

Supplementary Material

The Unexpected Reactivity of Zeise's Anion in Strong Basic Medium Discloses New Substitution Patterns at the Platinum Centre

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Experimental Section

Materials. All solvents and reagents, except otherwise stated, were purchased from Aldrich Chemical Company and used as received. Zeise's salt was prepared from potassium tetrachloroplatinate and ethylene gas as previously described.²⁰

Synthesis of complexes

[Pt(η^1 -C₂H₄OMe)Cl(Me₄en)], 7a. Zeise's salt (245 mg, 0.633 mmol) and KOH (71 mg, 1.3 mmol) were dissolved in 10 mL of cold MeOH (0 °C, ice bath); a white precipitate of KCl immediately formed and the colour of the solution changed from bright to pale yellow. After a couple of minutes **Me₄en** (74 mg, 0.64 mmol) was introduced in the reaction vessel and the mixture was stirred for about 3 hours; meanwhile the solution became completely colourless. The solvent was evaporated under vacuum and the solid residue was repeatedly extracted with CH₂Cl₂ (total used volume ~30 mL). The CH₂Cl₂ solution was kept stirring for few minutes over Na₂SO₄, then filtered on a celite bed and finally evaporated to dryness under vacuum. The white solid residue was **7a** (240 mg, 0.59

mmol). The isolated yield, referred to platinum, was 94 %. (Found: C, 26.6; H, 5.6; N, 7.0 %. $C_9H_{23}ClN_2OPt$ requires C, 26.6; H, 5.7; N, 6.9 %). $\delta_H(CDCl_3)$ 3.47 (m, 2H, *O*-CH₂-), 3.31 (s, 3H, *O*-CH₃), 2.89 (s, 3H, *N*-CH₃, $^3J_{Pt-H} = 51$ Hz), 2.78 (m, 2H, *N*-CH₂-), 2.71 (s, 3H, *N*-CH₃, $^3J_{Pt-H} = 13$ Hz), 2.54 (m, 2H, *N*-CH₂-), 1.62 (m, 2H, *Pt*-CH₂-, $^2J_{Pt-H} = 93$ Hz).

[Pt(η^1 -C₂H₄OMe)Cl(dip)], **7b**; **[Pt(η^1 -C₂H₄OMe)Cl(phen)]**, **7c**; **[Pt(η^1 -C₂H₄OMe)Cl(Me₂phen)]**, **7d**. The synthetic procedures were similar to that used for **7a**. However, in the present cases, a slightly higher base/platinum ratio and a lower temperature (-20 °C) were used. The used quantities were: MeOH, 5 mL; KOH, 300 mg (5.3 mmol); Zeise's salt, 500 mg (1.29 mmol); **dip**, 220 mg, or **phen**·H₂O, 283 mg, or **Me₂phen**, 297 mg (1.4 mmol in each case). The final products (**7b**, **7c**, and **7d**, respectively) have a limited solubility in the reaction medium and precipitate from solutions as yellow powders. After 3-5 hour stirring, the reaction mixture was filtered on a sintered glass filter, the solid was washed with abundant water to eliminate co-precipitated KCl, and dried under vacuum. 500 mg of **7b** (1.1 mmol, yield 87 %), 582 mg of **7c** (1.24 mmol, yield 96 %), and 280 mg of **7d** (0.56 mmol, yield 45 %) were obtained (isolated yields are referred to platinum). {(**7b**) Found: C, 35.3; H, 3.5; N, 6.2 %. $C_{13}H_{15}ClN_2OPt$ requires C, 35.0; H, 3.4; N, 6.3 %). $\delta_H(CDCl_3)$ 9.59 (d, 1H, CH, $^3J_{H-H} = 6$ Hz, $^3J_{Pt-H} = 15$ Hz); 9.23 (d, 1H, CH, $^3J_{H-H} = 6$ Hz, $^3J_{Pt-H} = 60$ Hz); 8.12 (m, 2H, CH); 7.99 (m, 2H, CH); 7.62 (m, 1H, CH); 7.50 (m, 1H, CH); 3.61 (m, 2H, *O*-CH₂); 3.39 (s, 3H, *O*-CH₃); 2.22 (m, 2H, *Pt*-CH₂-, $^2J_{Pt-H} = 90$ Hz)};²¹ {(**7c**) Found: C, 37.7; H, 2.9; N, 6.3 %. $C_{15}H_{15}ClN_2OPt$ requires C, 38.2; H, 3.2; N, 6.0 %). $\delta_H(CDCl_3)$ 9.81 (d, 1H, CH, $^3J_{H-H} = 6$ Hz, $^3J_{Pt-H} = 12$ Hz); 9.53 (d, 1H, CH, $^3J_{H-H} = 6$ Hz, $^3J_{Pt-H} = 57$ Hz); 8.65 (d, 1H, CH, $^3J_{H-H} = 9$ Hz); 8.55 (d, 1H, CH, $^3J_{H-H} = 9$ Hz); 7.95 (m, 3H, CH); 7.81 (d.d., 1H, CH, $^3J_{H-H} = 9$ Hz, $^3J_{H-H} = 6$ Hz); 3.70 (m, 2H, CH₂); 3.42 (s, 3H, OCH₃); 2.41 (m, 2H, *Pt*-CH₂-, $^2J_{Pt-H} = 90$ Hz)};²¹ {(**7d**) Found: C, 40.5; H, 3.6; N, 5.5 %. $C_{17}H_{19}ClN_2OPt$ requires C, 41.0; H, 3.9; N, 5.6 %). $\delta_H(CDCl_3)$ 8.33 (d, 1H, CH, $^3J_{H-H} = 9$ Hz); 8.28 (d, 1H, CH, $^3J_{H-H} = 9$ Hz); 7.75 (s, 1H, CH); 7.74 (s,

1H, CH); 7.59 (d, 1H, CH, $^3J_{\text{H-H}} = 9$ Hz); 7.56 (d, 1H, CH, $^3J_{\text{H-H}} = 9$ Hz); 3.71 (m, 2H, *O*-CH₂); 3.33 (s, 3H, *O*-CH₃); 3.19 (s, 3H, *N*-CH₃); 2.98 (s, 3H, *N*-CH₃); 2.33 (m, 2H, *Pt*-CH₂, $^2J_{\text{Pt-H}} = 95$ Hz)}.²¹

[PtCl(η^2 -C₂H₄)(Me₄en)]BF₄, 8a. Synthesis of **8a** can be carried out according to previously described methods.¹⁸

[PtCl(η^2 -C₂H₄)(dip)]BF₄, 8b. 0.464 g (1.04 mmol) of [Pt(CH₂CH₂OMe)Cl(**dip**)] (**7b**) were dissolved in CH₂Cl₂ (250 mL). To the solution was added first absolute EtOH (2.5 mL) and then concentrated HBF₄ (≈ 70 % in H₂O) until pH ~ 1 . During the acidification process the colour of the solution turned from yellow to pale yellow and a light yellow precipitate separated out. The solvent was evaporated under vacuum (no heating was applied to the reaction vessel) and from time to time absolute EtOH was added to the mixture so that the volume of the liquid phase never became less than 25 mL (in this way all the CH₂Cl₂ could be removed while the residual EtOH prevented the concentration of excess HBF₄ to reach levels that could have caused product decomposition). The precipitate was separated by filtration of the solution, washed with abundant absolute ethanol (until the apparent pH of the washing ethanol was neutral) and dried. 469 mg (0.93 mmol) of **8b** were obtained; the isolated yield, referred to platinum, was 90 %. (Found: C, 28.1; H, 2.4; N, 5.7 %. C₁₂H₁₃BClF₄N₂Pt requires C, 28.7; H, 2.6; N, 5.6 %). $\delta_{\text{H}}(\text{d}_6\text{-Acetone})$ 9.47 (d, 1H, CH, $^3J_{\text{H-H}} = 6$ Hz, $^3J_{\text{Pt-H}} = 36$ Hz); 8.85 (d, 1H, CH, $^3J_{\text{H-H}} = 6$ Hz); 8.78 (d, 1H, CH, $^3J_{\text{H-H}} = 9$ Hz); 8.71 (t, 1H, CH, $^3J_{\text{H-H}} = 6$ Hz); 8.59 (m, 2H, CH); 8.18 (m, 1H, CH); 7.97 (m, 1H, CH); 5.29 (s, 4H, CH₂, $^3J_{\text{Pt-H}} = 54$ Hz).²¹

[PtCl(η^2 -C₂H₄)(phen)]BF₄, 8c. The preparative procedure was analogous to that used for **8b**. Being **7c** less soluble in chlorinated solvents than **7b**, 504 mg (1.07 mmol) of [Pt-(CH₂CH₂OMe)Cl(**phen**)] required 500 ml of CH₂Cl₂ to be completely dissolved. All the operations were performed as described for **8b**. 532 mg (1.01 mmol) of **8c** were obtained; the isolated yield, referred to platinum, was 94 %. (Found: C, 31.5; H, 2.3; N, 5.4 %. C₁₄H₁₃BClF₄N₂Pt requires C, 31.9; H, 2.5; N, 5.3 %). $\delta_{\text{H}}(\text{d}_6\text{-Acetone})$ 9.71 (d, 1H, CH, $^3J_{\text{H-H}} = 6$ Hz, $^3J_{\text{Pt-H}} = 36$ Hz); 9.33 (d, 1H,

CH, $^3J_{\text{H-H}} = 8$ Hz); 9.21 (d, 1H, CH, $^3J_{\text{H-H}} = 9$ Hz); 9.04 (d, 1H, CH, $^3J_{\text{H-H}} = 6$ Hz, $^3J_{\text{Pt-H}} = 38$ Hz);
8.5 (m, 3H, 3CH); 8.28 (d.d., 1H, CH, $^3J_{\text{H-H}} = 8$ Hz, $^3J_{\text{H-H}} = 6$ Hz); 5.45 (s, 4H, 2CH₂, $^3J_{\text{Pt-H}} = 60$
Hz).²¹

Notes and references

20 Chock, J. Halpern and F. E. Paulik, *Inorg. Synth.*, 1990, **28**, 349.

21 The small splitting due to $^4J_{\text{H-H}}$ has been neglected.