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Syntheses of platinum(II) complexes of cyclo-octenyl group and isolation of a self-assembled oxo-bridged macrocyclic complex $[Pt_4(Spy)_4(C_8H_{12}\text{-}O\text{-}C_8H_{12})_2]$

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ABSTRACT

Reactions of $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (**1**) ($C_8H_{12}OMe$ = 8-methoxy-cyclooct-4-ene-1-yl) with various anionic chalcogenolate ligands have been investigated. The reaction of **1** with $Pb(Spy)_2$ (HSpy = pyridine-2-thiol) yielded a binuclear complex $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (**2**). A trinuclear complex $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (**3**) was isolated by a reaction between **2** and $[Pt(Spy)_2]_n$. The reaction of **1** with HSpy in the presence of NaOMe generated **2** and its demethylated oxo-bridged tetranuclear complex $[Pt_4(Spy)_4(C_8H_{12}\text{-}O\text{-}C_8H_{12})_2]$ (**4**). Treatment of **1** with ammonium diisopropyldithiophosphate completely replaced $C_8H_{12}OMe$ resulting in $[Pt(S_2P\{OPr^i\}_2)_2]$ (**5**), whereas non-rigid 5-membered chelating ligand, $Me_2NCH_2\text{-}CH_2E^-$, produced mononuclear complexes $[Pt(ECH_2CH_2NMe_2)(C_8H_{12}OMe)]$ (E = S (**6**), Se (**7**)). These complexes have been characterized by elemental analyses, NMR (^1H, $^{13}C\{^1H\}$, $^{195}Pt\{^1H\}$) and absorption spectroscopy. Molecular structures of **2**, **3**, **4**, **5** and **7** were established by single crystal X-ray diffraction analyses. Thermolysis of **2**, **6** and **7** in HDA gave platinum nanoparticles.

1. Introduction

The chemistry of cyclometalated palladium and platinum complexes has been extensively explored for about five decades. There are several obvious reasons for this sustained interest as these complexes find numerous applications in many fields such as organic synthesis [1–3], metallomesogens [4–6], solar cells [7,8], opto-electronic devices [9–11] and materials science [12–14], etc. Platinum complexes such as $[Pt_2(\mu\text{-}OR)_2(C_8H_{12}OMe)_2]$ (R = Me, Ac) [14] and $PtMe_2(COD)$ (COD = cycloocta-diene) [15,16] have been used to prepare platinum thin films and nanoparticles.

Cyclometalated binuclear palladium and platinum complexes $[M_2(\mu\text{-}X)_2(L^{\cap}C)_2]$ (M = Pd or Pt; X = Cl or OAc; L = N, P, etc.), undergo a wide range of reactions. These can broadly be clubbed into (i) bridge cleavage reactions by neutral donor ligands; (ii) reaction at the metal–carbon bond, and (iii) substitution of the bridging Cl/OAc with another ionic ligand. The latter reaction yields a myriad of complexes. Structure of the resulting complex is governed by the nature of L, metal atom and the incoming anionic ligand. Recently we have described reactions of $[Pt_2(\mu\text{-}Cl)_2\{Bu^t_2PC(Me_2)CH_2\}_2]$ [17] and $[Pt_2(\mu\text{-}Cl)_2(ppy)_2]$ (ppy = metalated 2-phenylpyridine) [18] with a variety of anionic ligands. The nature of L (N or P) and the size of the metalacycle greatly influenced the reactivity as well as the structural features of the resulting complex. In pursuance of our work on cyclometalated platinum complexes and development of platinum group metal chalcogenolates as precursors for the synthesis of platinum group metal chalcogenides [19,20], we have chosen a precursor with a very large metalacycle ring (6-membered) and a weak L ligand (π-olefinic group) as in $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ and explored its reactions with a variety of chalcogenolate ligands. The results of this work are reported herein.

2. Experimental

2.1. General procedures

Solvents were dried and distilled prior to use by standard methods. All reactions were carried out in Schlenk flasks under a nitrogen atmosphere. The compounds 2-mercaptopyridine (HSpy), $Me_2NCH_2CH_2SH\cdot HCl$ and other reagents were procured from commercial sources. The compounds, $(Me_2NCH_2CH_2Se)_2$ [21], K_2PtCl_4 [22], $PtCl_2(COD)$ [23] and $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (**1**) [24] were prepared according to the literature methods. Syntheses and analytical data for $[Pb(Spy)_2]$ and $[Pt(Spy)_2]$ are given in Supplementary information, Fig. S2.

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were carried out on a Carlo-Erba

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EA-1110 CHN-O instrument. Electronic spectra were recorded on a Chemito Spectrascan UV 2600 spectrophotometer. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{77}Se\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance II-300 NMR spectrometer operating at 300, 75.47, 121.5, 57.24 and 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 ^{1}H and 77.0 for ^{13}C), external Me_2Se for $^{77}Se\{^{1}H\}$ (secondary reference Ph_2Se_2 in $CDCl_3$ δ 463 ppm) and Na_2PtCl_6 in D_2O for $^{195}Pt\{^{1}H\}$. TG curves were obtained at a heating rate of 10 °C min^{-1} under flowing argon on a Setaram Setsys evolution-1750 instrument. Powder XRD patterns were recorded on a Philips PW1820 using Cu-Kα radiation.

2.2. Synthesis of $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (**2**)

(a) To a benzene solution (20 mL) of $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (0.206 g, 0.278 mmol), solid $Pb(Spy)_2$ (0.122 g, 0.285 mmol) was added and stirred for 2 h. A yellow solution containing a white precipitate of $PbCl_2$ was obtained. The reaction mixture was filtered through celite and the filtrate was concentrated to 3 mL and 1 mL of hexane was added and cooled at 10 °C to yield yellow crystals of **2** (0.172 g, 0.193 mmol, 69%). [In some preparations a few red crystals were also formed which were separated manually and characterized as $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (**3**) (see later).]

Data of **2**. m.p. 182 °C (darkens above 165 °C). Anal. Calcd. for $C_{28}H_{38}N_2O_2Pt_2S_2$: C, 37.8; H, 4.3; N, 3.1; S, 7.2. Found: C, 37.9; H, 4.3; N, 3.0; S, 7.3%. ^{1}H NMR (300 MHz, C_6D_6): δ = 8.26 (m), 8.03, 7.88 (br, s) (2H, H-6), 7.45 (m, 2H, H-4), 6.56 (m, 2H, H-5), 6.13, 6.02 (br s, 2H, H-3), 5.58 (br s, $^{2}J_{HPt}$ = 73.2 Hz), 5.48 (br s, $^{2}J_{HPt}$ = 67.8 Hz), 4.84 (br s, $^{3}J_{HPt}$ = 53.1 Hz), 3.99 (br s) (4H, CH=CH), 4.49, 4.12 (br s, 2H, MeOCH), 3.70, 3.64, 3.61 (each s, 6H, OMe), 2.85–1.80 (m, 8H, CH_2); $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ = 171.5, 170.3 (br s, $\Delta 1/2$ = 40 Hz, C-2), 150.6, 150.1, 149.8 (s, C-6), 134.9, 134.8 (s, C-4), 131.0, 130.6, 130.0 (s, C-3), 120.3, 119.9, 119.5 (s, C-5), 88.9, 87.6, 86.6, 86.3, 85.0, 84.7, 83.9, 83.6, 81.0, 80.6 (C=C, COMe) (The platinum satellites could not be assigned), 56.4, 56.2 (s, *COMe*), 36.2 (s, $^{3}J_{CPt}$ = 38.1 Hz; *CH*$_2$COMe), 34.8 (s, *CH*$_2$CH$_2$COMe), 31.0, 30.6 (s, *CH*$_2$CH$_2$CHPt), 29.4 (m, *CH*$_2$CHPt), 25.4, 24.1, 23.2 (each s, $^{1}J_{CPt}$ = 628, 620, 632 Hz respectively; Pt–C); $^{195}Pt\{^{1}H\}$ NMR (64 MHz, C_6D_6): −3508 ($\Delta 1/2$ = 272 Hz); −3541 ($\Delta 1/2$ = 679 Hz) ppm (2:1) ratio; UV/Vis (CH_2Cl_2) λ_{max} (ε): 277 (18,000), 324 (8000), 371 nm (sh, 3000 M^{-1} cm^{-1}); ESI–MS, *m/z* (%): 778 ($[M-(Spy)]^+$, 100%), 748 ($[Pt_2(Spy)_2(C_8H_{12}OMe)-H]^+$, 20%), 638 ([Pt2(Spy)(C8H12OMe) − H]+, 13%), 413 ($[Pt(Spy)_2-2H]^+$, 49%) (Supplementary information, Fig. S1).

(b) To a methanolic solution (15 mL) of NaSpy (freshly prepared by reaction between HSpy (0.062 g, 0.563 mmol) and NaOMe in methanol (1.1 mL, 0.53 N, 0.572 mmol)), a dichloromethane solution (10 mL) of $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (0.209 g, 0.282 mmol) was added and stirred for 3 h. The solvents were evaporated under reduced pressure and the residual solid was chromatographed on a silica gel column (3 × 40 cm), 30:70 v/v ethylacetate/hexane to elute $[Pt_4(Spy)_4(C_8H_{12}\text{-}O\text{-}C_8H_{12})_2]$ (**4**) and 10:90 v/v methanol/chloroform to elute **2**. The solvent was removed from the product containing fractions by rotary evaporation and oil pump vacuum to give yellow crystalline solid of **2** (0.160 g, 0.180 mmol, 64%), m.p. 184 °C. The volume of fraction containing **4** was made up to 5 mL, few drops of diethylether added to yield pale yellow crystals of **4**·OEt_2 (0.037 g, 0.021 mmol, 15%).

2.3. Synthesis of $[Pt_3(Spy)_4(C_8H_{12}OMe)_2]$ (**3**)

To a benzene solution (15 mL) of $PtCl_2(COD)$ (0.027 g, 0.072 mmol), solid $Pb(Spy)_2$ (0.030 g, 0.070 mmol) was added and stirred. After 30 min, benzene solution (10 mL) of $[Pt_2(Spy)_2(C_8H_{12}OMe)_2]$ (0.060 g, 0.067 mmol), was added and the contents were further stirred for 3 h. The reaction mixture was dried by evaporating the solvents under vacuum, washed with ether (2 × 2 mL) and hexane (2 × 2 mL), and extracted from dichloromethane. The latter on volume reduction to 3 mL followed by refrigeration gave reddish solid of **3** (0.043 g, 0.032 mmol, 48%), m.p. 145 °C. Anal. Calcd. for $C_{38}H_{46}N_4O_2Pt_3S_4$: C, 35.0; H, 3.5; N, 4.3; S, 9.8. Found: C, 34.8; H, 3.5; N, 4.3; S, 9.2%; UV/Vis (CH_2Cl_2) λ_{max} (ε): 275 (21,000), 297 nm (16,000 M^{-1} cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46, 8.35 (br m, 4H, H-6), 7.63 (br s, 4H, H-4), 7.15 (m, 4H, H-5), 6.95, 6.57 (m, 4H, H-3), 5.61 (s, $^{2}J_{HPt}$ = 66.9 Hz, 4H, CH=CH), 3.71 (br, 2H, MeOCH), 3.50, 3.48, 3,36 (s, 6H, OMe), 2.92–2.40 (m, 8H, CH_2), 2.27 (d, $^{3}J_{HH}$ = 9 Hz, PtCH), 2.05–1.55 (m, 8H, CH_2); $^{195}Pt\{^{1}H\}$ NMR (64 MHz, $CDCl_3$): δ = −3470 ($\Delta 1/2$ = 458 Hz), −3333, other minor broad peaks at −3447, −3454 and −3481 ppm; ESI-MS, *m/z* (%): 859 [M − Pt(Spy)($C_8H_{12}OMe$)] (5%), 415 $[\{Pt(Spy)_2\}]^+$ (100%) (Supplementary information, Fig. S2).

Data of $[Pt_4(Spy)_4(C_8H_{12}\text{-}O\text{-}C_8H_{12})_2]$ (**4**). M.p. 198 °C (dec.). Anal. Calcd. for $C_{56}H_{74}N_4O_3Pt_4S_4$ (**4**·OEt_2): C, 38.2; H, 4.2; N, 3.2; S, 7.3. Found: C, 38.3; H, 4.0; N, 3.1; S, 7.7%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (m, 4H, 6-H), 7.46 (m, 4H, H-4), 7.07 (m, 4H, H-5), 6.54 (m, 4H, H-3), 5.58 (br s, 8H, CH=CH), 3.68 (br s, 4H, OCH), 2.85–1.45 (m, 36H, CH_2 + PtCH). The peaks at δ 4.12 (q), 1.26 (t) are due to the solvated Et_2O in the crystals of **4**; $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 170.1 (br s, C-2), 150.3 (s), 149.5, 149.0 (br s, C-6), 134.62 (s), 134.60 (br s, C-4), 129.8, 128.8 (br s, C-3), 119.6, 119.5 (br s, C-5), 87.3 (s, MeO*CH*), 80.6, 79.7 (s, C=C), 35.8, 30.0, 29.7, 28.3, 26.8 (s, CH_2), 25.05, 24.9 (br s, PtC); $^{195}Pt\{^{1}H\}$ NMR (64 MHz, $CDCl_3$): δ = −3495 (major, $\Delta 1/2$ = 312 Hz), other minor broad peaks at −3523, −3554, −3607 (each approx. of $\Delta 1/2$ = 624 Hz) ppm.

2.4. Synthesis of $[Pt(S_2P\{OPr^i\}_2)_2]$ (**5**)

To a dichloromethane (10 mL) solution of $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (0.104 g, 0.140 mmol), methanolic (5 mL) $NH_4S_2P(OPr^i)_2$ (0.065 g, 0.280 mmol) was added. The color of the solution turned yellow and the whole reaction mixture was stirred for 2 h. The solvents were evaporated under reduced pressure and the residue was extracted with dichloromethane (2 × 5 mL) and passed through a Florisil column. The filtrate was concentrated to 3 mL and 1 mL of hexane was added to yield yellow crystals of **5** (0.125 g, 0.201 mmol, 71%), m.p. 123 °C (dec.). Anal. Calcd. for $C_{12}H_{28}O_4P_2PtS_4$: C, 23.2; H, 4.5; S, 20.6. Found: C, 23.2; H, 4.4; S, 20.0%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.98 (hep, $^{3}J_{HH}$ = 6 Hz, 4H, *CH*Me$_2$), 1.41 (d, $^{3}J_{HH}$ = 6 Hz, 24H, CH*Me*$_2$); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 74.2 (s, *CH*Me$_2$), 23.8 (s, CH*Me*$_2$); $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ = 97.4 (t, $^{4}J_{PP}$ = 10.2 Hz, $^{2}J_{PPt}$ = 441 Hz); $^{195}Pt\{^{1}H\}$ NMR (64 MHz, $CDCl_3$): δ = −3981 ($^{2}J_{PPt}$ = 441 Hz) ppm.

2.5. Synthesis of $[Pt(SCH_2CH_2NMe_2)(C_8H_{12}OMe)]$ (**6**)

To a methanolic solution of $Me_2NCH_2CH_2SH$·HCl (0.072 g, 0.508 mmol), NaOMe in methanol (1.95 mL, 0.52 N) was added and stirred for 15 min. To this reaction mixture $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OMe)_2]$ (0.187 g, 0.248 mmol) was added and the whole was further stirred for 2 h. The solvent was evaporated to dryness and the residual solid was extracted with dichloromethane (3 × 6 mL) to yield **6** as a colorless solid (0.184 g, 0.419 mmol, 83%), m.p. 178 °C (dec.). Anal. calcd for $C_{13}H_{25}NOPtS$: C 35.6, H 5.7, N 3.2, S 7.3; found: C 35.6, H 5.7, N 3.0, S 6.3%; UV/Vis (CH_2Cl_2) λ_{max} (ε): 275 (sh) (4400), 293 nm (5400 M^{-1} cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.23 (t, $^{3}J_{HH}$ = 8.7 Hz, $^{2}J_{HPt}$ = 70 Hz, 1H, CH_2CH=CH), 3.90–3.87 (m, $^{2}J_{HPt}$ = 62 Hz, 1H, CH_2CH=C*H*), 3.50 (m, 1H, MeO*CH*), 3.24 (s, 3H, OMe), 2.92 (m, 2H, NCH_2), 2.84 (t, $^{3}J_{HH}$ = 5.4 Hz, 2H, SCH_2),