

SUPPLEMENTARY MATERIALS

Cationic intermediates in Oxidative Addition Reactions of Cl₂ to [PtCl₂(*cis*-1,4-DACH)].

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Figure S1. ¹H-NMR spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(*O*-DMF)](CF₃SO₃) in Acetone-d₆.

Figure S2. [¹H-¹⁹⁵Pt]-HMQC spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(*O*-DMF)](CF₃SO₃) in Acetone-d₆.

Figure S3. 2D COSY NMR spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(DMSO)]Cl in DMSO-d₆.

Figure S4. ¹H-NMR spectra: **a**, [PtCl₂(*en*)] in DMSO-d₆; **b**, soon after addition of Cl₂ in CCl₄; **c**, after 20 h; **d**, after 14 days.

Figure S5. ¹H-NMR spectrum of [PtCl₂(*cis*-1,4-DACH)] in Acetone-d₆ soon after addition of Cl₂ at 203 K.

Figure S6. 2D COSY NMR of *fac*-[PtCl₃(*cis*-1,4-DACH){O=C(CH₃)₂}]Cl in Acetone-d₆ at 203 K.

Figure S7. [¹H-¹⁹⁵Pt] HMQC spectrum of [PtCl₂(*cis*-1,4-DACH)] in Acetone-d₆ at 203 K soon after addition of Cl₂.

Figure S8. ¹H-NMR (600 MHz) spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] in DMSO-d₆.

Figure S9. [¹H-¹⁹⁵Pt] HSQC spectrum (300 MHz, ¹H) of *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] in DMSO-d₆.

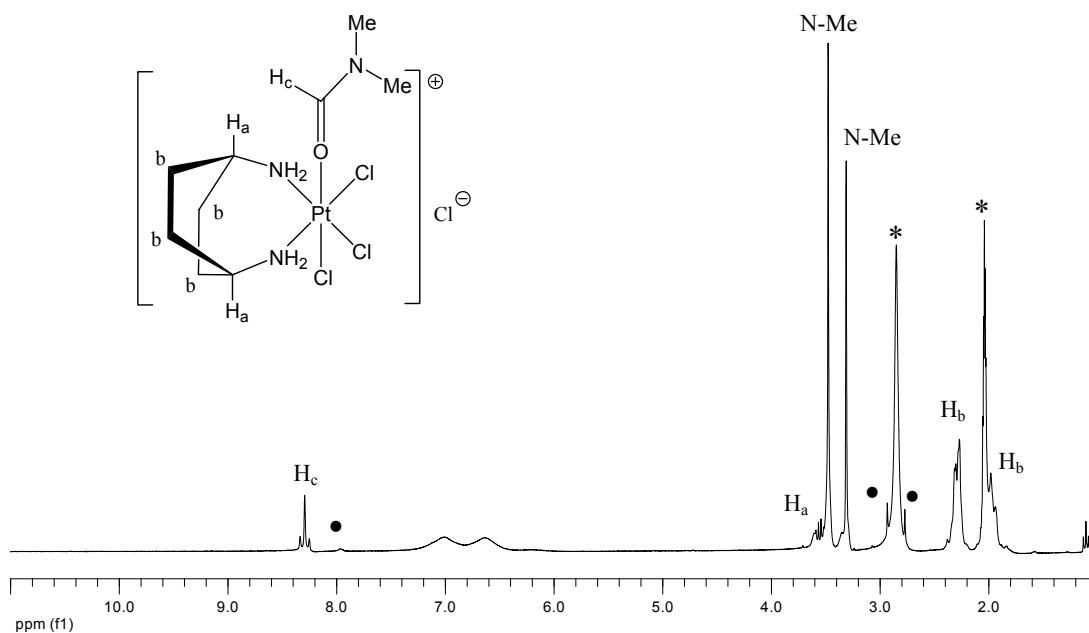


Figure S1. $^1\text{H-NMR}$ spectrum of $\text{fac-}[\text{PtCl}_3(\text{cis-1,4-DACH})(\text{O-DMF})](\text{CF}_3\text{SO}_3)$ in Acetone- d_6 .

Peaks belonging to free DMF are marked with •. The asterisks indicate residual solvent peaks.

The spectrum exhibits a pseudotriplet (singlet with platinum satellites) at 8.30 ppm ($^3J_{\text{Pt-H}} = 25$ Hz) and two singlets at 3.48 and 3.32 ppm assigned, respectively, to the amidic proton and to the two methyl groups of coordinated DMF. The two broad multiplets around 7.01 and 6.64 ppm (amine protons), the pseudotriplet at 3.48 ppm ($^3J_{\text{Pt-H}} = 75$ Hz, methynic protons), and the two multiplets centered at 2.30 and 1.96 ppm (methylene protons) are assigned to the *cis*-1,4-DACH ligand. Three very weak singlets at 7.97, 2.94, and 2.78 ppm are assigned, respectively, to the amidic proton and to the methyl protons of free DMF.

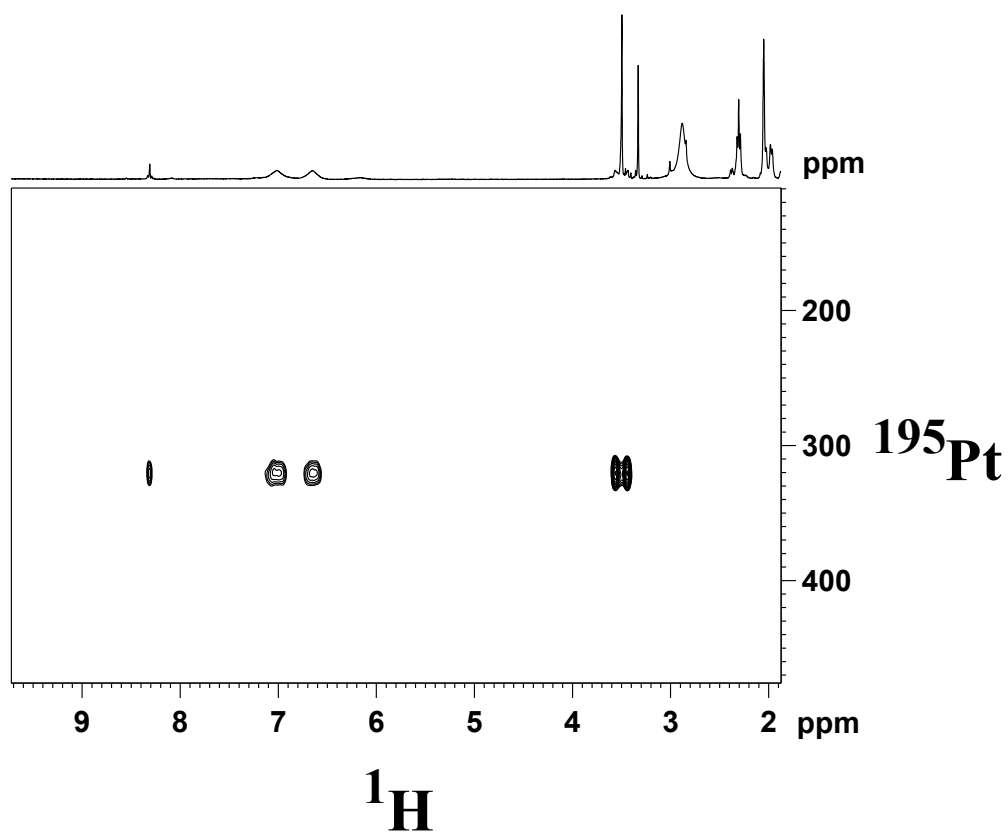


Figure S2. [^1H - ^{195}Pt]-HMQC spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(*O*-DMF)](CF₃SO₃) in Acetone-*d*₆.

The spectrum shows cross peaks between the signal of the Pt atom falling at 320 ppm (Table 1) and those of the aminic protons of DACH and of the amidic and methyl protons of DMF (see also Figure S1).

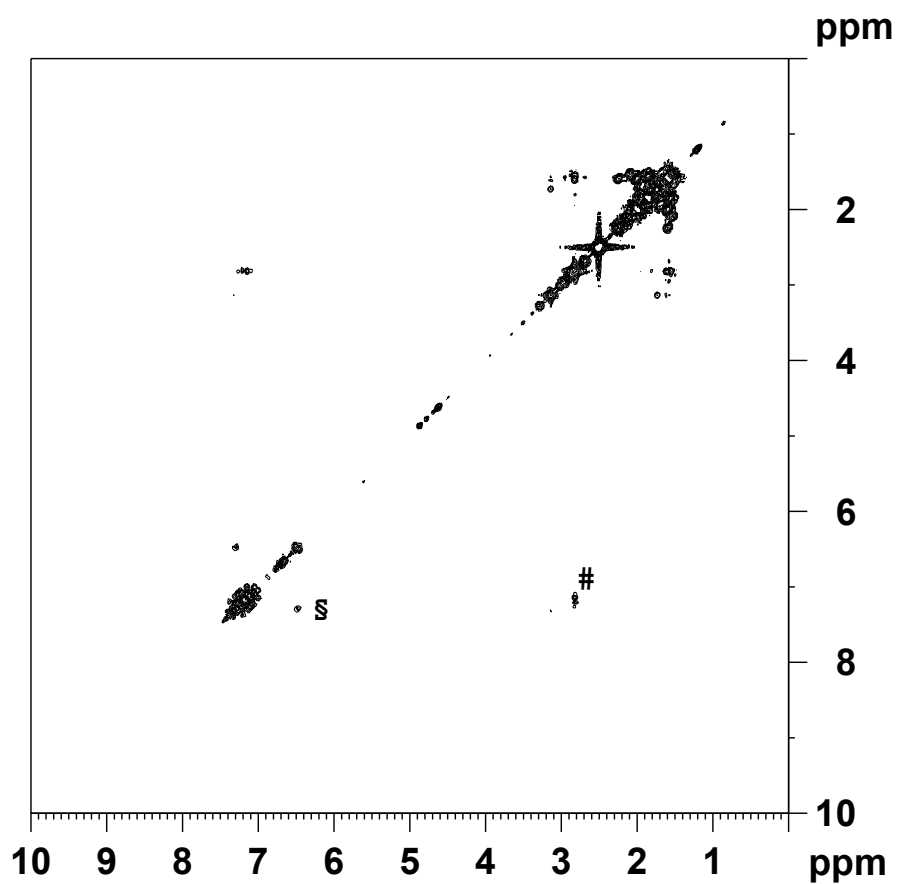


Figure S3. 2D COSY NMR spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(DMSO)]Cl in DMSO-d₆. § indicates the cross peak between the signal at *ca.* 7.30 ppm (partially overlapping with the more intense signal at 7.18 ppm) and the signal at 6.48 ppm. # indicates the cross peak between the multiplet at 7.18 ppm and the signal at 2.81 ppm

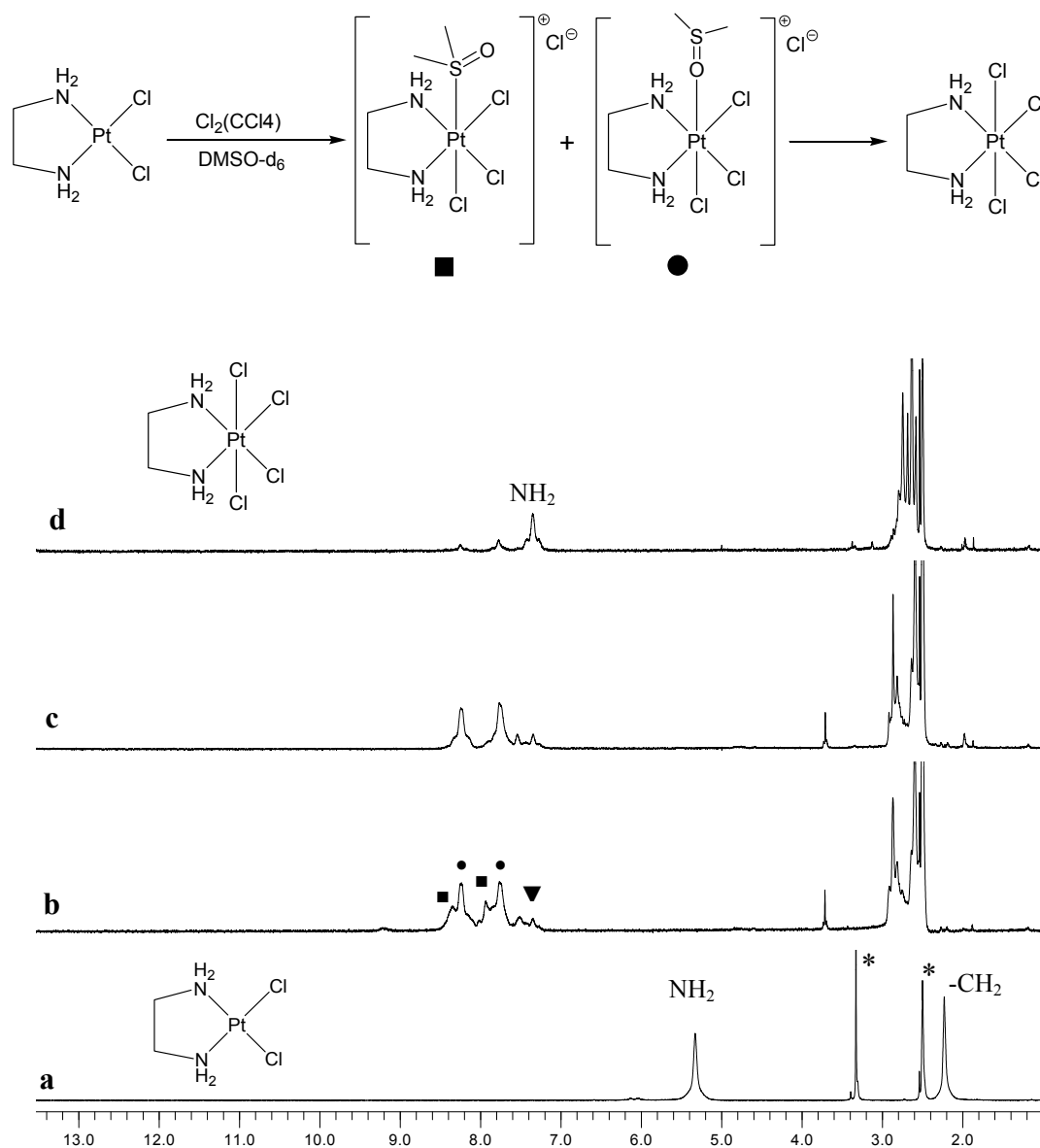


Figure S4. Top, reaction scheme. Bottom, $^1\text{H-NMR}$ spectra: **a**, $[\text{PtCl}_2(\text{en})]$ in DMSO-d_6 ; **b**, soon after addition of Cl_2 in CCl_4 ; **c**, after 20 h; **d**, after 14 days. The asterisks indicate residual solvent peaks.

The $^1\text{H-NMR}$ spectrum of a solution of the starting $[\text{PtCl}_2(\text{en})]$ complex in DMSO-d_6 (Figure S5-a) exhibits a broad singlet at 5.33 ppm assigned to the aminic protons and a singlet at 2.23 ppm assigned to the methylene protons of the coordinated ethylenediamine. After addition of Cl_2 (Figure S5-b) the signals of the starting Pt(II) complex disappear and three new sets of signals appear in the region of aminic protons between 9 and 7 ppm. The first set (marked by ■ in Figure S5-b) consists of two multiplets centered at 8.35 and 7.93 ppm; the second set (marked by ●) consists of two multiplets centered at 8.24 and 7.76 ppm; finally, the third set (marked by ▼) consists of one multiplet centered at 7.34 ppm. The last signal coincides with the aminic protons of the tetrachlorido end product $[\text{PtCl}_4(\text{en})]$, which was found to be the main species after 14 days (Figure S5-d). The two intermediate species (marked by ■ and ●) most likely are the Pt^{IV} complexes having the DMSO molecule coordinated to a metal center through the oxygen (●, more stable) or the sulphur atom (■, less stable) as already observed in the case of $[\text{PtCl}_2(\text{cis-1,4DACH})]$ (see **Figure 4**).

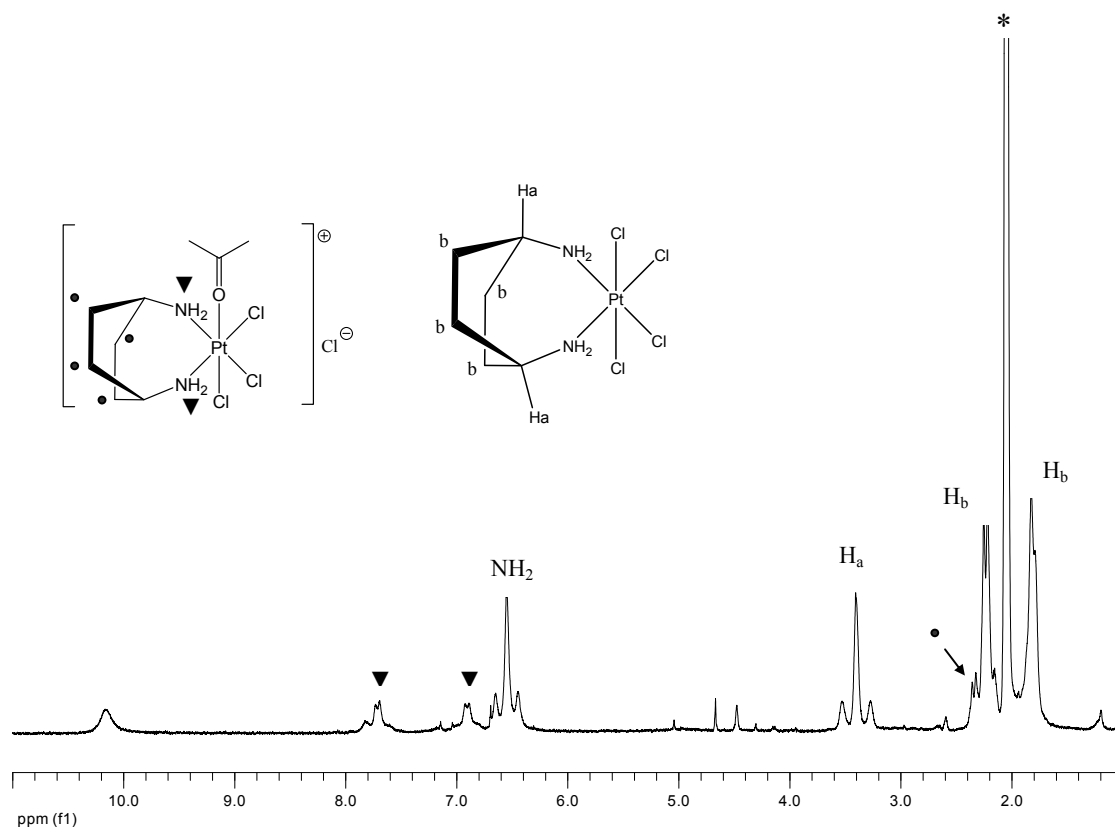


Figure S5. $^1\text{H-NMR}$ spectrum of $[\text{PtCl}_2(\text{cis-1,4-DACH})]$ in Acetone-d_6 soon after addition of Cl_2 at 203 K. The asterisk indicates residual solvent peak.

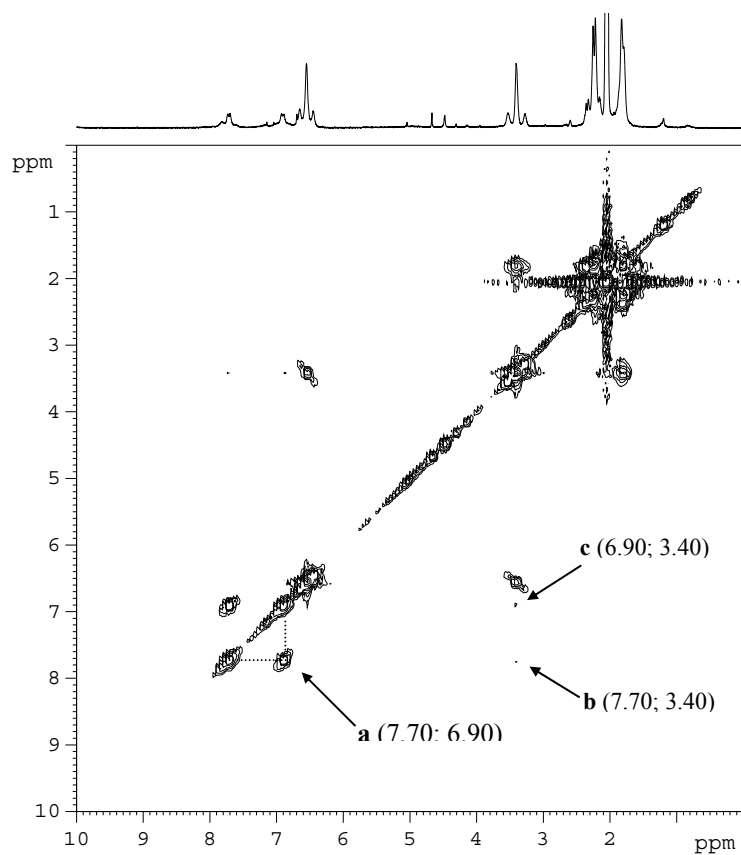


Figure S6. 2D COSY NMR of *fac*-[PtCl₃(*cis*-1,4-DACH){O=C(CH₃)₂}]Cl in Acetone-d₆ at 203 K. The spectrum shows a cross peak (indicated by **a**) which correlates the signals at 7.70 and 6.90 ppm assigned to the aminic protons of the intermediate Pt^{IV} solvato species (the aminic protons of the cyclohexane ring become magnetically non-equivalent because of the diversity of the two axial ligands). The spectrum also shows cross peaks (**b** and **c**) between the signals at 7.70 and 6.90 ppm and that at 3.40 ppm confirming that the methinic protons of the intermediate species resonate at the same frequency as those of the end product [PtCl₄(*cis*-1,4-DACH)].

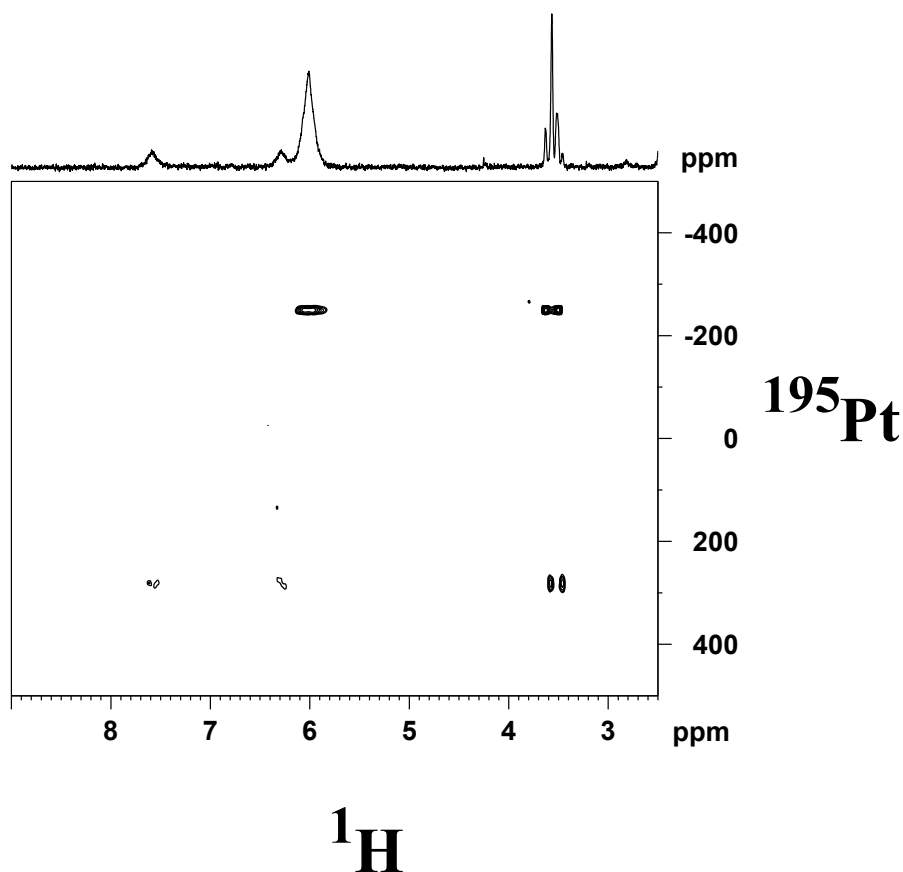


Figure S7. [^1H - ^{195}Pt] HMQC spectrum of $[\text{PtCl}_2(\text{cis-1,4-DACH})]$ in Acetone- d_6 at 203 K soon after addition of Cl_2 .

The spectrum shows two splitted cross-peaks ($^1\text{H}/^{195}\text{Pt}$) centered at 6.13/-250 and 3.54/-250 ppm which are assigned to the final $[\text{PtCl}_4(\text{cis-1,4-DACH})]$ product of the oxidation reaction and three cross-peaks ($^1\text{H}/^{195}\text{Pt}$) at 7.70/281, 6.90/281, and 3.40/281 ppm which are compatible with a $[\text{PtCl}_3(\text{cis-1,4-DACH})(\text{O-Acetone})]^+$ species.

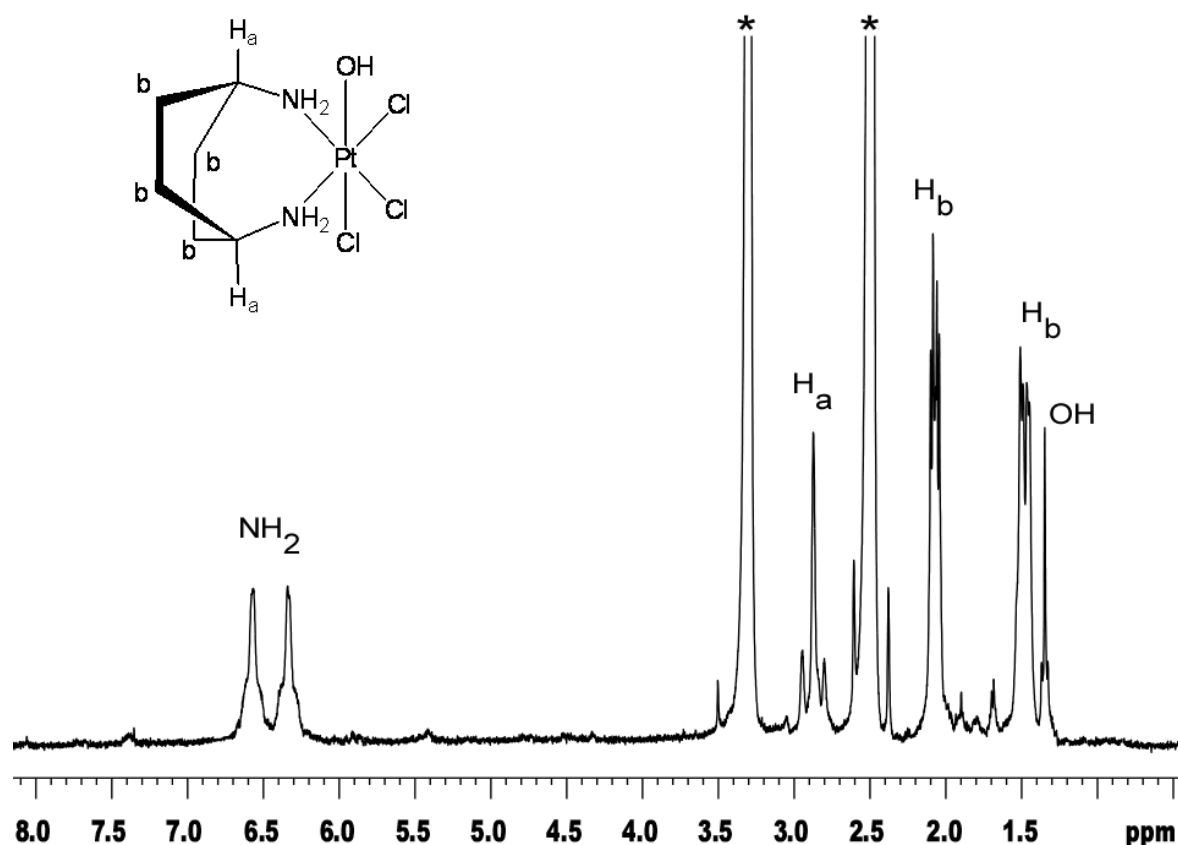


Figure S8. $^1\text{H-NMR}$ (600 MHz) spectrum of *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] in DMSO-*d*₆. The two broad pseudotriplets at 6.57 ($^2J_{\text{Pt-H}} = 63$ Hz) and 6.34 ($^2J_{\text{Pt-H}} = 63$ Hz) ppm are assigned to the NH₂ proton facing the axial OH and Cl ligands, respectively. The pseudotriplet at 2.87 ppm ($^3J_{\text{Pt-H}} = 88$ Hz) is assigned to H_a protons (numbering of protons reported in figure), while the two multiplets centered at 2.07 and 1.48 ppm are assigned to the eight H_b protons of the cyclohexane ring. The pseudotriplet at 1.35 ppm ($^2J_{\text{Pt-H}} = 25$ Hz) is assigned to the axial OH ligand. The asterisks indicate residual solvent peaks. *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] was also characterized by ESI-MS spectrometry (peak at *m/z* 454.8 assignable to the cation [PtCl₃(*cis*-1,4-DACH)(OH)+Na]⁺) and IR spectroscopy (peaks at 3480.7, $\nu(\text{O-H})$; 3181.7, $\nu(\text{N-H})$; and 332.2, $\nu(\text{Pt-Cl})$ cm⁻¹).

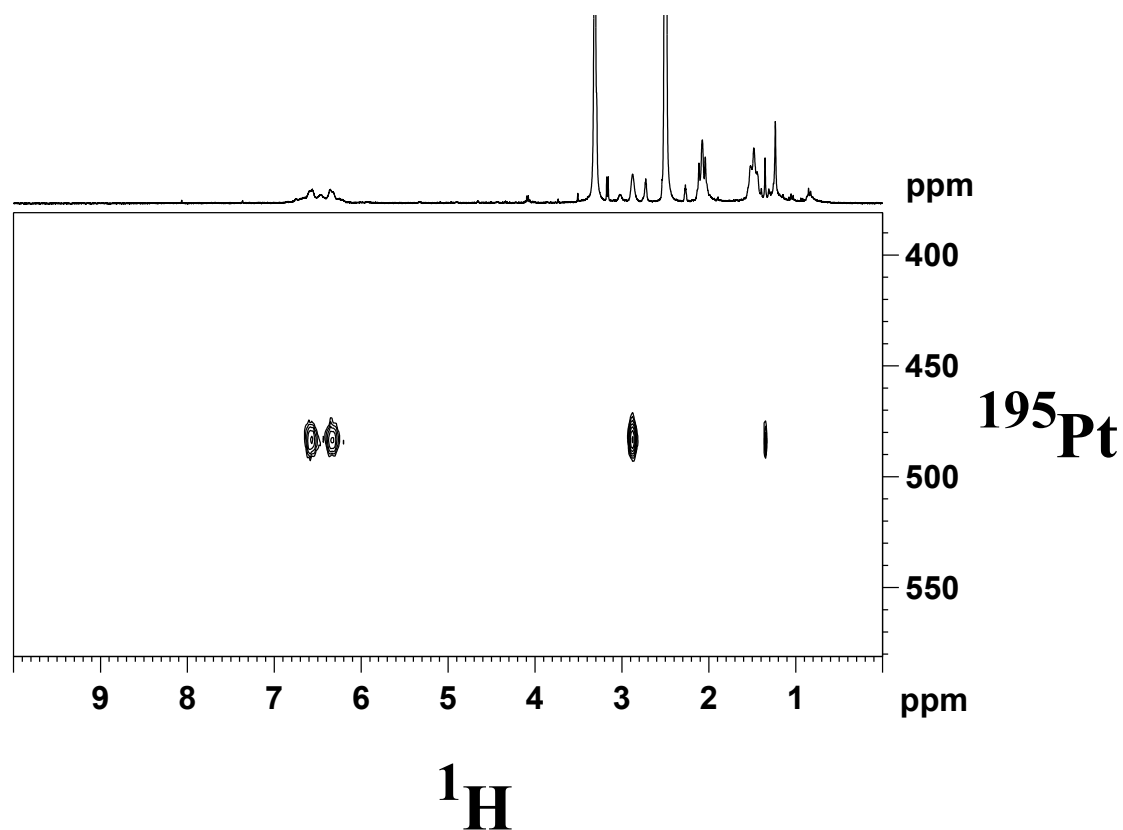


Figure S9. [^1H - ^{195}Pt] HSQC spectrum (300 MHz, ^1H) of *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] in DMSO-*d*₆.

The spectrum shows four cross-peaks ($^1\text{H}/^{195}\text{Pt}$) at 6.57/483, 6.34/483, 2.87/483, and 1.35/483 ppm. These cross-peaks correlate the ^1H peaks assigned to *fac*-[PtCl₃(*cis*-1,4-DACH)(OH)] to a Pt atom falling at 483 ppm, a chemical shift which is compatible with a Pt(IV) atom in a N₂Cl₃O coordination environment (Table 1).