

Supporting Information for:

Oxidative Addition of Arsenic Halides to Platinum(0)

*Jonas H. Muessig,^{a,b} Tom E. Stennett, Uwe Schmidt,^{a,b} Rian D. Dewhurst,^{a,b} Lisa Mailänder^{a,b}
and Holger Braunschweig^{a,b*}*

^a *Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.*

^b *Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.*

*To whom correspondence should be addressed. E-mail: h.braunschweig@uni-wuerzburg.de

Materials and Methods

General considerations. All reactions were performed under an atmosphere of dry argon using standard Schlenk or glovebox techniques. ^1H , ^{13}C , ^{31}P and ^{195}Pt NMR spectra were obtained at ambient temperature using either a Bruker Avance I 400 (operating at 400.1 MHz for ^1H , 128.4 MHz for ^{13}C , 162.0 MHz for $^{31}\text{P}\{^1\text{H}\}$ and 86.0 MHz for $^{195}\text{Pt}\{^1\text{H}\}$) or a Bruker Avance 500 NMR spectrometer (operating at 500.1 MHz for ^1H , 160.5 MHz for ^{13}C and 107.5 MHz for $^{195}\text{Pt}\{^1\text{H}\}$). ^1H NMR spectra were referenced via residual proton resonances of C_6D_6 (^1H , 7.16 ppm) or toluene- d_8 (^1H , 2.08, 6.97, 7.01, 7.09 ppm). ^{13}C NMR spectra were referenced to C_6D_6 (^{13}C , 128.06 ppm), toluene- d_8 (^{13}C , 20.43, 125.13, 127.96, 128.87, 137.48 ppm). $^{195}\text{Pt}\{^1\text{H}\}$ were referenced to $\text{Na}_2[\text{PtCl}_6]$ in D_2O . Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer.

All solvents were purified by distillation using the appropriate drying agents (potassium/benzophenone for diethyl ether; Na/K alloy for pentane and hexane; sodium for toluene, benzene), deoxygenated using three freeze-pump-thaw cycles and stored over molecular sieves under dry argon prior to use. Deuterated solvents used for NMR spectroscopy were purchased from Sigma-Aldrich, deoxygenated by three freeze-pump-thaw cycles and dried under an argon atmosphere over molecular sieves.

Reagents AsCl_3 and AsBr_3 were purchased from commercial sources. AsBr_3 was used as received and AsCl_3 was used after distillation. $[\text{Pt}(\text{PCy}_3)_2]$,¹ $[\text{Pt}(\text{PCy}_3)(\text{IMes})]$,² $[\text{Pt}(\text{IMes})_2]$,³ and IMes ⁴ were prepared by established methods.

Synthetic Details

***trans*-[(Cy₃P)₂PtCl(AsCl₂)] (4):** [Pt(PCy₃)₂] (135 mg, 178 μmol) was dissolved in Et₂O (5 mL) and a solution of AsCl₃ in Et₂O (1.19 mol/L, 0.18 mL, 214 μmol) was added at 0 °C. The reaction mixture was stirred for 1 h at ambient temperature, and the resulting precipitate filtered off and washed with Et₂O (3 x 4 mL) to yield the product (119 mg, 127 μmol, 69%) as a colourless powder.

¹H NMR (400.1 MHz, C₆D₆): δ = 3.12 (br m, 6H, Cy), 2.20 (br d, ³J_{H-H} = 12.5 Hz, 12H, Cy), 1.79–1.70 (br m, 24H, Cy), 1.61 (br d, ³J_{H-H} = 12 Hz, 6H, Cy), 1.36–1.26 (br m, 12H, Cy), 1.20–1.11 (br m, 6H, Cy) ppm.

¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ = 32.8 (vt, N = |¹J_{C-P} + ³J_{C-P}| = 25 Hz, C¹, Cy), 30.6 (s, C², C⁶, Cy), 27.9 (vt, N = |³J_{C-P} + ⁵J_{C-P}| = 11 Hz, C³, C⁵, Cy), 26.8 (s, C⁴, Cy) ppm.

³¹P{¹H} NMR (162.0 MHz, C₆D₆): δ = 22.0 (¹J_{P-Pt} = 2595 Hz) ppm.

¹⁹⁵Pt{¹H} NMR (86.0 MHz, C₆D₆): δ = -4053 (¹J_{P-Pt} = 2595 Hz) ppm.

Elemental analysis (%) calculated for C₃₆H₆₆P₂PtAsCl₃: C 46.14, H 7.10; found: C 46.47, H 7.18.

***trans*-[PtCl(AsCl₂)(IMes)(PCy₃)] (5):** [Pt(IMes)(PCy₃)] (20.0 mg, 25.6 μmol) was dissolved in toluene (0.6 mL) and a solution of AsCl₃ in Et₂O (0.12 mol/L, 0.23 mL, 27.0 μmol) was added at ambient temperature. The reaction mixture was stirred for 1 h and the resulting precipitate was filtered off and washed with Et₂O (3 x 1 mL) to yield **5** (18.2 mg, 18.9 μmol, 74%) as a colourless powder.

¹H NMR: (400.1 MHz, d₈-toluene): δ = 6.83 (s, 2H, *H*-Mes), 6.78 (s, 2H, *H*-Mes), 6.18 (s, 2H, NCHCHN), 2.85 (m, 3H, Cy), 2.49 (s, 6H, Me), 2.19 (s, 6H, Me), 2.16 (s, 6H, Me), 2.04 (m, 6H, Cy), 1.66 (m, 9H, Cy), 1.51 (m, 6H, Cy), 1.30 (m, 6H, Cy), 1.17 (m, 3H, Cy) ppm.

¹³C NMR: (86.0 MHz, d₈-toluene): δ = 139.1 (s, *ipso*-C_{Ar}, Mes), 138.0 (s, *p*-C_{Ar}, Mes), 135.2 (s, *o*-C_{Ar}, Mes), 134.8 (s, *o*-C_{Ar}, Mes), 129.9 (s, *m*-C_{Ar}, Mes), 129.5 (s, *m*-C_{Ar}, Mes), 123.5 (d, ⁴J_{C-P} = 4 Hz, NCHCHN), 32.7 (d, ¹J_{C-P} = 26 Hz, C¹, Cy), 30.5 (s, ²J_{C-P} = 1 Hz, C², C⁶, Cy), 27.9 (d, ²J_{C-P} = 11 Hz, C³, C⁵, Cy), 26.8 (d, ⁴J_{C-P} = 1 Hz, C⁴, Cy) ppm.

³¹P NMR: (162.0 MHz, d₈-toluene): δ = 13.5 ppm (¹J_{P-Pt} = 2665 Hz).

¹⁹⁵Pt NMR: (86.0 MHz, d₈-toluene): δ = -3860 ppm (¹J_{P-Pt} = 2665 Hz).

Elemental analysis (%) calculated for C₃₉H₅₈AsCl₃N₂PPt: C 48.68, H 6.08, N 2.91; found: C 48.34, H 6.02, N 2.54.

***trans*-[Pt(AsCl₂)Cl(IMes)₂] (6):** [Pt(IMes)₂] (24.5 mg, 30.4 μmol) was dissolved in benzene (0.6 mL) and a solution of AsCl₃ in Et₂O (0.24 mol/L, 0.13 mL, 30.4 μmol) was added at ambient temperature. The reaction mixture was stirred for 1 h and the resulting precipitate was filtered

off and washed with Et₂O (3 x 1 mL) to yield **6** (14.0 mg, 14.2 μmol, 46%) as a colourless powder.

¹H NMR: (500.1 MHz, C₆D₆): δ = 6.66 (s, 4H, *H*-Mes), 6.47 (s, 4H, *H*-Mes), 5.91 (s, 4H, NCHCHN), 2.55 (s, 12H, Me), 2.17 (s, 12H, Me), 1.67 (s, 12H, Me) ppm.

¹³C NMR: (125.75 MHz, C₆D₆): δ = 137.9 (s, *o*-C_{Ar}, Mes.), 137.6 (s, *o*-C_{Ar}, Mes), 137.5 (s, *ipso*-C_{Ar}, Mes.) 134.0 (s, *p*-C_{Ar}, Mes), 130.7 (s, *m*-C_{Ar}, Mes) 129.0 (s, *m*-C_{Ar}, Mes), 124.84 (d, ⁴J_{C-P} = 4 Hz, NCHCHN), 21.7 (s, CH₃), 21.1 (s, CH₃), 19.7 (s, CH₃) ppm.

¹⁹⁵Pt NMR: (107.5 MHz, C₆D₆): δ = -3188 ppm.

Elemental analysis (%) calculated for C₄₂H₅₀AsCl₃N₄Pt: C 51.10, H 5.11, N 5.68; found: C 51.43, H 5.31, N 5.91.

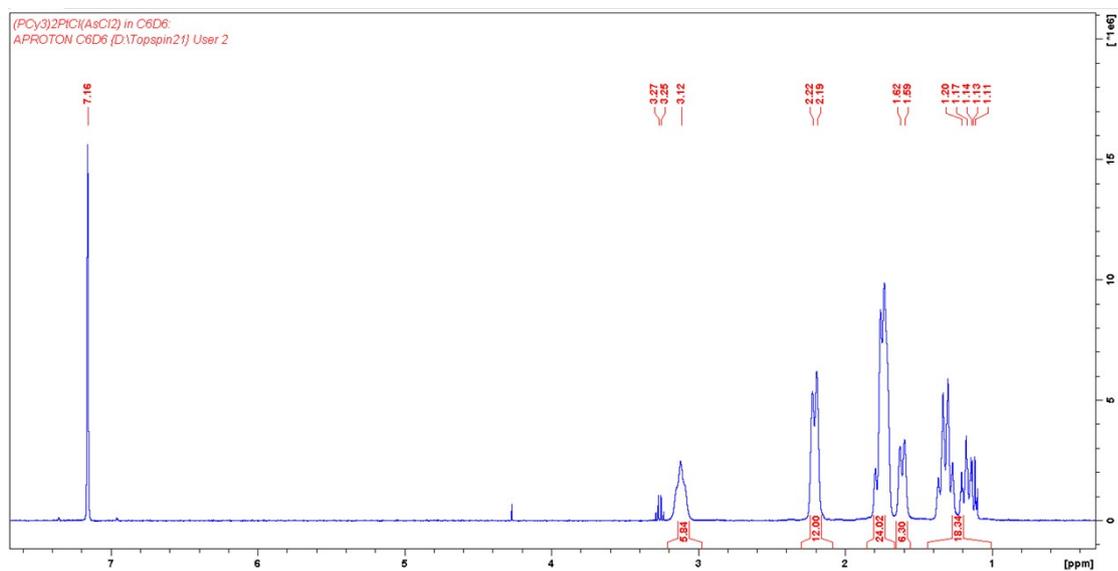
Attempted synthesis of *trans*-[PtBr(AsBr₂)(PCy₃)₂] (7**):** [Pt(PCy₃)₂] (20.0 mg, 26.4 μmol) was dissolved in Et₂O (0.6 mL) and AsBr₃ (8.34 mg, 26.4 μmol) was added at ambient temperature. ³¹P{¹H} NMR spectroscopy indicated immediate formation of *trans*-[PtBr(AsBr₂)(PCy₃)₂], together with *trans*-[(Cy₃P)₂PtBr₂]. After 30 minutes in solution further decomposition was observed by the appearance of several peaks in the ³¹P{¹H} NMR, and compound **7** could not be successfully isolated. During several attempts to crystallise **7**, X-ray quality crystals of the cluster compound [(PCy₃)₂Pt(μ₃-As)₂{PtBr(PCy₃)₂}] (**8**) were repeatedly obtained. Deep red **8** was the only arsenic-containing compound identified by X-ray diffraction.

³¹P NMR of **7 from mixture:** (162.0 MHz, Et₂O): δ = 18.6 ppm (¹J_{P-Pt} = 2613 Hz).

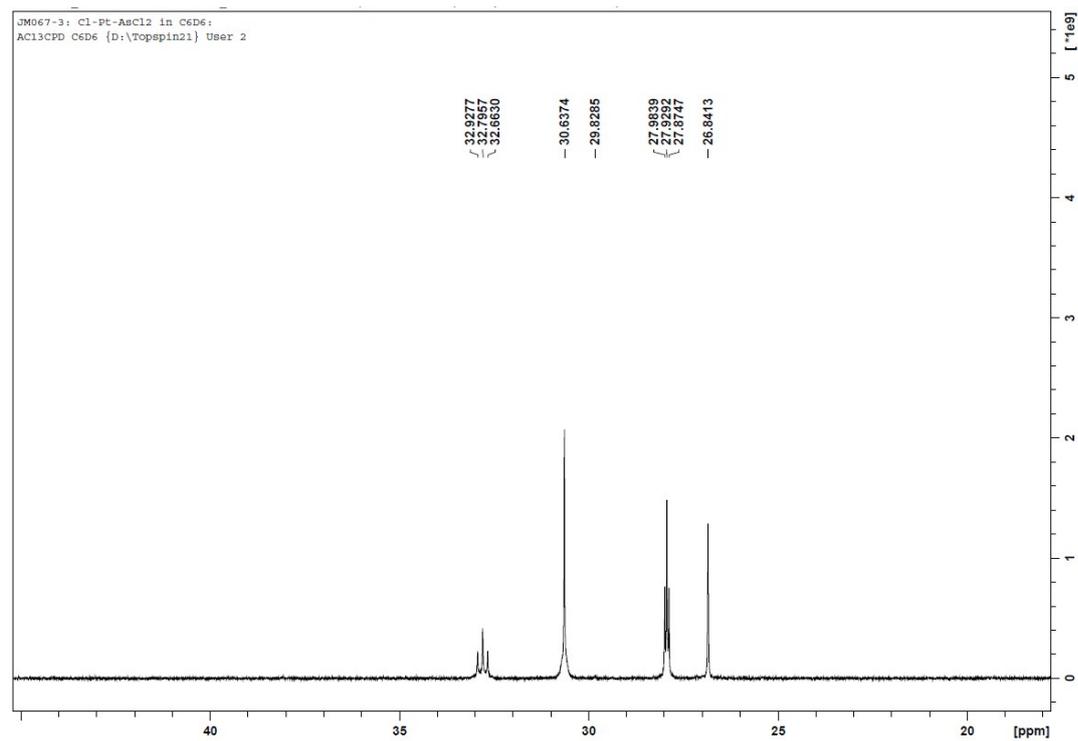
NMR Spectra:

trans-[(C₃P)₂PtCl(AsCl₂)] (4)

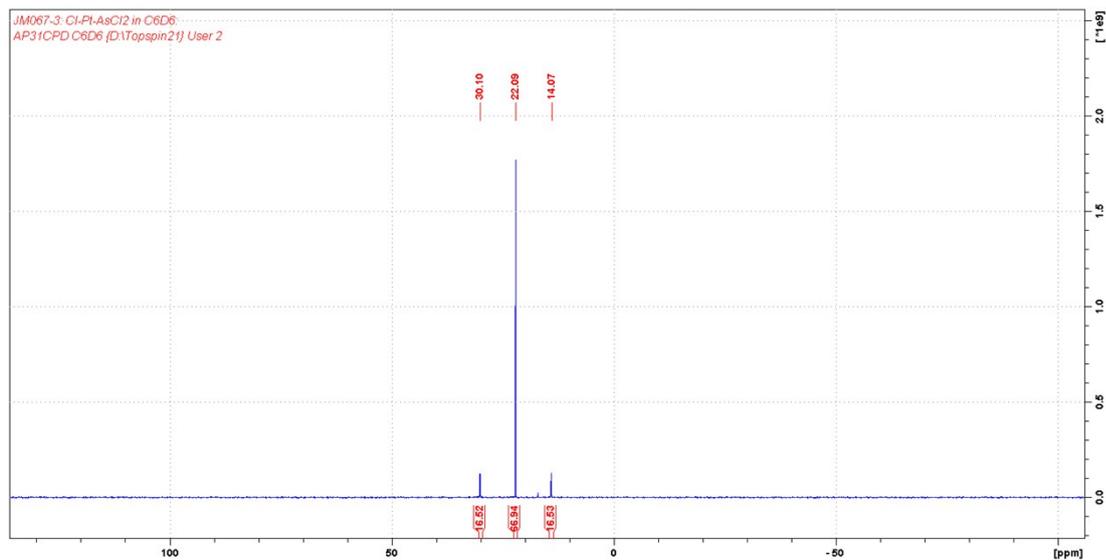
¹H NMR



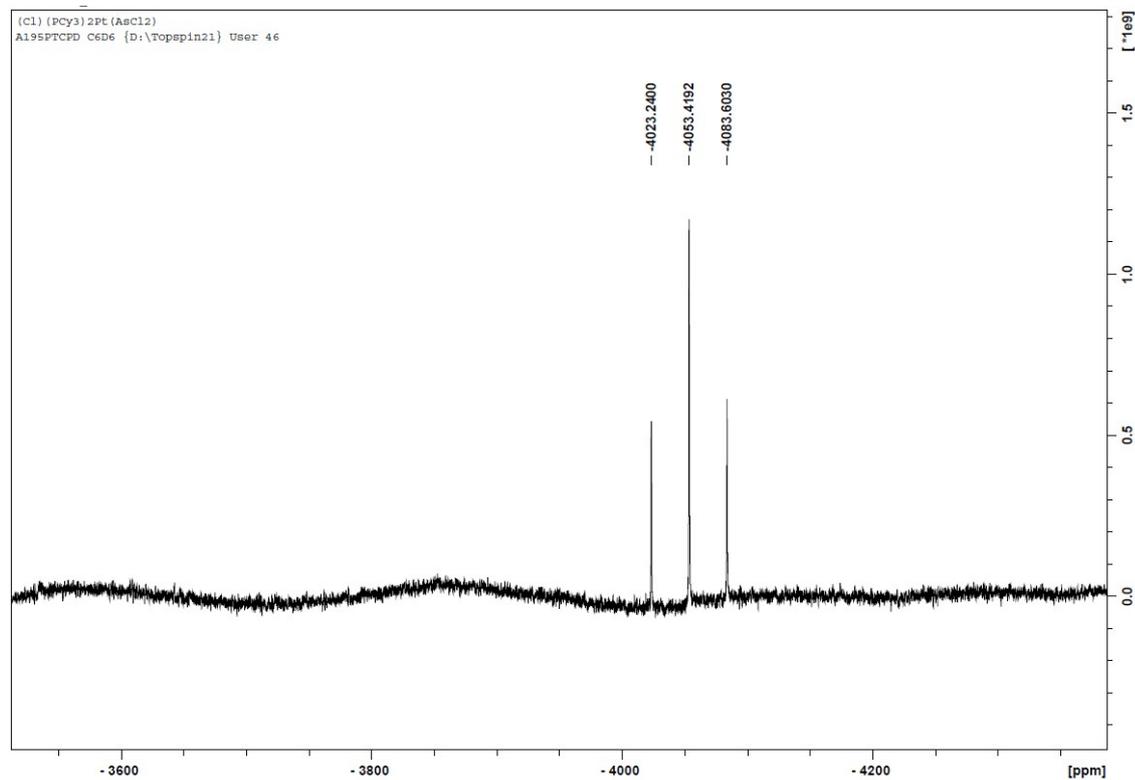
¹³C{¹H} NMR



$^{31}\text{P}\{^1\text{H}\}$ NMR

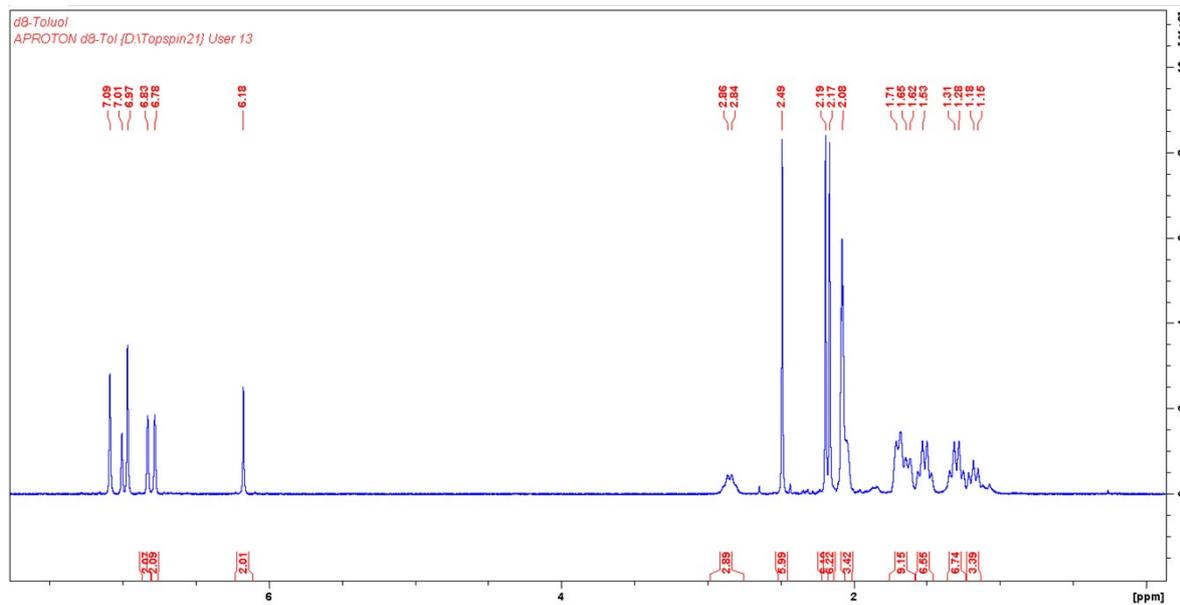


$^{195}\text{Pt}\{^1\text{H}\}$ NMR:

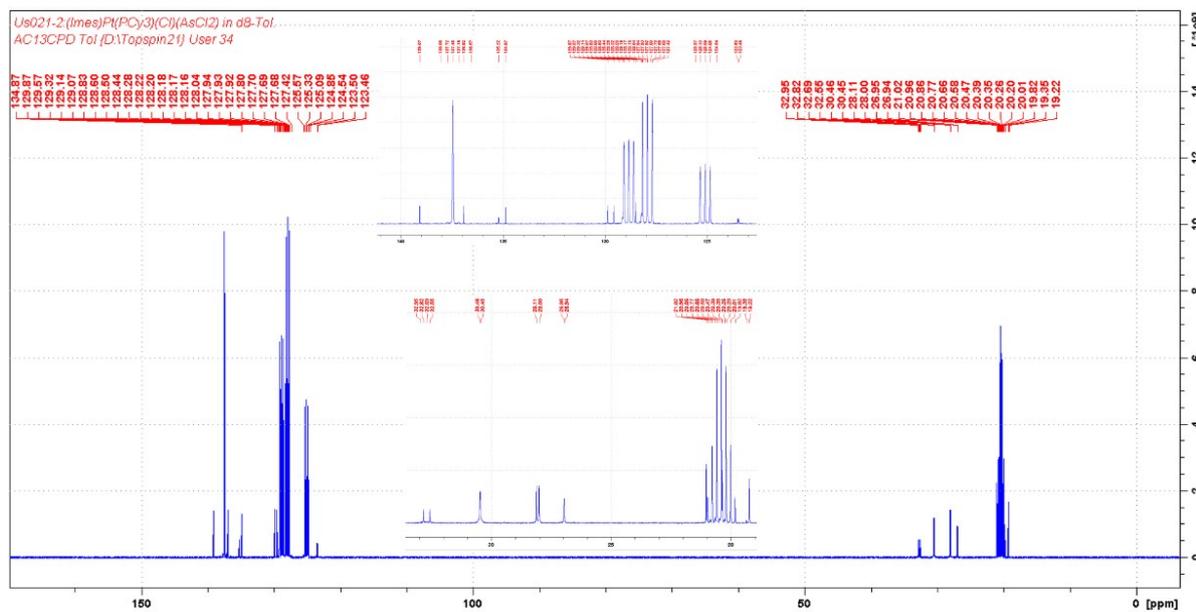


trans-[PtCl(AsCl₂)(IMes)(PCy₃)] (5)

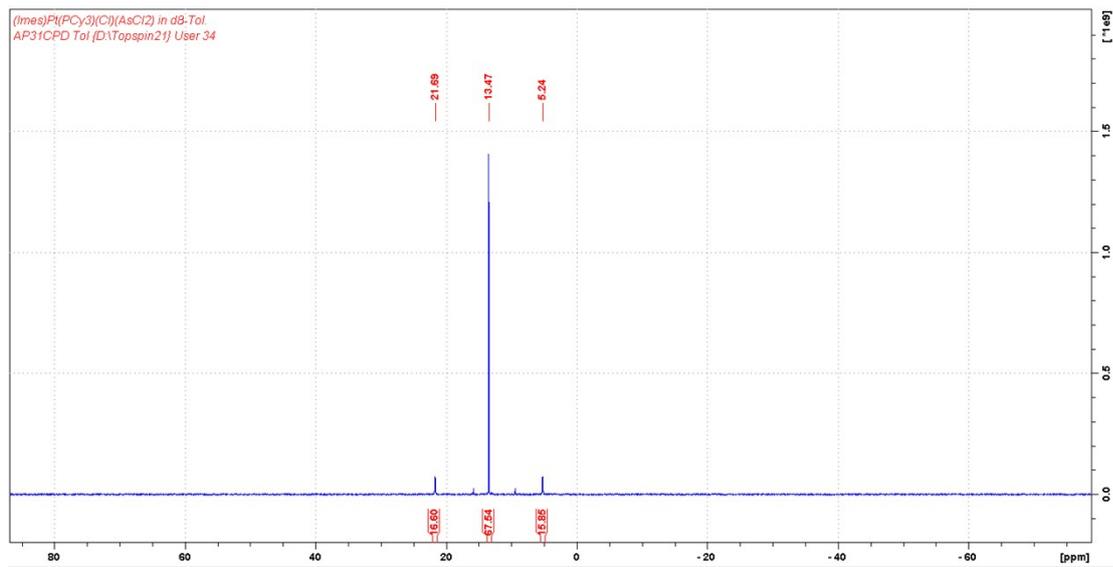
¹H NMR:



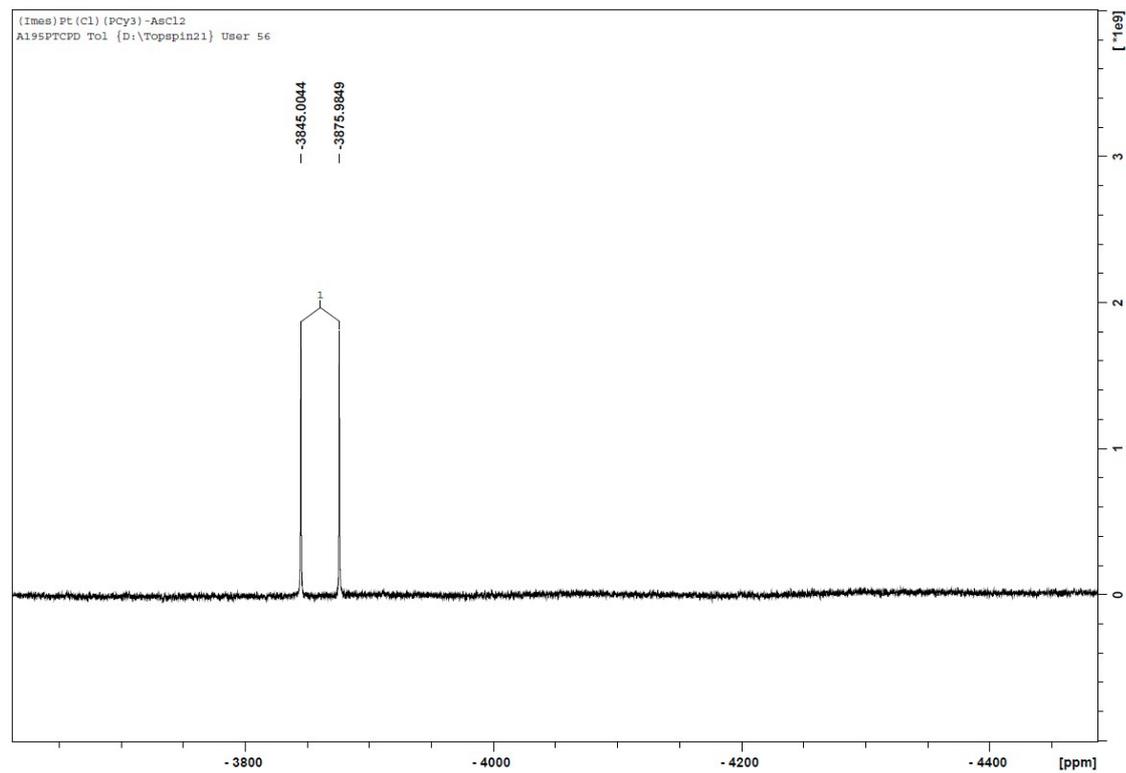
¹³C{¹H} NMR:



$^{31}\text{P}\{^1\text{H}\}$ NMR:

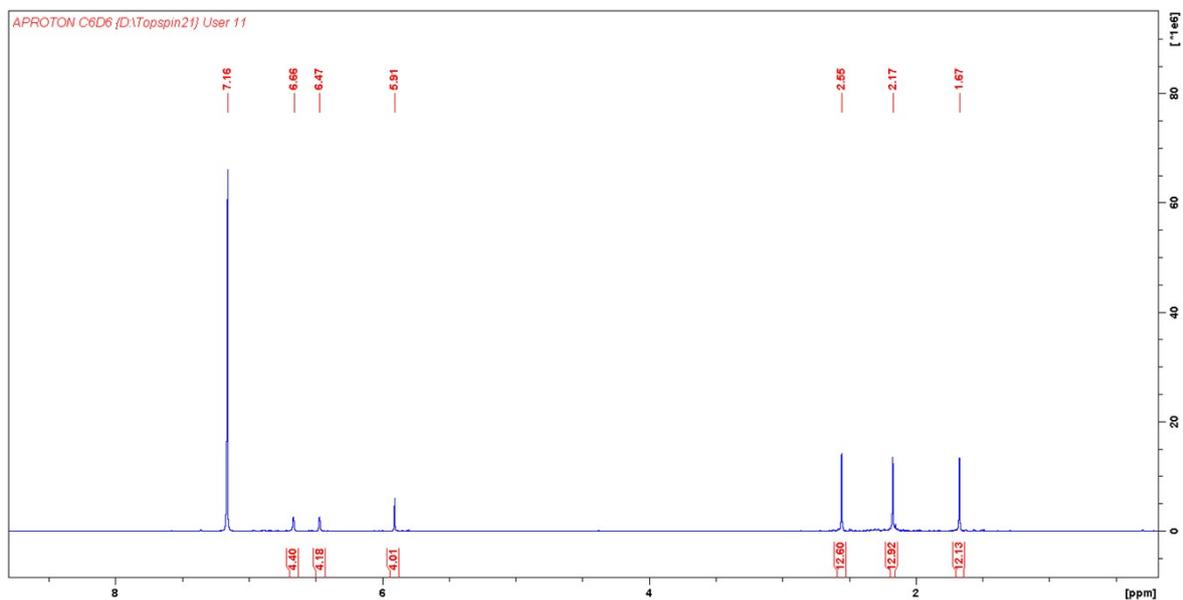


$^{195}\text{Pt}\{^1\text{H}\}$ NMR:

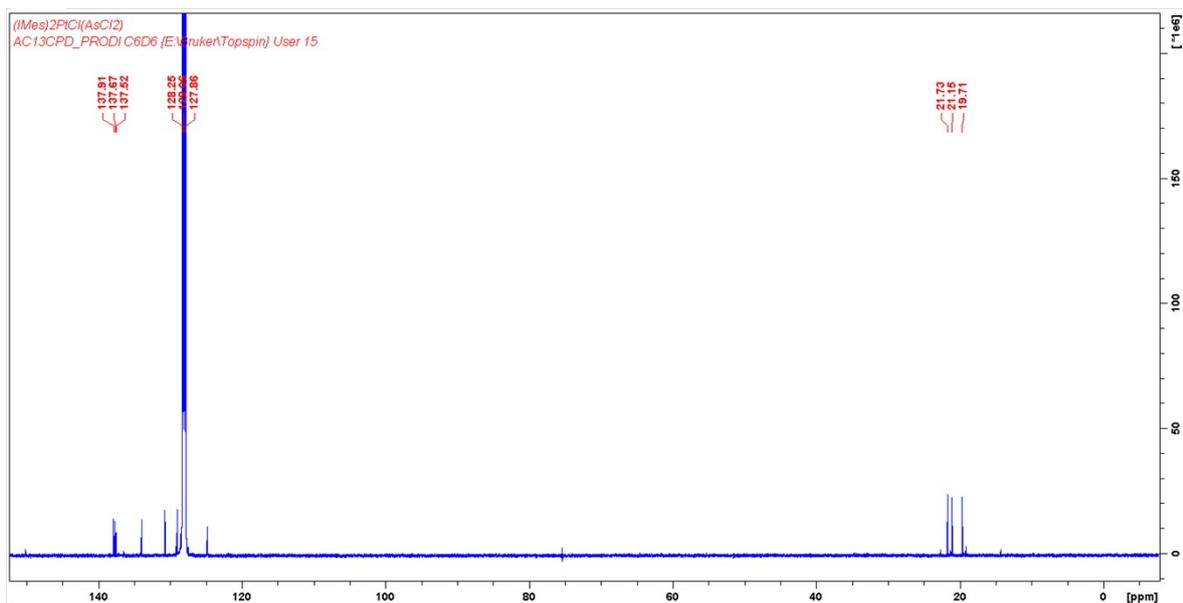


trans-[Pt(AsCl₂)Cl(IMes)₂] (6)

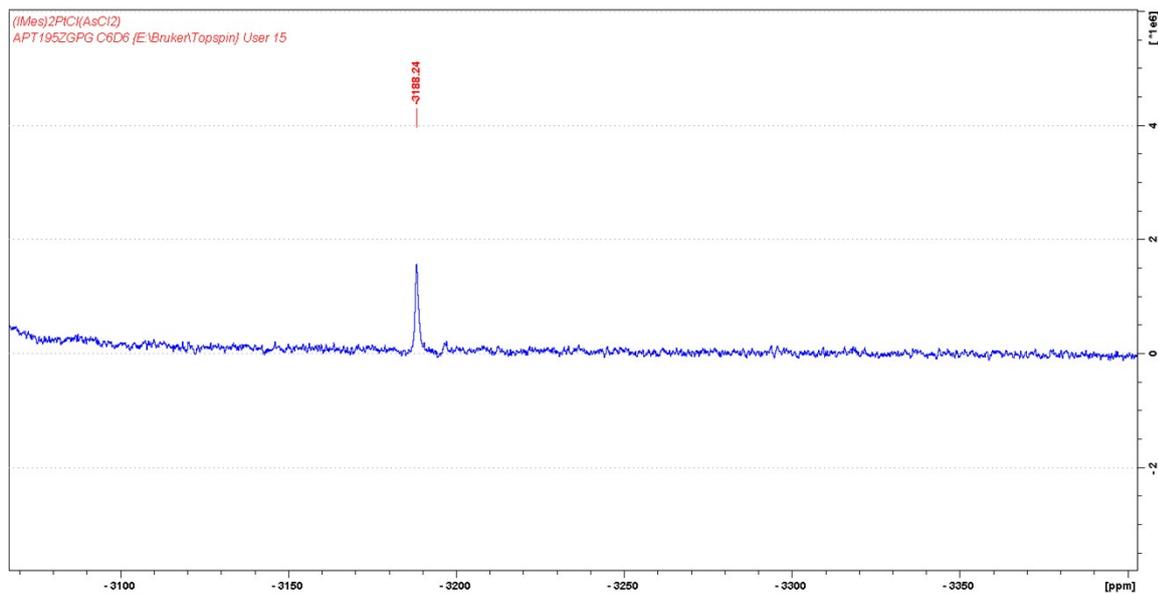
¹H NMR:



¹³C{¹H} NMR:



$^{195}\text{Pt}\{^1\text{H}\}$ NMR



Crystallographic Details

The crystal data of *trans*-[(Cy₃P)₂PtCl(AsCl₂)] (**4**) and *trans*-[(Cy₃P)(IMes)PtCl(AsCl₂)] (**5**) were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated MoK α radiation. The structures were solved using the intrinsic phasing method,⁵ refined with the SHELXL program⁶ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized positions.

Crystal data for *trans*-[(Cy₃P)₂PtCl(AsCl₂)] (**4**): C₃₆H₆₆AsCl₃P₂Pt, $M_r = 937.18$, yellow needle, 0.234×0.069×0.069 mm³, triclinic space group $P\bar{1}$, $a = 10.0229(4)$ Å, $b = 13.4142(5)$ Å, $c = 15.1155(6)$ Å, $\alpha = 89.3400(10)^\circ$, $\beta = 89.1100(10)^\circ$, $\gamma = 74.4180(10)^\circ$, $V = 1957.28(13)$ Å³, $Z = 2$, $\rho_{calcd} = 1.590$ g·cm⁻³, $\mu = 4.734$ mm⁻¹, $F(000) = 948$, $T = 100(2)$ K, $R_1 = 0.0171$, $wR^2 = 0.0378$, 7947 independent reflections [$2\theta \leq 52.746^\circ$] and 388 parameters.

Crystal data for *trans*-[(Cy₃P)(IMes)PtCl(AsCl₂)] (**5**): C₃₉H₅₇AsCl₃N₂PPt, $M_r = 961.19$, colorless plate, 0.21×0.126×0.057 mm³, triclinic space group $P\bar{1}$, $a = 10.255(2)$ Å, $b = 10.607(3)$ Å, $c = 19.408(6)$ Å, $\alpha = 81.416(18)^\circ$, $\beta = 78.469(16)^\circ$, $\gamma = 71.452(12)^\circ$, $V = 1952.7(9)$ Å³, $Z = 2$, $\rho_{calcd} = 1.635$ g·cm⁻³, $\mu = 4.710$ mm⁻¹, $F(000) = 964$, $T = 100(2)$ K, $R_1 = 0.0273$, $wR^2 = 0.0519$, 9623 independent reflections [$2\theta \leq 56.562^\circ$] and 430 parameters.

Crystal data for **8**: C₇₇H₁₄₄As₂Br₂P₄Pt₃, $M_r = 2088.72$, red block, 0.09×0.08×0.04 mm³, Monoclinic space group $P2_1/n$, $a = 15.239(6)$ Å, $b = 26.032(8)$ Å, $c = 21.255(7)$ Å, $\beta = 101.68(2)^\circ$, $V = 8257(5)$ Å³, $Z = 4$, $\rho_{calcd} = 1.680$ g·cm⁻³, $\mu = 6.949$ mm⁻¹, $F(000) = 4144$, $T = 103(2)$ K, $R_1 = 0.0495$, $wR^2 = 0.0630$, 17605 independent reflections [$2\theta \leq 53.592^\circ$] and 842 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers 1885931 (**4**), 1885930 (**5**) and 1885932 (**8**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Literature

- 1 T. Yoshida, S. Otsuka and T. Matsuda, *Inorg. Synth.*, 1990, **28**, 113–123.
- 2 F. Hupp, M. Ma, F. Kroll, J. O. C. Jimenez-Halla, R. D. Dewhurst, K. Radacki, A. Stasch, C. Jones and H. Braunschweig, *Chem. Eur. J.*, 2014, **20**, 16888-16898.
- 3 A. J. Arduengo III, S. F. Gamper, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1994, **116**, 4391-4394.
- 4 A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641-6649.
- 5 G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
- 6 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.