Electronic Supplementary Information (ESI)

Unprecedented twofold intramolecular hydroamination in diam(m)ine-
dicarboxylatodichloridoplatinum(IV) complexes – ethane-1,2-diamine

versus ammine ligands

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EXPERIMENTAL

All reagents and solvents were obtained from commercial suppliers, and were used as received. For column chromatography, silica gel 60 (Fluka) was used. The starting compounds (OC-6-33)-dichlorido(ethane-1,2-diamine)dihydroxoplatinum(IV) 1 and (OC-6-33)-diamminedichloridodihydroxoplatinum(IV) 2 were synthesized according to standard literature procedures.\textsuperscript{[1,2]} \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{15}N, \textsuperscript{195}Pt and two-dimensional TOCSY, HMQC, HSQC, and HMBC NMR spectra were recorded with a Bruker Avance DPX 400 or a Bruker Avance III 500 MHz NMR spectrometer, using the solvent residual peak for \textsuperscript{1}H and \textsuperscript{13}C as internal standard. \textsuperscript{15}N chemical shifts were referenced relative to external NH\textsubscript{4}Cl, whereas \textsuperscript{195}Pt chemical shifts were referenced relative to external K\textsubscript{2}[PtCl\textsubscript{4}]. Half height line widths of \textsuperscript{195}Pt resonances are given in parentheses. All infrared spectra were obtained from a KBr matrix (4000-400 cm\textsuperscript{-1}) using a Bruker Vertex 70 FTIR spectrometer. Electrospray ionization mass spectrometry was carried out with a Bruker Esquire 3000 instrument using MeOH as solvent. Elemental analyses were performed using a Perkin-Elmer 2400 CHN-Elemental Analyser by the microlaboratory of the Institute of Physical Chemistry, University of Vienna. The elemental analyses of the \textsuperscript{15}N labeled complexes 4 and 6 did not consider the high isotopic purity of the nitrogen. Therefore both, the corrected as well as the measured values are given.

\textit{(OC-6-33)-Bis(2Z-3-carboxyacrylato)dichlorido(ethane-1,2-diamine)platinum(IV)} (3):

Maleic anhydride (167.5 mg, 1.708 mmol) was added to a suspension of enPtCl\textsubscript{2}(OH)\textsubscript{2} (150 mg, 0.417 mmol) in DMF (4 mL) and the reaction mixture was stirred at 70 °C for 3 h. During this time the solid material dissolved to form a brown solution. DMF was then removed under reduced pressure. The residue was dissolved in acetone and filtered to give a clear, light brown solution. This solution was concentrated under reduced pressure, and
subsequent addition of diethyl ether led to precipitation of a brown solid. The product was dried in vacuo. Yield: 120 mg (52%). C\textsubscript{10}H\textsubscript{14}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{8}Pt (556.21): calcd. C 21.59, H 2.54, N 5.04; found C 21.32, H 2.65, N 5.19. ESI-MS: m/z 578.9 [M+Na\textsuperscript{+}], 594.9 [M+K\textsuperscript{+}], 555.0 [M−H\textsuperscript{−}]. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3548 (\(\nu_{\text{COO-H}}\)), 3200 m, 1698 s, 1657 s, 1623 s, 1542 m, 1381 m, 1050 s, 828 m, 577 m. \(\delta\)H (400.13 MHz, \textit{d}\textsubscript{7}-DMF) 13.49 (bs, 2 H, COO\textit{H}), 8.69 (s, \(J_{\text{H,Pt}} = 52.4\) Hz, 4 H, NH\textsubscript{2}), 6.96 (d, \(J_{\text{H,H}} = 11.9\) Hz, 2 H, 2−H/3−H), 6.24 (d, \(J_{\text{H,H}} = 11.9\) Hz, 2 H, 2−H/3−H), 3.38 (bs, 4 H, 5−H).

\(\delta\)C (100.62 MHz, \textit{d}\textsubscript{7}-DMF) 173.0, 165.1 (C−1/C−4), 123.3, 133.3 (C−2/C−3), 47.5 (C−5). \(\delta\)N (40.55 MHz, \textit{d}\textsubscript{7}-DMF) −2.8. \(\delta\)Pt (86.11 MHz, \textit{d}\textsubscript{7}-DMF) 2610 (430 Hz).

\((\text{OC}-6-33)-\text{Diamminebis}(2Z-3\text{-carboxyacrylato})\text{dichloridoplatinum(IV)}\) (4): The synthesis was carried out as described for 3, but the reaction time was only 1 h. Yield: 97.2 mg (62 %). C\textsubscript{8}H\textsubscript{12}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{8}Pt·0.5DMF (568.71): calcd. C 20.06, H 2.74, N 6.51; found (without consideration of \(\textsuperscript{15}N\) labeling) C 20.34, H 2.54, N 5.91; found (calcd. with consideration of \(\textsuperscript{15}N\) labeling) C 20.27, H 2.53, N 6.25. ESI-MS: m/z 530.4 [M−H\textsuperscript{−}]. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3277 (\(\nu_{\text{N-H}}\)), 3130 m, 1692 m, 1620 m, 1576 s, 1525 m, 1485 m, 1301 s, 862 s. \(\delta\)H (400.13 MHz, \(d\)\textsubscript{7}-DMF) 13.74 (bs, 2 H, OH), 6.92 (d, \(J_{\text{H,N}} = 75.4\) Hz, \(J_{\text{H,Pt}} = 51.9\) Hz, 6 H, NH\textsubscript{3}), 6.69 (d, \(J_{\text{H,H}} = 11.9\) Hz, 2 H, 2−H/3−H), 6.27 (d, \(J_{\text{H,H}} = 11.9\) Hz, 2 H, 3−H). \(\delta\)C (100.62 MHz, \(d\)\textsubscript{7}-DMF) 172.2 (\(J_{\text{C,Pt}} = 26.1\) Hz, C−1), 165.3 (C−4), 131.8 (\(J_{\text{C,Pt}} = 41.5\) Hz, C−2), 125.5 (C−3). \(\delta\)N (50.68 MHz, \(d\)\textsubscript{7}-DMF) −41.0 (q, \(J_{\text{N,H}} = 76.3\) Hz, \(J_{\text{N,Pt}} = 251\) Hz). \(\delta\)Pt (107.51 MHz, \(d\)\textsubscript{7}-DMF) 2777 (t, \(J_{\text{P,PL}} = 252\) Hz).
1,1’-Carbonyldiimidazole (CDI; 132.7 mg, 0.818 mmol) in DMF (8 mL) was added to a solution of 3 (222 mg, 0.399 mmol) in DMF (4 mL) and the mixture was heated to 60 °C. After 10 min stirring, the solution was cooled down to room temperature and CO$_2$ was removed by flushing with argon. Propylamine (64.5 µL, 0.818 mmol) in DMF (12 mL) was added to the solution and stirred for 24 h at room temperature. DMF was then removed under reduced pressure to form a brown oil. The crude product was purified by column chromatography (EtOAc/MeOH, 6:1) to yield a pale-yellow solid. Yield: 42 mg (16%).


ν$_{\text{max}}$(KBr)/cm$^{-1}$: 3278 (ν$\text{N-H}$), 3018 w, 2937 w, 2876 w, 1678, 1647 (ν$\text{as C=O}$), 1561 m, 1299 m, 667 w.

δ$^1$H (400.13 MHz, d$_7$-DMF) 10.05 (m, $J_{\text{H,Pt}} = 44.5$ Hz, 2 H, C−8−N$\text{H}$), 8.22 (m, 2 H, C−4−N$\text{H}$), 4.75 (dd, $J_{\text{H,H}} = 10.8$ Hz, $J_{\text{H,Pt}} = 36$ Hz, 2 H, 2−H), 4.04 (dd, $J_{\text{H,H}} = 9.6$ Hz, $J_{\text{H,Pt}} = 37.4$ Hz, 2 H, 8−H), 3.51 (m, 2 H, 3−H), 3.40 (m, 2 H, 8−H), 3.32 (m, 4 H, 5−H), 3.04 (m, 2 H, 3−H), 1.67 (m, 4 H, 6−H), 1.06 (t, $J_{\text{H,H}} = 7.4$ Hz, 6 H, 7−H). δ$^13$C (100.62 MHz, d$_7$-DMF) 182.4 (C−1), 167.2 (C−4), 62.4 (C−2), 56.6 (C−8), 39.6 (C−5), 38.0 (C−3), 21.0 (C−6), 9.5 (C−7). δ$^15$N (40.55 MHz, d$_7$-DMF) 94.8 (C−4−NH), 21.0 (C−8−NH). δ$^\text{Pt}$ (86.11 MHz, d$_7$-DMF) 2224 (332 Hz).

The synthesis was carried out as described for 5. The crude product was first purified by column chromatography (EtOAc/MeOH, 6:1); afterwards, the pure product was obtained via vapor diffusion of diethyl ether into a solution of 6 in acetone. Yield: 15.3 mg (7 %). C$_{14}$H$_{26}^{15}$N$_2$N$_2$O$_6$Pt (614.35): calcd. C 27.37, H 4.27, N 9.44; found
(without consideration of $^{15}$N labeling) C 27.58, H 4.30, N 8.95; found (calcd. with consideration of $^{15}$N labeling) C 27.49, H 4.29, N 9.27. ESI-MS: $m/z$ 637.3 [M+Na$^+$]$^+$, 613.2 [M–H$^-$]. $v_{\text{max}}$(KBr)/cm$^{-1}$ 3344 m, 3272 w, 3046 m, 2970 w, 2880 w, 1696, 1638 ($\nu_{\text{as}}$ C=O), 1571 m, 1225 m, 870 w. $\delta_H$(500.32 MHz, $d_7$-DMF) 9.87 (dt, $J_{HH} = 8.6$ Hz, $J_{HN} = 77.9$ Hz, $J_{HPt} = 55.9$ Hz, 1 H, C–2–NH), 8.64 (t, $J_{HH} = 5.5$ Hz, 2 H, C–4–NH), 6.77 (d, $J_{HN} = 74.3$ Hz, $J_{HPt} = 49.5$ Hz, 3 H, NH$_3$), 4.90 (m, 2 H, 2–H), 3.33 (m, 2 H, 3–H), 3.27 (m, 4 H, 5–H), 3.25 (m, 2 H, 3–H), 1.63 (m, 4 H, 6–H), 1.03 (t, $J_{HH} = 7.4$ Hz, 6 H, 7–H). $\delta_C$(125.81 MHz, $d_7$-DMF) 179.9 (d, $J_{CN} = 1.8$ Hz, 1–C), 169.4 (4–C), 63.1 (d, $J_{CN} = 4.0$ Hz, 2–C), 39.5 (5–C), 35.5 (3–C), 21.0 (6–C), 9.6 (7–C). $\delta_N$(50.68 MHz, $d_7$-DMF) 0.3 (d, $J_{NH} = 78.1$ Hz, $J_{NPt} = 215$ Hz, 1 N, C–2–NH), -31.3 (q, $J_{NH} = 74.4$ Hz, $J_{NPt} = 277$ Hz, 1 N, NH$_3$). $\delta_Pt$(107.55 MHz, $d_7$-DMF) 2302 (dd, $J_{Pt,N} = 274$ Hz, $J_{P,N} = 218$ Hz)
Selected NMR spectra of complex 5

Figure S1. $^1$H–$^1$H TOCSY NMR spectrum of complex 5.

Figure S2. $^1$H–$^{13}$C HMQC NMR spectrum of complex 5.
Figure S3. \(^1\text{H}-^{13}\text{C}\) HMBC NMR spectrum of complex 5.

Figure S4. \(^1\text{H}-^{15}\text{N}\) HMQC NMR spectrum of complex 5.
Figure S5. $^{195}$Pt NMR spectrum of complex 5.

Selected NMR spectra of complex 6

Figure S6. $^1$H–$^1$H COSY NMR spectrum of complex 6.
Figure S7. $^1$H–$^1$H TOCSY NMR spectrum of complex 6.

Figure S8. $^1$H–$^{13}$C HSQC NMR spectrum of complex 6.
Figure S9. $^1$H–$^{13}$C HMBC NMR spectrum of complex 6.

Figure S10. $^{195}$Pt{$^1$H} NMR spectrum of complex 6.

References