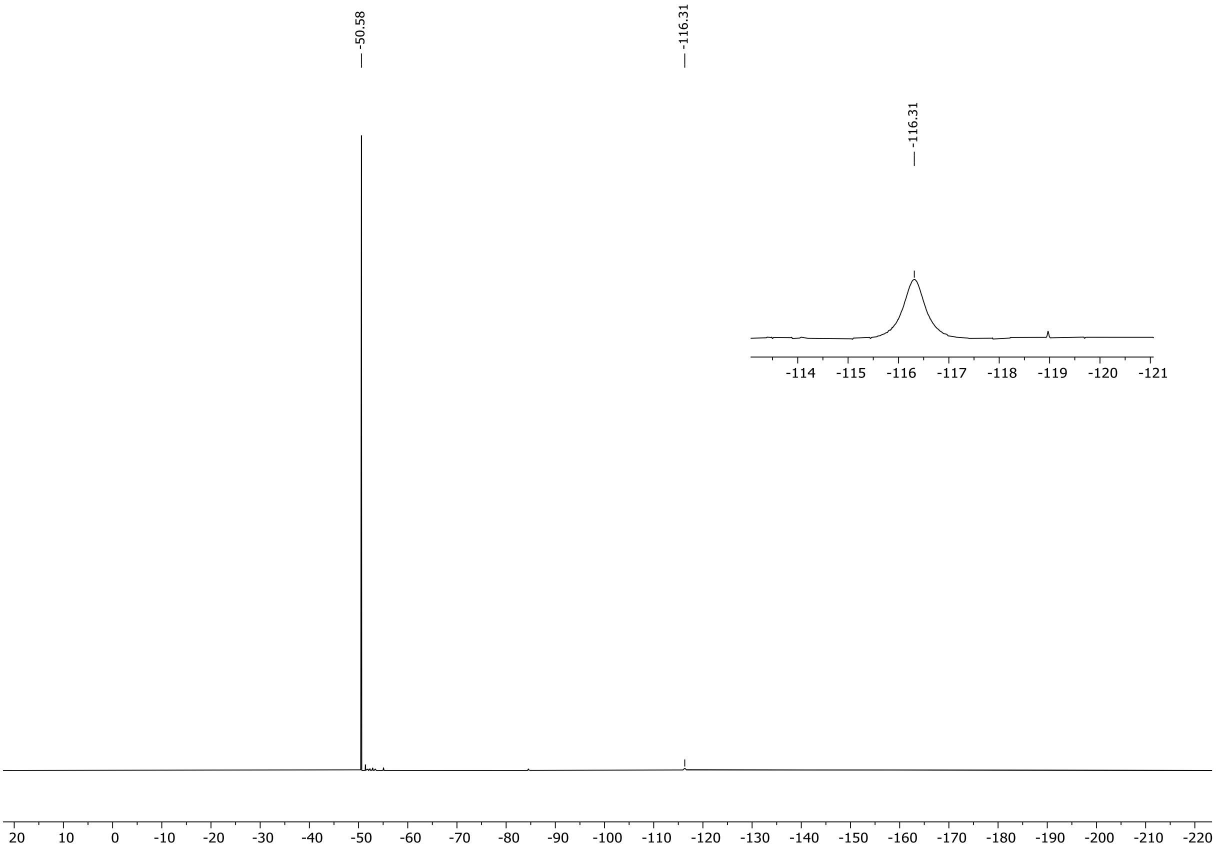

Figure 19: ^{19}F NMR (565 MHz, CD_2Cl_2, rt) spectrum of $[Rh(COD)(3,5\text{-}C_5H_3F_2N)_2][C_5(CF_3)_5]$.

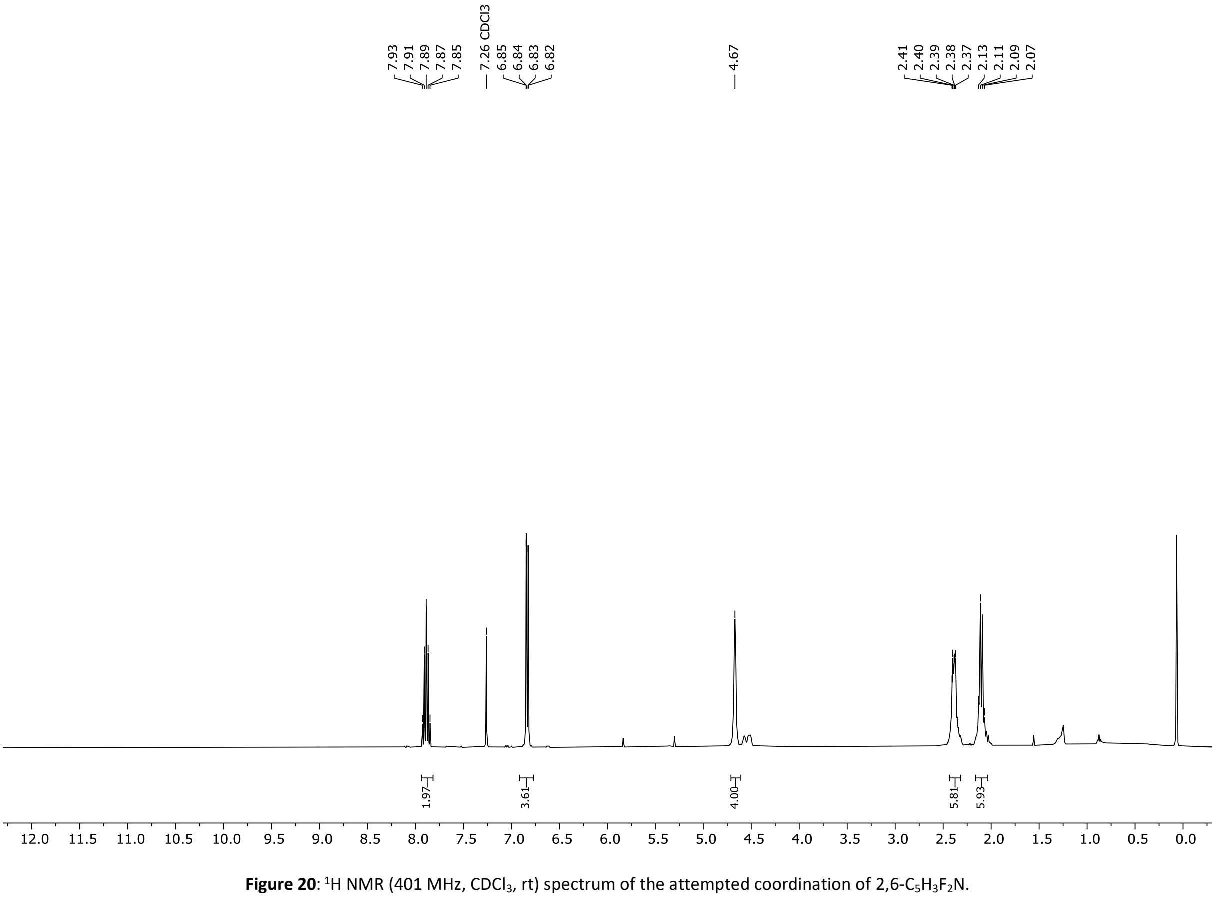

Figure 20: ^{1}H NMR (401 MHz, $CDCl_3$, rt) spectrum of the attempted coordination of $2,6\text{-}C_5H_3F_2N$.

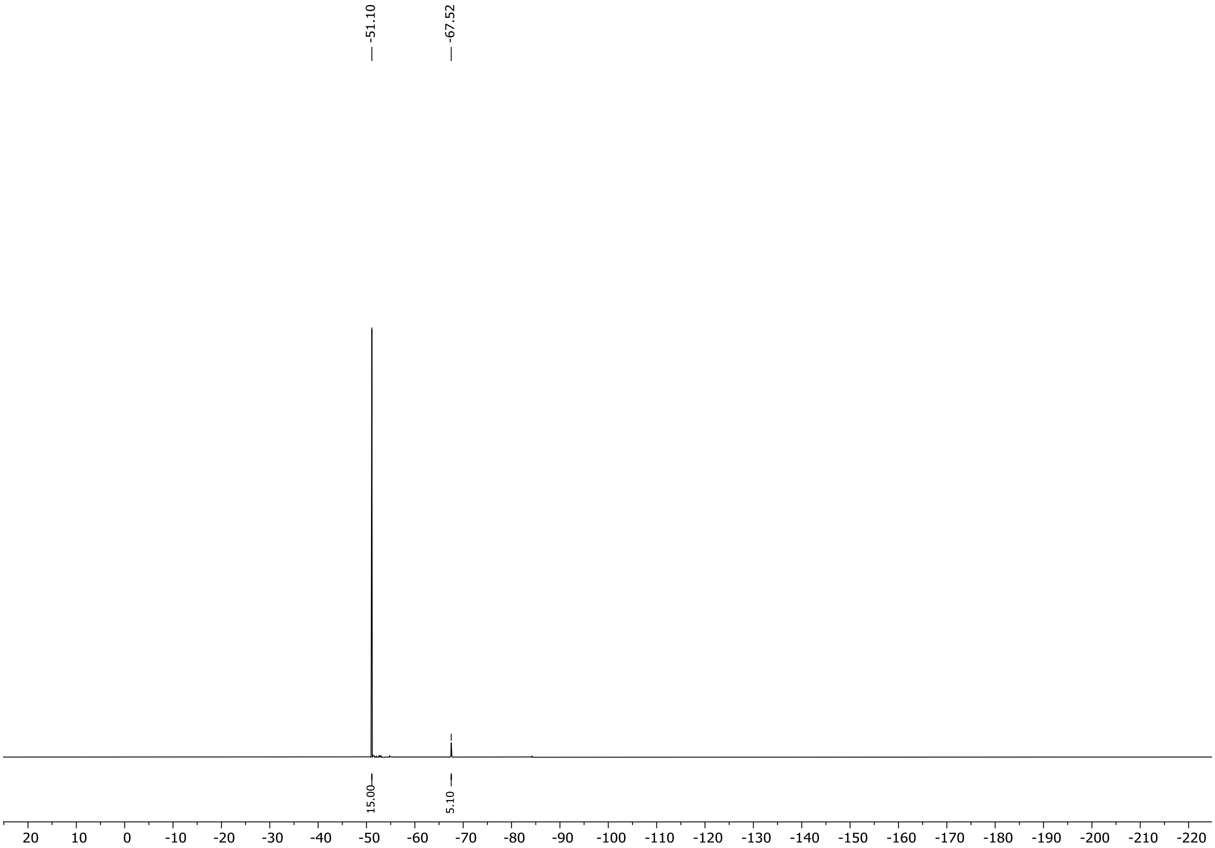

Figure 21: ^{19}F NMR (377 MHz, $CDCl_3$, rt) spectrum of the attempted coordination of 2,6-$C_5H_3F_2N$.

Crystallographic Data

Table 1: Crystallographic data of [Rh(COD)(MeCN)$_2$][C$_5$(CF$_3$)$_5$].

Identification code	2240962
Empirical formula	$C_{22}H_{18}F_{15}N_2Rh$
Formula weight	698.29
Temperature/K	104.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7638(4)
b/Å	21.5907(8)
c/Å	10.9819(4)
α/°	90
β/°	90.1520(10)
γ/°	90
Volume/Å^3	2552.16(16)
Z	4
ρ_{calc}g/cm^3	1.817
μ/mm^{-1}	0.794
F(000)	1376.0
Crystal size/mm^3	0.52 × 0.177 × 0.146
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 55.818
Index ranges	$-14 \leq h \leq 13$, $-28 \leq k \leq 25$, $-14 \leq l \leq 14$
Reflections collected	23894
Independent reflections	5683 [R_{int} = 0.0262, R_{sigma} = 0.0309]
Data/restraints/parameters	5683/0/580
Goodness-of-fit on F^2	1.173
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1265
Final R indexes [all data]	R_1 = 0.0875, wR_2 = 0.1354
Largest diff. peak/hole / e Å^{-3}	0.73/-1.27

Table 2: Crystallographic data of [Rh(COD)(3-$C_5H_4FN)_2$][$C_5(CF_3)_5$].

Identification code	2240960
Empirical formula	$C_{56}H_{40}F_{34}N_4Rh_2$
Formula weight	1620.74
Temperature/K	112.0
Crystal system	triclinic
Space group	P-1
a/Å	14.3033(16)
b/Å	14.7648(13)
c/Å	15.3305(13)
α/°	112.269(4)
β/°	91.270(3)
γ/°	104.241(3)
Volume/Å^3	2879.9(5)
Z	2
ρ_{calc}g/cm^3	1.869
μ/mm^{-1}	0.728
F(000)	1600.0
Crystal size/mm^3	0.29 × 0.22 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.1 to 55.09
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
Reflections collected	67365
Independent reflections	13238 [R_{int} = 0.0535, R_{sigma} = 0.0369]
Data/restraints/parameters	13238/0/1009
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	1.15/-1.07

DFT calculations

C_5H_5N

Neutral, diamagnetic, E = −248.3961737 Hartree.

Table 3: Structure optimized coordinates (x, y, z) for C_5H_5N.

N	-0.0000190000	-1.4116200000	0.0000030000
C	1.1933760000	0.6694620000	0.0000000000
C	0.0000200000	1.3786320000	-0.0000010000
C	-1.1933570000	0.6694940000	0.0000010000
C	-1.1394010000	-0.7194570000	-0.0000050000
C	1.1393790000	-0.7194900000	-0.0000020000
H	2.1483550000	1.1778330000	0.0000010000
H	0.0000320000	2.4611300000	0.0000000000
H	-2.1483200000	1.1778940000	0.0000060000
H	-2.0537360000	-1.3036540000	0.0000040000
H	2.0536990000	-1.3037100000	0.0000020000

$C_5H_5NH^+$

Monocationic, diamagnetic, E = −248.7663175 Hartree.

Table 4: Structure optimized coordinates (x, y, z) for $C_5H_5NH^+$.

N	-1.3034540000	-0.0034810000	0.0000000000
C	-0.6604940000	-1.1860300000	0.0000000000
C	-0.6665640000	1.1828530000	0.0000010000
C	0.7101370000	1.2079560000	0.0000000000
C	1.4087180000	0.0035610000	0.0000000000
C	0.7166590000	-1.2042280000	-0.0000010000
H	-1.2741860000	-2.0747360000	-0.0000010000
H	-1.2853800000	2.0679680000	0.0000020000
H	1.2243110000	2.1578540000	0.0000010000
H	2.4905690000	0.0064950000	-0.0000010000
H	1.2355660000	-2.1515390000	-0.0000010000
H	-2.3174390000	-0.0063440000	0.0000010000

$3\text{-}C_5H_4FN$

Neutral, diamagnetic, E = −347.6759702 Hartree.

Table 5: Structure optimized coordinates (x, y, z) for $3\text{-}C_5H_4FN$.

F	2.2549060000	0.0228550000	0.0000000000
N	-1.0983260000	-1.2459770000	-0.0000040000
C	0.2308420000	-1.1880490000	-0.0000040000
C	-1.7782150000	-0.0993110000	0.0000140000
C	-1.1672070000	1.1491860000	-0.0000050000
C	0.2196730000	1.2182260000	0.0000020000
C	0.9081040000	0.0215510000	0.0000040000
H	0.7838310000	-2.1206150000	-0.0000040000
H	-2.8589620000	-0.1820370000	-0.0000130000
H	-1.7644260000	2.0510510000	-0.0000200000
H	0.7545040000	2.1581310000	-0.0000010000

$3\text{-}C_5H_4FNH^+$

Monocationic, diamagnetic, E = −348.0357583 Hartree.

Table 6: Structure optimized coordinates (x, y, z) for $3\text{-}C_5H_4FNH^+$.

F	-2.2733780000	-0.0229660000	-0.0000040000
N	1.0840160000	-1.1213930000	0.0000010000
C	-0.9558120000	0.0158060000	-0.0000020000
C	-0.2837640000	1.2317160000	0.0000000000
C	1.1049730000	1.2273200000	0.0000030000
C	1.7844700000	0.0258150000	0.0000030000
C	-0.2595510000	-1.1759200000	-0.0000020000
H	-0.8486330000	2.1548060000	0.0000000000
H	1.6626130000	2.1524770000	0.0000050000
H	2.8606710000	-0.0576300000	0.0000060000
H	-0.7392360000	-2.1433830000	-0.0000030000
H	1.5949880000	-1.9982510000	0.0000010000

$2\text{-}C_5H_4FN$

Neutral, diamagnetic, E = −347.6865708 Hartree.

Table 7: Structure optimized coordinates (x, y, z) for $2\text{-}C_5H_4FN$.

F	2.2334970000	-0.0334360000	0.0003860000
N	0.3067200000	-1.1916060000	-0.0003170000
C	0.2450350000	1.2066750000	-0.0002660000
C	-1.1393390000	1.1809330000	-0.0000200000
C	-1.7966610000	-0.0466840000	0.0003250000
C	-1.0312410000	-1.2016520000	-0.0001360000

C	0.8910210000	-0.0235540000	-0.0000890000
H	0.8125320000	2.1257800000	-0.0008970000
H	-1.6992060000	2.1069720000	-0.0001420000
H	-2.8759590000	-0.1055080000	0.0013500000
H	-1.4987650000	-2.1793780000	-0.0004500000

2-$C_5H_4FNH^+$

Monocationic, diamagnetic, E = −348.0391073 Hartree.

Table 8: Structure optimized coordinates (x, y, z) for 2-$C_5H_4FNH^+$.

F	2.2221830000	-0.0136880000	0.0003490000
N	0.2867980000	1.1058490000	0.0000130000
C	0.9183390000	-0.0764570000	0.0001430000
C	-1.0649360000	1.2011650000	-0.0001970000
C	-1.8168010000	0.0549370000	-0.0003090000
C	-1.1689220000	-1.1843090000	-0.0001390000
C	0.2160030000	-1.2611800000	0.0000920000
H	-1.4752100000	2.1998870000	-0.0002880000
H	-2.8943320000	0.1239260000	-0.0005040000
H	-1.7512170000	-2.0961740000	-0.0002270000
H	0.7545830000	-2.1976310000	0.0001820000
H	0.8568360000	1.9473140000	0.0000710000

3,5-$C_5H_3F_2N$

Neutral, diamagnetic, E = −446.9547002 Hartree.

Table 9: Structure optimized coordinates (x, y, z) for 3,5-$C_5H_3F_2N$.

F	2.3504410000	-0.9389460000	-0.0000040000
F	-2.3504410000	-0.9389460000	-0.0000010000
N	0.0000000000	1.7645360000	-0.0000030000
C	-1.1467690000	1.0905940000	-0.0000010000
C	1.1467690000	1.0905940000	0.0000050000
C	1.1709240000	-0.2960550000	0.0000040000
C	0.0000000000	-1.0301880000	0.0000030000
C	-1.1709240000	-0.2960550000	0.0000020000
H	-2.0723930000	1.6532640000	-0.0000030000
H	2.0723930000	1.6532630000	-0.0000030000
H	0.0000000000	-2.1105940000	0.0000010000

3,5-$C_5H_3F_2NH^+$

Monocationic, diamagnetic, E = −447.3042530 Hartree.

Table 10: Structure optimized coordinates (x, y, z) for 3,5-$C_5H_3F_2NH^+$.

F	2.3414180000	-0.9725210000	0.0000000000
F	-2.3413400000	-0.9726010000	-0.0000010000
N	-0.0000280000	1.6679390000	0.0000020000
C	1.1864320000	-0.3427440000	0.0000000000
C	0.0000410000	-1.0605990000	-0.0000010000
C	-1.1864560000	-0.3427180000	-0.0000010000
C	-1.1873900000	1.0413410000	0.0000010000
C	1.1872330000	1.0413980000	0.0000010000
H	0.0001030000	-2.1431820000	-0.0000020000
H	-2.0888050000	1.6350850000	0.0000020000
H	2.0887550000	1.6349920000	0.0000020000
H	0.0002900000	2.6835560000	0.0000020000

2,6-$C_5H_3F_2N$

Neutral, diamagnetic, E = −446.9753461 Hartree.

Table 11: Structure optimized coordinates (x, y, z) for 2,6-$C_5H_3F_2N$.

F	-2.2442400000	1.0320990000	-0.0000490000
F	2.2442400000	1.0320990000	-0.0001370000
N	0.0000000000	1.0036860000	0.0000890000
C	-1.1163140000	0.3141550000	-0.0000070000
C	1.1163140000	0.3141550000	0.0002300000
C	1.2025050000	-1.0687040000	0.0000270000
C	0.0000000000	-1.7633740000	-0.0000270000
C	-1.2025050000	-1.0687040000	-0.0000060000
H	2.1625820000	-1.5618160000	-0.0000790000
H	0.0000000000	-2.8451060000	-0.0001120000
H	-2.1625820000	-1.5618170000	-0.0000550000

2,6-$C_5H_3F_2NH^+$

Monocationic, diamagnetic, E = −447.3107349 Hartree.

Table 12: Structure optimized coordinates (x, y, z) for 2,6-$C_5H_3F_2NH^+$.

F	-2.2324090000	1.0267150000	-0.0000340000
F	2.2324070000	1.0267150000	-0.0000210000
N	0.0000010000	0.9270290000	-0.0000270000
C	1.2159750000	-1.1064700000	0.0000340000
C	0.0000110000	-1.7857620000	0.0000520000
C	-1.2159740000	-1.1064760000	0.0000290000
C	-1.1759530000	0.2640620000	-0.0000160000
C	1.1759420000	0.2640840000	-0.0000030000
H	2.1701350000	-1.6122320000	0.0000530000
H	0.0000160000	-2.8676970000	0.0000830000
H	-2.1701250000	-1.6122570000	0.0000430000
H	-0.0000150000	1.9454840000	-0.0000650000

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