# Selective Synthesis of *Cis*- and *Trans*-[$(NHC^{Me})_2PtCl_2$] and [$NHC^{Me}Pt(cod)Cl$][$NHC^{Me}PtCl_3$] using $NHC^{Me}SiCl_4$

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Electronic Supplementary Information

**Experimental Details**

**General Procedures**

All reactions were carried out under an atmosphere of argon using common Schlenk techniques in flame-dried glassware. Unless stated otherwise, all reagents were purchased from available commercial sources. Acetonitrile and dichloromethane were distilled from $CaH_2$ under argon and stored over 4 Å molecular sieves. Tetrahydrofuran, diethyl ether and toluene were distilled from sodium wire under argon and stored over sodium wire. $NHC^{Me}SiCl_4$ was prepared according to the literature method.[1]

**Thermo Gravimetric Analysis**: TA Instruments SDT Q600 thermobalance. Sample size of 15-25 mg. Ramp method: 5 °C/min.

**NMR Spectroscopy**: NMR spectra were recorded on a JEOL ECX 400 MHz spectrometer at room temperature using 5 mm tubes. The solvent signals were used as references and the chemical shifts converted to the TMS scale. For $^{195}Pt$ NMR, $K_2[PtCl_4]$ was used as external standard ($\delta$ $^{195}Pt$ = -1612.67). Operating frequency: $^{1}H$ 400.53 MHz, $^{13}C$ 100.71 MHz, $^{195}Pt$ 86.10 MHz.

**XRD Measurements:** Crystals were mounted on a Hampton cryoloop in paratone oil under nitrogen at 100 K. Indexing and data collection were performed on a Bruker D8 SMART APEX II CCD diffractometer with κ geometry and Mo Kα radiation (graphite mono- chromator, λ = 0.71073 Å), using Apex2 suite. Data integration was performed using the SAINT Plugin software. Multi-scan absorption correction was applied using the SADABS Plugin software, alongside routine Lorentz and polarization corrections. The SHELX-97 software package was used for structure solution and refinement. Refinements were full-matrix least-squares against $F^2$ using all data. In the final refinement, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. Crystallographic data are summarized in Table 1.

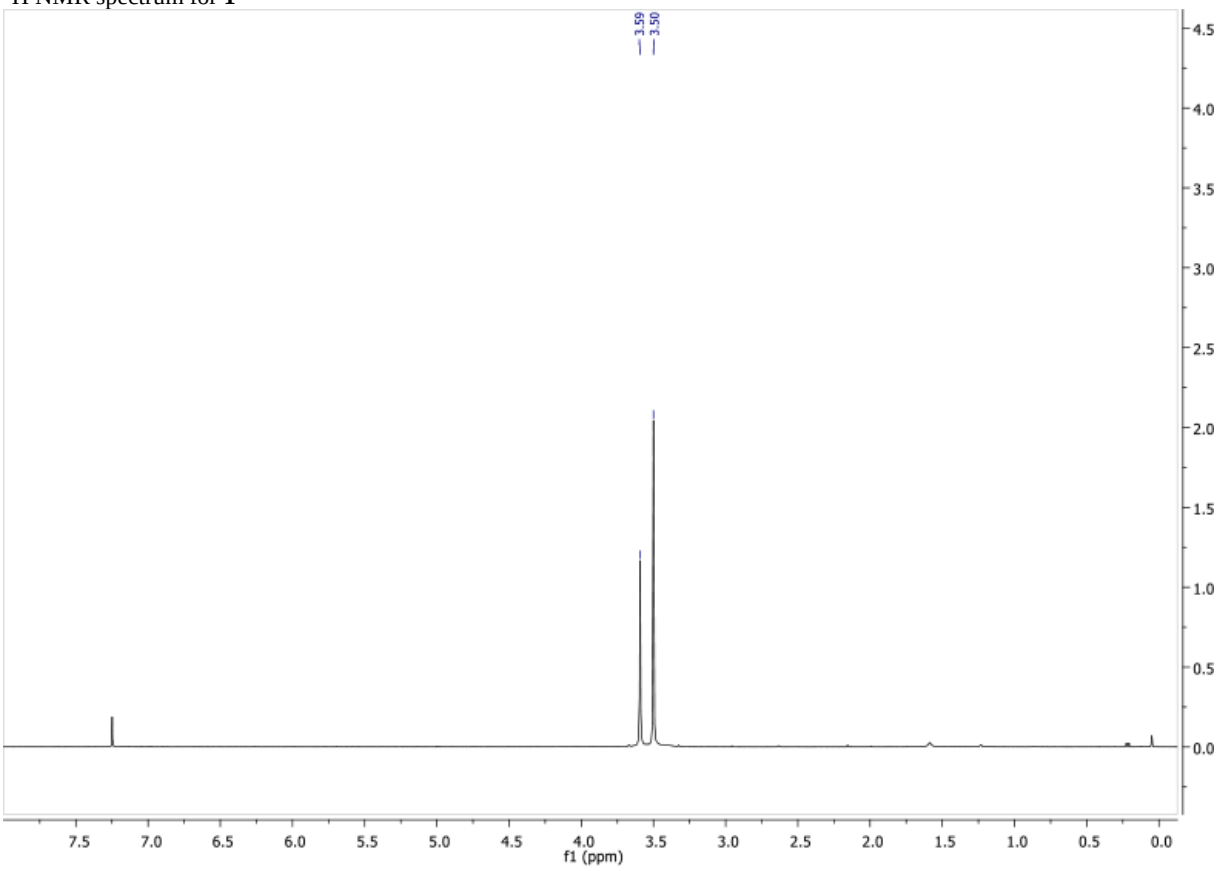
**Elemental Analysis**: Elemental analysis was performed by the "Analytische Laboratorien" in Industriepark Kaiserau (Haus Heidbruch), 51789 Lindlar, Germany.

**Synthesis of *trans*-[$(NHC^{Me})_2PtCl_2$] (1):** $NHC^{Me}SiCl_4$ (1.10 g, 4.1 mmol) and $PtCl_2$ (0.50 g, 1.86 mmol) were stirred vigorously in refluxing tetrahydrofuran (30 ml) under an argon atmosphere overnight. All volatile components were removed under reduced pressure at room temperature. The solid residue was dissolved in dichloromethane, filtered through celite and the solvent removed under reduced pressure to give *trans*-[$(NHC^{Me})_2PtCl_2$] (0.49 g, 1.04 mmol). The product was recrystallised by slow evaporation of toluene. $^{1}H$ NMR ($CDCl_3$): $\delta$ = 3.50 (s, 12H, $-CH_3$), 3.59 (s, 8H, $-CH_2-$) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 36.5 (s, 4C, $-CH_3$), 51.44 (s, 4C, $-CH_2-$), 194.24 (s, carbene-C, $^{1}J_{CPt}$= 860 Hz) ppm; $^{195}Pt$ NMR ($CDCl_3$): $\delta$ = -3271.09 ppm. Elemental analysis calcd (%) for C10H20Cl2N4Pt: C 25.98, H 4.36, N 12.12; found: C 25.75, H 4.36, N 11.89

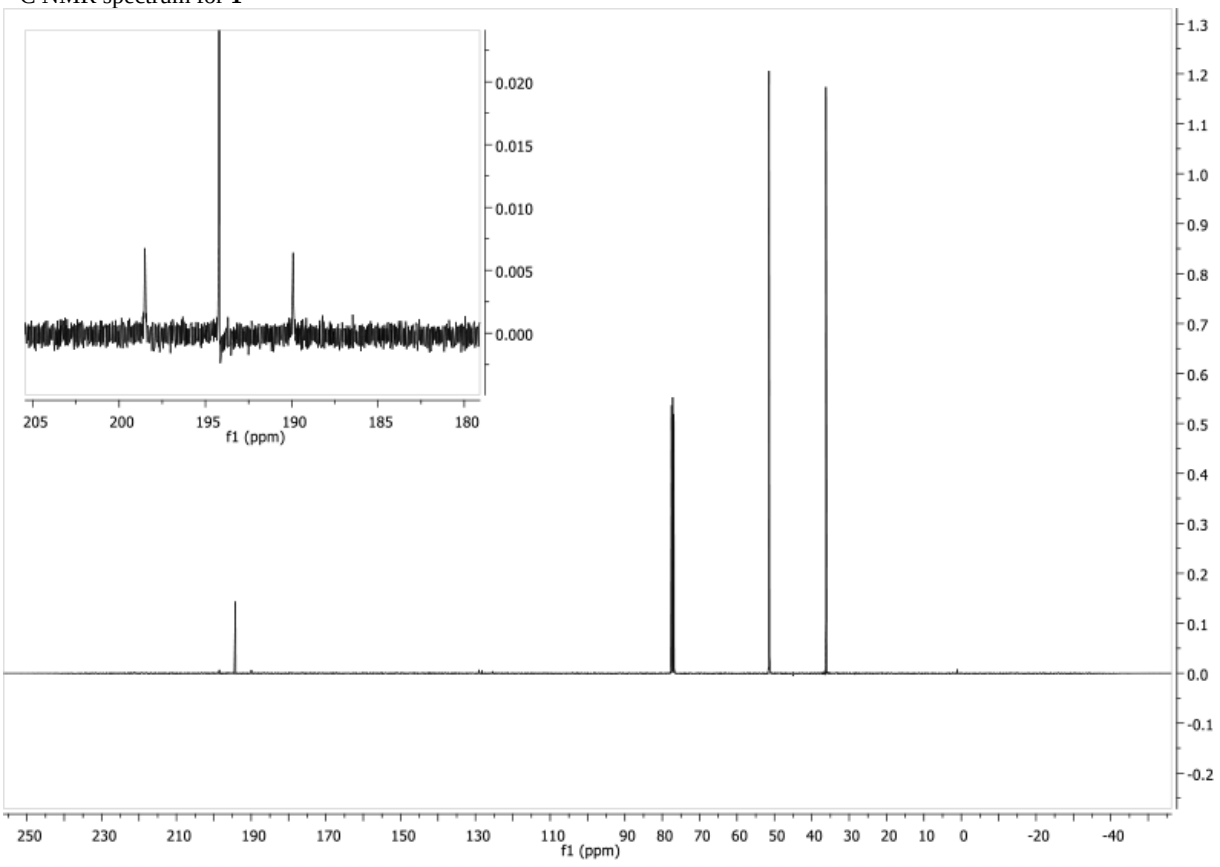
**Synthesis of *cis*-[$(NHC^{Me})_2PtCl_2$] (2):** $NHC^{Me}SiCl_4$ (1.05g, 3.92 mmol) and $[Pt(cod)Cl_2]$ (0.637g, 1.70 mmol) were stirred vigorously in refluxing tetrahydrofuran (30 ml) under an argon atmosphere overnight. All volatile components were removed under reduced pressure at room temperature. The residue was washed with cold acetonitrile, then diethyl ether and the product dried under reduced pressure. *Cis*-[$(NHC^{Me})_2PtCl_2$] (0.534g, 1.15 mmol) was recrystallised by cooling of its hot acetonitrile solution. $^{1}H$ NMR ($CDCl_3$): $\delta$ = 3.37 (s, 12H, $-CH_3$), 3.61 (m, 8H, $-CH_2-$) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 37.76 (s, 4C, $-CH_3$, $^{3}J_{CPt}$= 33 Hz), 51.53 (s, 4C, $-CH_2-$, $^{3}J_{CPt}$= 43 Hz), 175.37 (s, carbene-C, $^{1}J_{CPt}$= 1379 Hz) ppm; $^{195}Pt$ NMR ($CDCl_3$): $\delta$ = -3730.20 ppm. Elemental analysis calcd (%) for C10H20Cl2N4Pt: C 25.98, H 4.36, N 12.12; found: C 25.92, H 4.34, N 12.08

**Synthesis of [$(NHC^{Me})Pt(cod)Cl$][$(NHC^{Me})PtCl_3$] (3):** $NHC^{Me}SiCl_4$ (1.18 g, 4.40 mmol) and $[Pt(cod)Cl_2]$ (1.50 g, 4.0 mmol) were stirred vigorously in refluxing acetonitrile (30 ml) under an argon atmosphere over 3 days. The reaction mixture was filtered and all volatile components were removed under reduced pressure at room temperature. The solid residue was dissolved in deionised water and filtered. The product (0.5139 g, 0.66 mmol) was extracted with dichloromethane, dried with $MgSO_4$, filtered and isolated by solvent removal under reduced pressure. [$(NHC^{Me})Pt(cod)Cl$][$(NHC^{Me})PtCl_3$] was recrystallised from dichloromethane/pentane. $^{1}H$ NMR ($CDCl_3$): $\delta$ = 2.45-2.75 (m, 8H, $-CH_2$ of cod), 3.33 (s, 6H, carbene-$CH_3$ in $[Pt]^+$), 3.51 (s, 6H, carbene-$CH_3$ in $[Pt]^-$), 3.59 (s, 4H, carbene-$CH_2$ in $[Pt]^-$), 3.61 (t, 2H, carbene-$CH_2$ in $[Pt]^+$), 4.42 (t, 2H, carbene-$CH_2$ in $[Pt]^+$), 5.80-5.90 (m, 4H, olefinic CH of cod)ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 28.40 (s, 2C, $CH_2$ of cod), 32.30 (s, 2C, $CH_2$ of cod), 36.72 (s, 2C, $-CH_3$), 36.73 (s, 2C, $-CH_3$), 51.04 (s, 2C, $-CH_2-$ of carbene in $[Pt]^-$), 52.43 (s, 2C, $-CH_2-$ of carbene in $[Pt]^+$), 96.35 (s, 2C, olefinic C of cod trans to Cl, $^{1}J_{CPt}$= 154.01 Hz), 117.60 (s, 2C, olefinic C of cod trans to C, $^{1}J_{CPt}$= 55.34 Hz), 170.52 (s, carbene-C,), 174.47 (s, carbene-C,) ppm; $^{195}Pt$ NMR ($CDCl_3$): $\delta$ = -3542.34 (s, $[Pt]^+$), $\delta$ = -2930.61 (s, $[Pt]^-$)ppm. Elemental analysis calcd (%) for C18H32Cl4N4Pt2: C 25.85, H 3.86, N 6.70; found: C 25.63, H 3.77, N 6.63

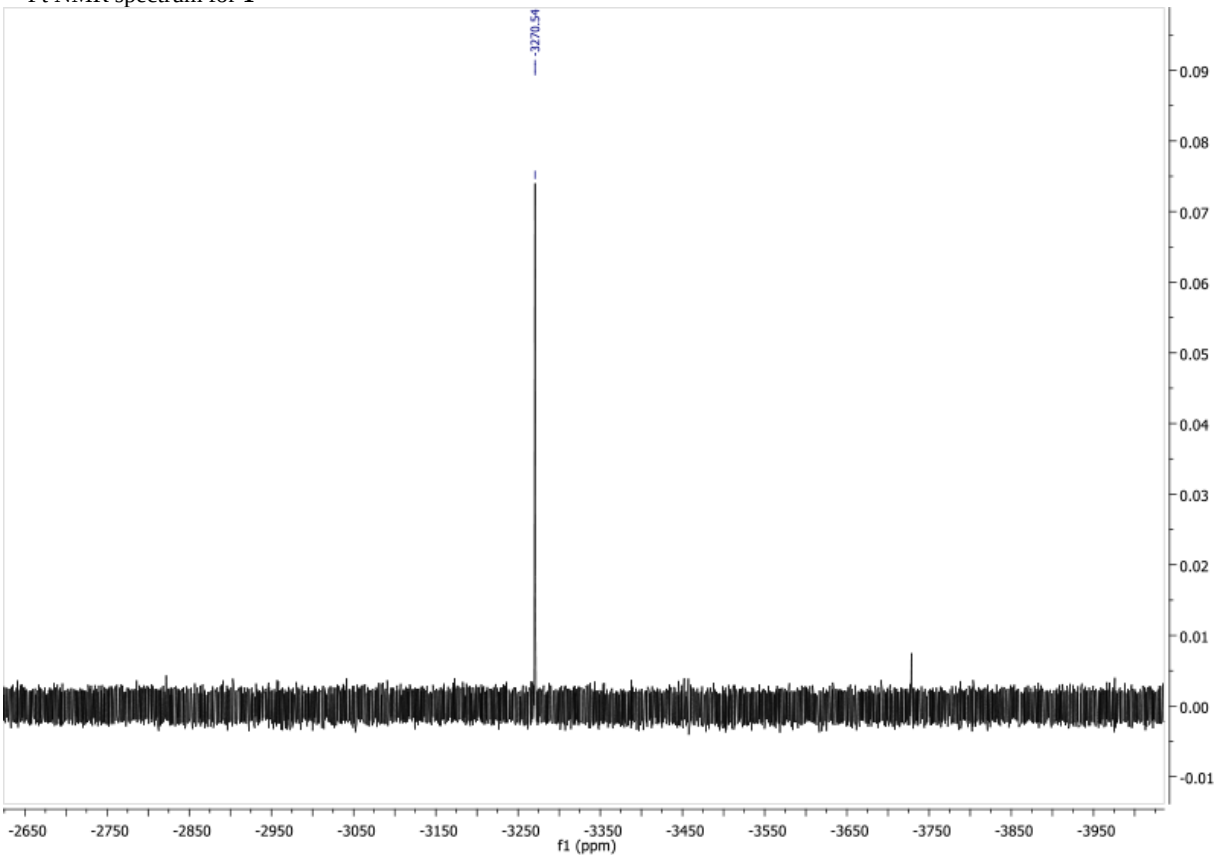
$^{1}$H NMR spectrum for **1**



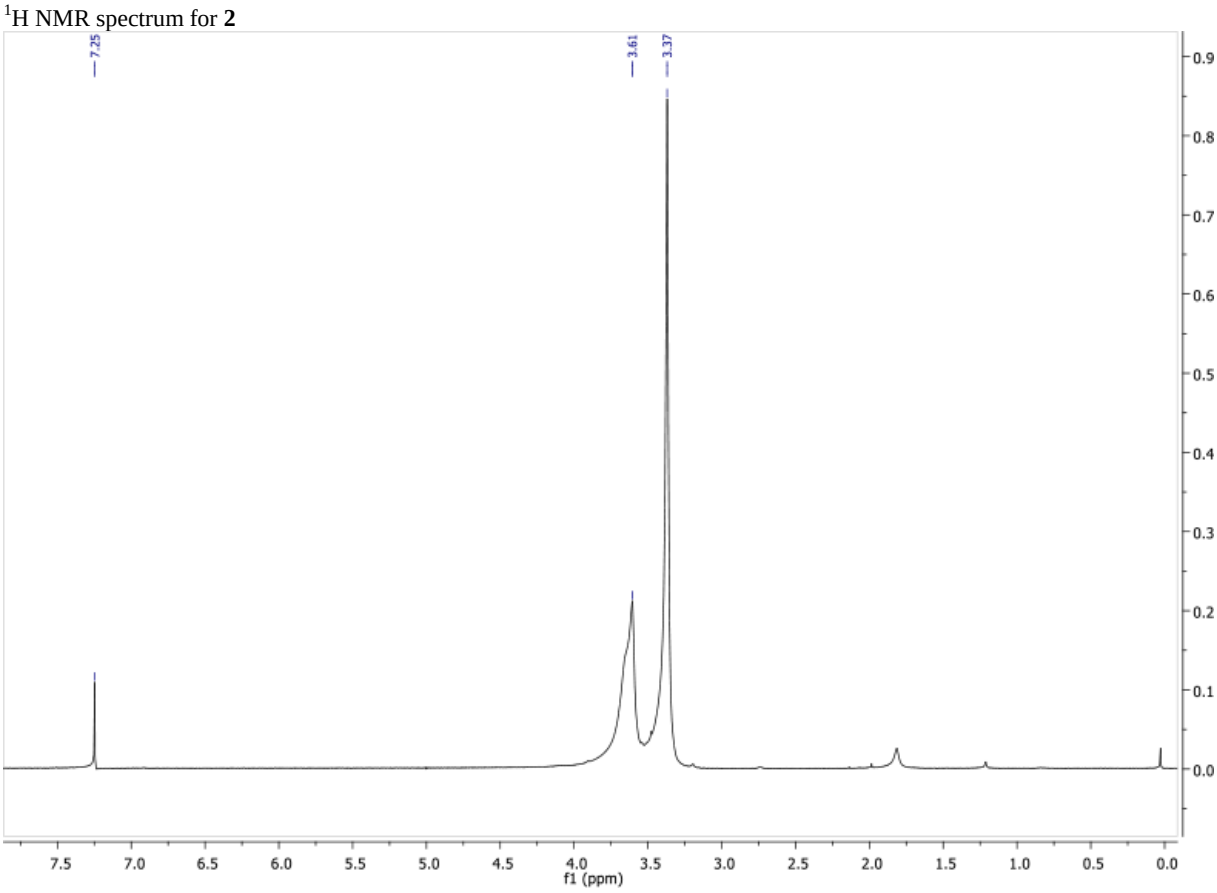

$^{13}$C NMR spectrum for **1**



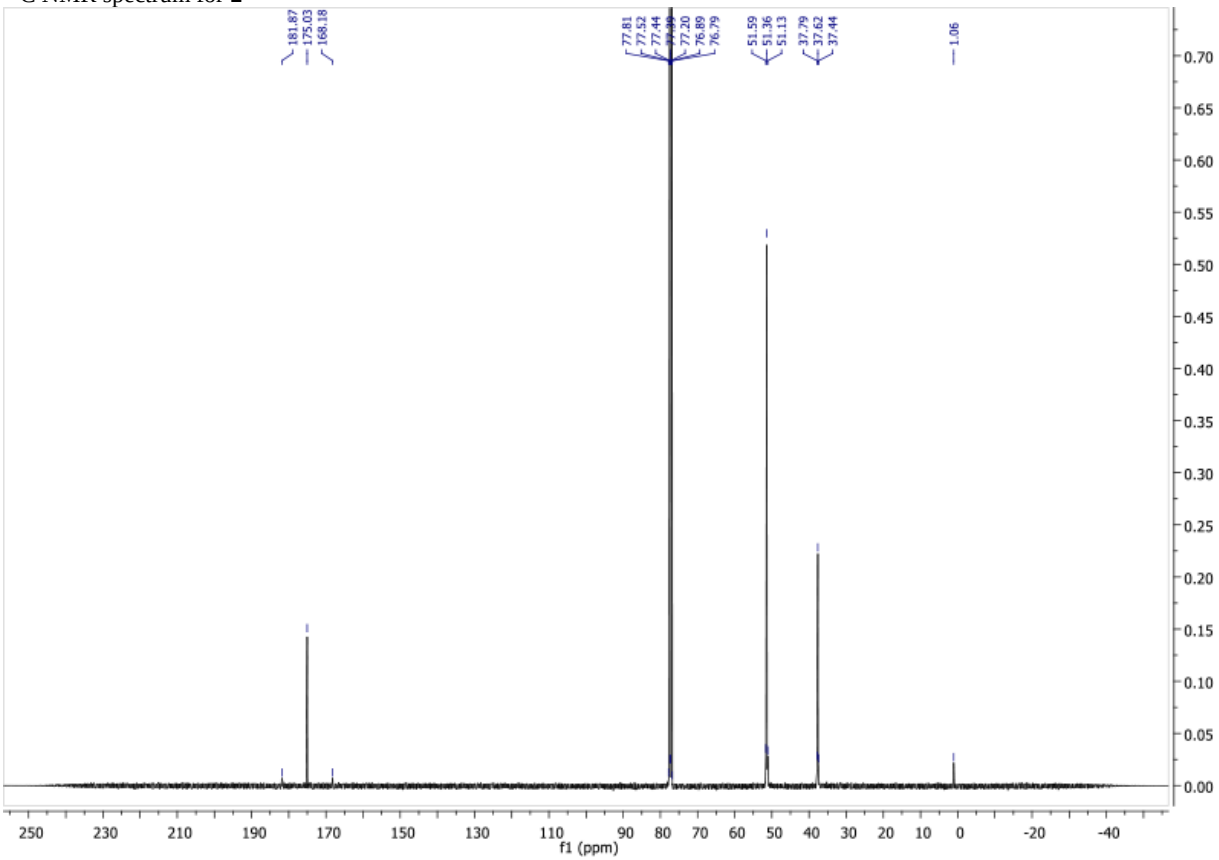
$^{195}$Pt NMR spectrum for **1**



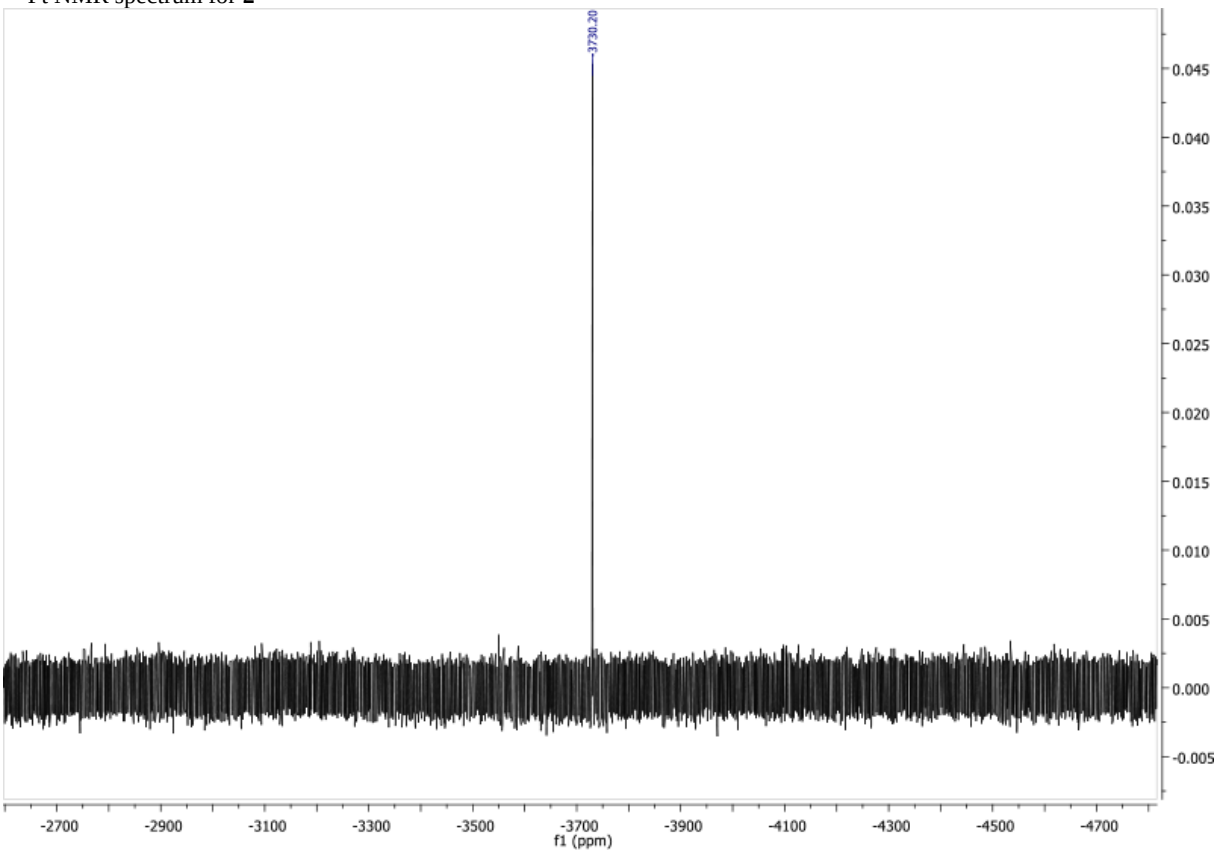

$^{1}$H NMR spectrum for **2**



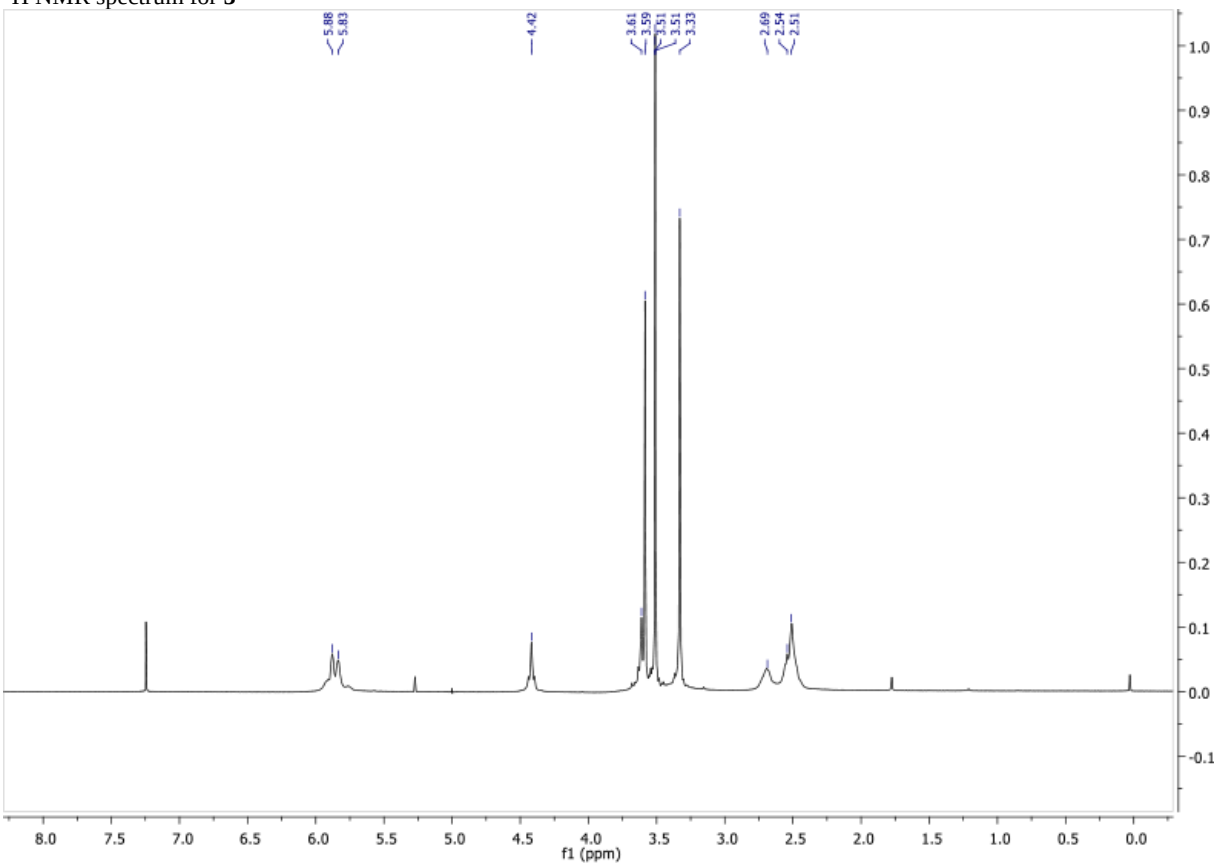
$^{13}$C NMR spectrum for **2**



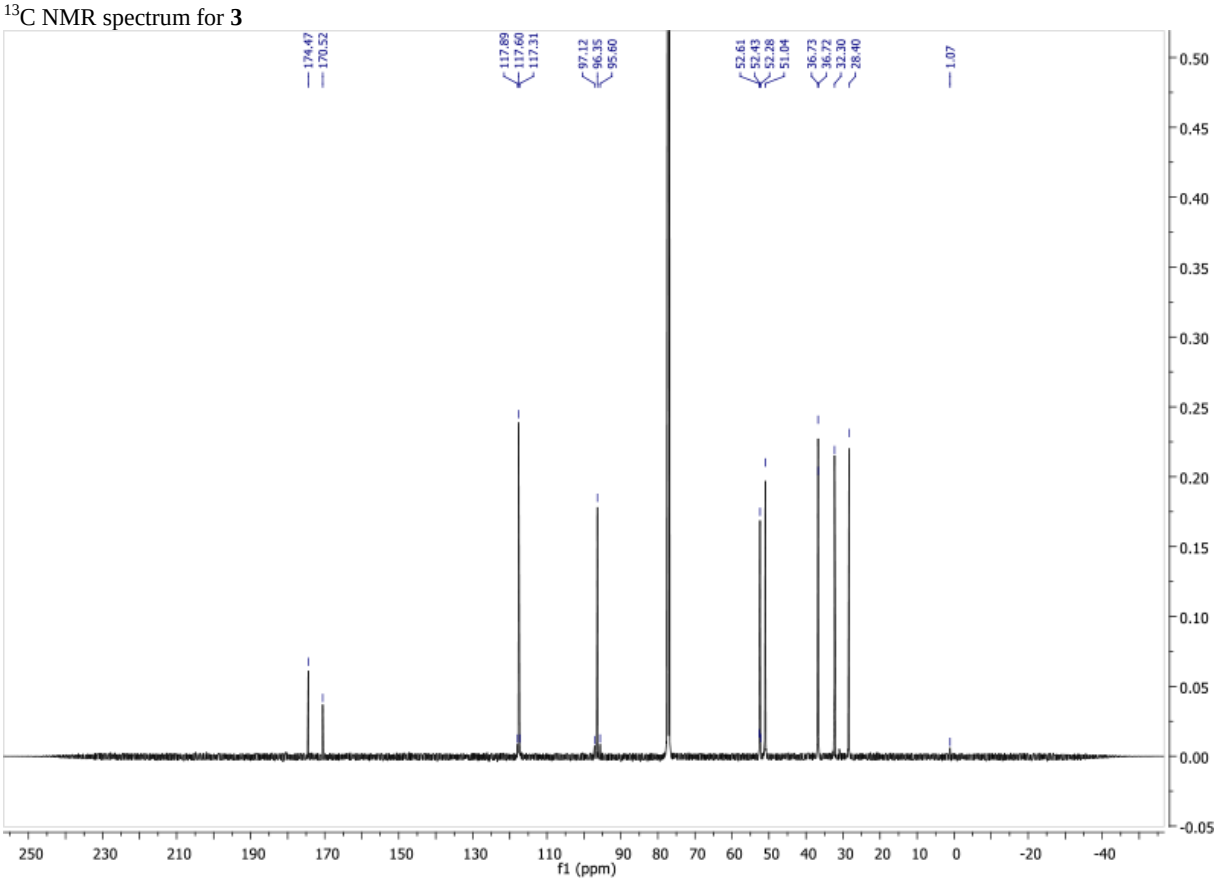

$^{195}$Pt NMR spectrum for **2**



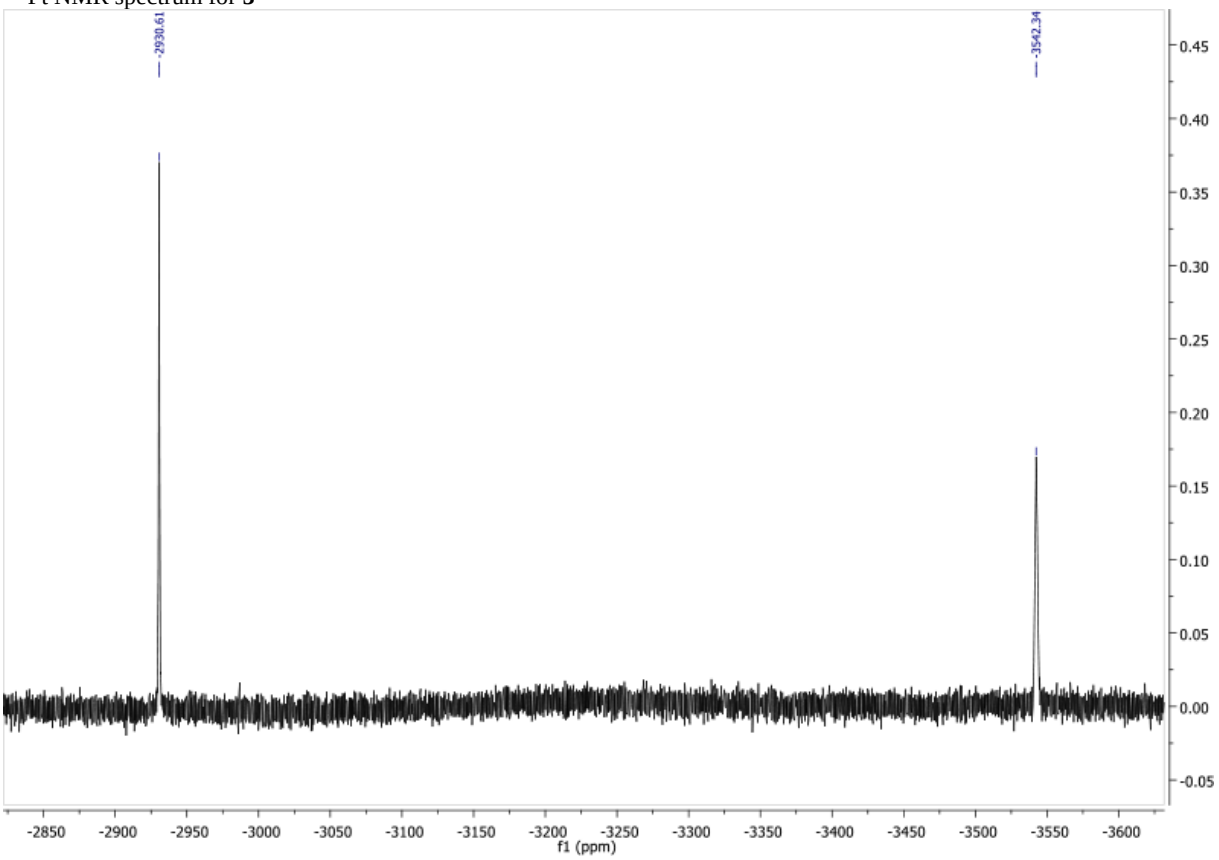
$^{1}$H NMR spectrum for **3**



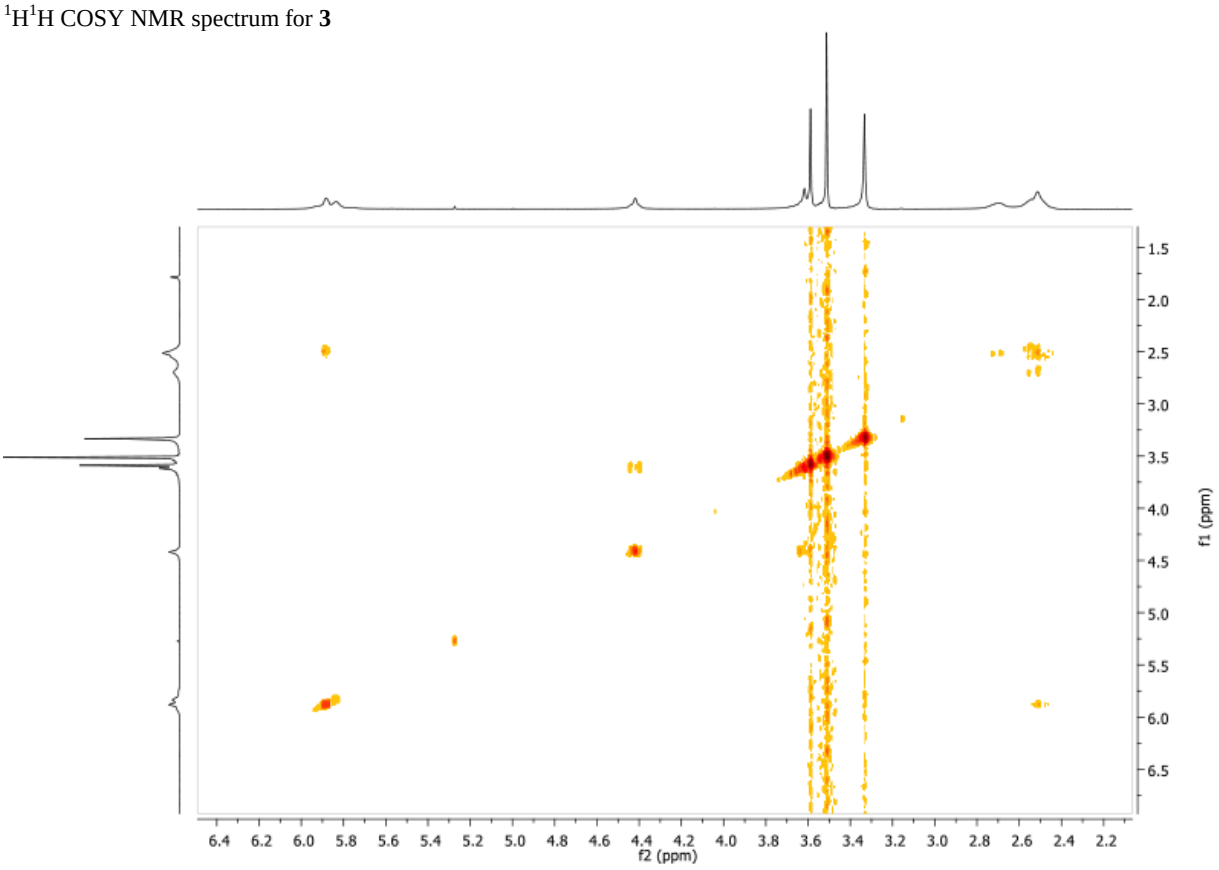

$^{13}$C NMR spectrum for **3**



$^{195}$Pt NMR spectrum for **3**




$^{1}$H$^{1}$H COSY NMR spectrum for **3**



$^{1}H^{13}C$ HETCOR NMR spectrum for **3**

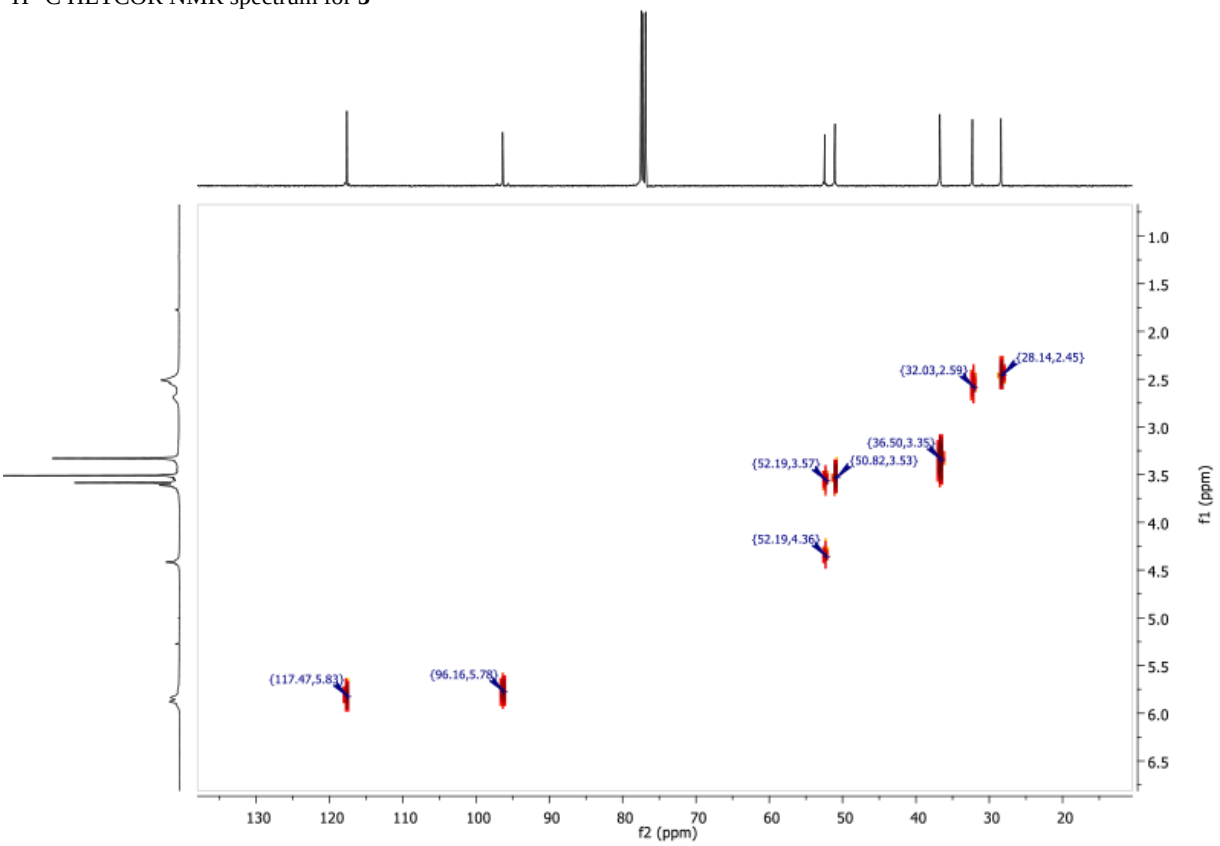


Table 1: Crystallographic data for compounds **1**, **2** and **3**

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| Formula Unit | $C_{10}H_{20}Cl_2N_4Pt$ | $C_{30}H_{60}C_{l6}N_{12}Pt_3$ | $C_{18}H_{32}Cl_4N_4Pt_2$ |
| Formula weight (g/mol) | 462.29 | 1386.87 | 836.46 |
| Crystal System | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| a (Å) | 15.474(3) | 19.905(2) | 13.568(3) |
| b (Å) | 7.0663(14) | 11.9335(11) | 14.159(3) |
| c (Å) | 14.061(3) | 18.0082(18) | 12.365(2) |
| α (°) | 90 | 90 | 90.00 |
| β (°) | 110.334(7) | 98.522(6) | 95.771(10) |
| δ (°) | 90 | 90 | 90.00 |
| Volume ($Å^3$) | 1441.7(5) | 4230.3(7) | 2363.4(8) |
| Z | 4 | 4 | 4 |
| $D_{calc}$ ($g/cm^3$) | 2.130 | 2.178 | 2.351 |
| Abs. Coeff. μ ($mm^{-1}$) | 10.089 | 10.315 | 12.290 |
| Temperature | 100(2) K | 100(2) K | 100(2) K |
| Total reflections | 90085 | 278310 | 194137 |
| Min-max θ (°) | 3.77 – 30.51 | 3.41 – 30.51 | 3.50 – 30.51 |
| Unique reflections | 4387 | 12879 | 7209 |
| Calculated reflection (I > 2σ) | 3481 | 11140 | 6877 |
| Final R1* | 0.0224 | 0.0200 | 0.0184 |
| wR2* | 0.0720 | 0.0510 | 0.0527 |
| $R_{int}$ | 0.0491 | 0.0593 | 0.0524 |
| Goodness of Fit | 1.037 | 1.010 | 1.015 |
| Parameters | 157 | 460 | 253 |
| Restraints | 0 | 0 | 0 |
| Largest Peak/ Deepest Hole | 1.844/-2.197 | 1.041-1.096 | 1.272 / -1.246 |

$* R1 = \Sigma \| F(obs) | - | F(calc) \| / \Sigma | F(obs) |$ ; $wR2 = \{ \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] \}^{1/2}$

1. T. Bottcher, B. S. Bassil, L. Zhechkov, T. Heine and G.-V. Roschenthaler, *Chem. Sci.*, 2013, **4**, 77-83.