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Synthesis and reactivity of (2-amine-5-nitrophenyl)platinum(II) complexes

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Abstract

Reaction of $[HgR_2]$ ($R = C_6H_3NH_2$-2, NO_2-5) with $[PtCl_2(COD)]$ (COD = cycloocta-1,5-diene) yields *cis*-$[PtCl(R)(COD)]$, which reacts with PPh_3 to give *trans*-$[PtCl(R)(PPh_3)_2]$. The latter reacts with $AgClO_4$ to give solutions from which the complexes *trans*-$[PtI(R)(PPh_3)_2]$ or *trans*-$[Pt(CO)(R)(PPh_3)_2]ClO_4$ can be isolated. Treatment of some of these complexes with acetic anhydride gives the 2-acetamido-5-nitrophenyl ($R^\star$) derivatives $[PtCl(R^\star)L_2]$ (L_2 = COD, L = PPh_3), and these, in turn react with $AgClO_4$ to give complexes *cis*-$[Pt(R^\star)L_2]ClO_4$ in which the $R^\star$ group acts as a chelating ligand. The main features of the structures of these complexes have been established by IR and NMR spectroscopy.

Introduction

We are developing the use of organomercury compounds as transmetallating agents in preparing functional aryl complexes of gold [1], palladium [2], platinum [3], rhodium [4] and tin [5]. The interest in this subject arises from the unavailability of the corresponding Grignard or organolithium derivatives, that provide the usual reagents for preparing aryl complexes, and from the possibility of studying the reactions and coordinating properties of the group attached to the phenyl ring.

In this paper we report the synthesis of (2-amine-5-nitrophenyl)platinum(II) complexes as a good example of the synthetic value of the organomercuric route when the classical one is not available. In addition, the availability of this new type of aryl complexes makes possible a study of the reactions of the amine group. We have acetylated it, and shown that the resulting acetamido group can be coordinated to the metal centre.

Results and discussion

Synthesis

Reaction between equimolar amounts of $[PtCl_2(COD)]$ and $[HgR_2]$ ($R = C_6H_3NH_2$-2,NO_2-5) in acetone at room temperature gives *cis*-$[PtCl(R)(COD)]$ (**1**),

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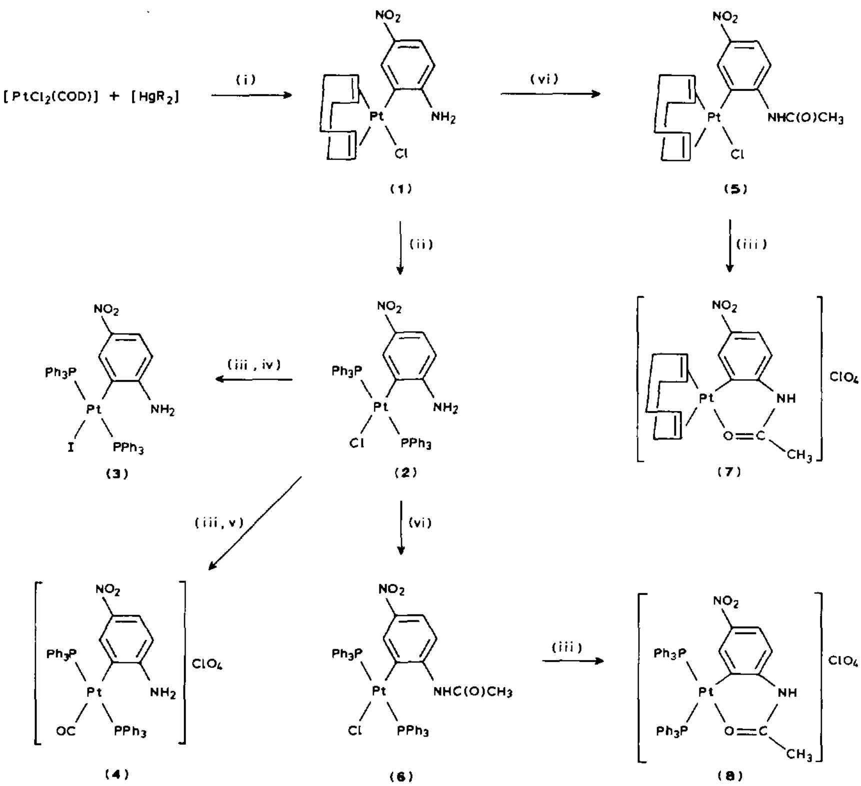

Scheme 1. (i) $-HgClR$; (ii) $2PPh_3$, $-COD$; (iii) $AgClO_4$, $-AgCl$; (iv) I^-; (v) CO; (vi) $(CH_3CO)_2O$.

(see Scheme 1). When the resulting solution has been evaporated to dryness, complex **1** will not redissolve in acetone, and so it can be separated from the formed [HgCl(R)] by washing of the solid mixture with that solvent. Attempts to prepare a diaryl complex by use of a 1/2 molar ratio were unsuccessfull and **1** was always obtained.

Complex **1** reacts with a 2 molar proportion of PPh_3 to give *trans*-$[PtCl(R)(PPh_3)_2]$ (**2**). Both **1** and **2** are yellow air-stable solids, and poorly soluble in most of the common organic solvents. Complex **2** reacts with a 1 molar proportion of $AgClO_4$ in acetone to give AgCl and a yellow solution from which various species can be isolated depending on the experimental conditions, and none of these gives elemental analyses corresponding to any reasonable formulation. However, the acetone solution can be used as if it did contain $Pt(ClO_4)(R)(PPh_3)_2$. Thus, addition of NaI (1/1 molar ratio) or bubbling of CO through the solution leads to attachment of I^- or CO ligands at the coordination sites previously occupied by ClO_4^- or by the NH_2 or the NO_2 group in the intermediate(s), to give *trans*-$[PtI(R)(PPh_3)_2]$ (**3**) or *trans*-$[Pt(R)(CO)(PPh_3)_2][ClO_4]$ (**4**).

Complexes **3** and **4** are also yellow air-stable solids. Only **4** is sufficiently soluble in organic solvents to be studied in solution. Its molar conductivity in acetone (ca. 10^{-4} mol dm^{-3}) is consistent with its formulation as a 1/1 electrolyte (94 Ω^{-1} cm^2 mol^{-1}).

Complexes **1** and **2** can be acetylated by heating their suspensions in acetic anhydride (see Scheme 1) to give the corresponding 2-acetamido-5-nitrophenyl complexes, *cis*-[PtCl(R*)(COD)] (**5**) and *trans*-$[PtCl(R^*)(PPh_3)_2]$ (**6**) (R^* = $C_6H_3NHC(O)CH_3$-2, NO_2-5). Treatment of these complexes with $AgClO_4$ gives the cationic complexes *cis*-$[Pt(R^*)(COD)]ClO_4$ (**7**) and *cis*-$[Pt(R^*)(PPh_3)_2]ClO_4$ (**8**). Spectroscopic data show that the acetamido-aryl group in **7** and **8** acts as a chelating ligand (see below).

Complexes **5** and **7** are cream and yellow, respectively, whereas **6** and **8** are white. The molar conductivities of all four species in acetone are consistent with their formulations (the values for **5**, **6**, **7** and **8** are 3, 0, 112 and 144 Ω^{-1} cm^2 mol^{-1}, respectively). However, **7** and **8** are non-conducting in dichloromethane, while typical 1/1 electrolytes have molar conductivities of around 16 Ω^{-1} cm^2 mol^{-1} in this solvent. It is likely that there is some association of the perchlorate anion with the cationic complexes in solution. The IR spectra also point to the presence of such interactions in the solid state (see below).

IR and NMR spectra

The most significant bands in the IR spectra of these complexes are those assignable to the mode ν(NH) in the 3200–3500 cm^{-1} range. Complexes **1**–**4** show three bands, at ca. 3450(m), 3350(m) and 3200(w) cm^{-1}. This is a similar pattern to that observed for $[HgR_2]$ and *p*-nitroaniline. Complexes **5** and **6** show only a medium band at 3330 cm^{-1}, attributable to ν(NH), and another at ca. 1700(vs) cm^{-1} assignable to ν(CO), confirming that both are acetamidoaryl complexes. The 100 cm^{-1} lowering of the frequency of this band in complexes **7** and **8** support our proposal that there is coordination of the carbonyl group in these complexes, giving a six-membered metallacycle (see Scheme 1).

The bands at 1090(vs, br) and 620(s) cm^{-1} in **4** can be assigned to $\nu(T_2)$ and $\delta(T_2)$, respectively, of the ClO_4^- ion (Td). The first band in **7** and **8** is split into two, the second is broadened, and a new one is present at ca. 930 (m-w) cm^{-1}. This is a clear indication of the lowering of symmetry of the perchlorate anion in these complexes. It is likely that the anion–cation interaction suggested for solutions also occurs in the solid state. The 50 cm^{-1} lowering in the ν(NH) frequency in these complexes, with respect to **5** and **6** suggests that the hydrogen bonding $N-H\ldots OClO_3$ may be responsible for the interaction.

Complex **2** shows a band at 293(m) cm^{-1} that disappears when the chloro ligand is replaced by iodo or CO in **3** or **4**, respectively, and so can be assigned to ν(PtCl). The corresponding band in **1** is at 309 cm^{-1}, which is consistent with the weaker *trans*-influence of an olefinic than of an aryl ligand. The same order is observed on comparison of the ν(PtCl) frequencies in complexes **5** (315(m) cm^{-1}) and **6** (290(m) cm^{-1}).

The band assignable to ν(CO) in the carbonyl complex **4** appears at 2105(vs) cm^{-1} in dichloromethane solution.

The absence of a band at 550 ± 5 cm^{-1} for the bis(triphenylphosphine) complexes other than **8** permits the assignment to them of a *trans* geometry in the solid state [6]. The presence of such a band in **8** supports our assignment of a *cis* geometry for this complex.

Complexes **4**, **6** and **8** are the only ones sufficiently soluble in organic solvents to be studied by NMR spectroscopy. Their $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ show (a) for **4** and **6**, singlets at δ 14.8 and 24 ppm (aqueous H_3PO_4 as reference) with platinum satellites corresponding to ^1J(PtP) coupling of 2492 and 2795 Hz, respectively, and (b) for **8** two doublets at δ 13.2 and 25.7 ppm with ^2J(PP) 19 and ^1J(PtP) 4662 and 1940 Hz, respectively. Thus the complexes have the same geometry in solution as in the solid state.

The ^{1}H NMR spectrum of **4** in $CDCl_3$ shows a singlet at δ 4.63 ppm (TMS as reference) arising from the NH_2 group. The NH proton resonance of the acetylated complex **6** appears at lower field (δ 8.67 ppm), and even lower in complex **8** (δ 10.77 ppm). This large shift can be due to the postulated hydrogen bond between the NH group and the ClO_4^- anion. The signals from the methyl group in complexes **6** and **8** are at δ 1.57 and 1.62 ppm, respectively.

Experimental

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 1430 and Nicolet MX-1 spectrophotometers with Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 10^{-4} mol dm^{-3} solutions with a Philips 9501 conductimeter. Solvents were distilled before use. Melting points were determined on a Reichert apparatus and are uncorrected. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer. NMR spectra were recorded on a Varian XL-200 spectrometer. The starting compounds $[PtCl_2(COD)]$ [7] and $[Hg(C_6H_3NH_2\text{-}2,NO_2\text{-}5)_2]$ [8] made by published methods. All reactions were carried out at room temperature with magnetic stirring and without any special precautions to exclude air, moisture or light, unless otherwise stated.

cis-$[PtCl(C_6H_3NH_2\text{-}2,NO_2\text{-}5)(COD)]$ *(1)*

Solid $[Hg(C_6H_3NH_2\text{-}2,NO_2\text{-}5)_2]$ (634 mg, 1.34 mmol) was added to a suspension of $[PtCl_2(COD)]$ (500 mg, 1.34 mmol) in acetone (100 cm^3). After 6 h, the solvent was evaporated off and the residual solid was washed with acetone, then air dried to give **1**. Further similar treatment of the mother liquor gave further amounts of **1** (total yield 546 mg, 86%); m.p. 185 °C dec. ν(NH): 3436(m), 3336(m), 3195(w) cm^{-1}; Anal. Found: C, 35.62; H, 3.50; N, 5.45. $C_{14}H_{17}ClN_2O_2Pt$ calcd.: C, 35.34; H, 3.60; N, 5.89%.

trans-$[PtCl(C_6H_3NH_2\text{-}2,NO_2\text{-}5)(PPh_3)_2]$ *(2)*

Solid PPh_3 (200 mg, 0.76 mmol) was added to a suspension of **1** (180 mg, 0.38 mmol) in acetone (30 cm^3). After 1.5 h the suspended yellow solid was filtered off, then washed with diethyl ether and dried in an oven at 90 °C for 6 h to give **2** (268 mg, 79% yield); m.p. 299 °C. ν(NH): 3479(m), 3364(m), 3150(w) cm^{-1}; Anal. Found: C, 56.40; H, 4.02; N, 2.75. $C_{42}H_{35}ClN_2O_2P_2Pt$ calcd.: C, 56.54; H, 3.95; N, 3.14%.

trans-$[PtI(C_6H_3NH_2\text{-}2,NO_2\text{-}5)(PPh_3)_2]$ *(3)*

Solid $AgClO_4$ (34 mg, 0.18 mmol) was added to a suspension of **2** (145 mg, 0.18 mmol) in acetone (20 cm^3), protected from light. After 4 h the suspension was filtered and NaI (32 mg, 0.22 mmol) added to the filtrate. After 30 min the suspended solid was filtered off, washed with acetone and diethyl ether, then dried in an oven at 90 °C for 6 h to give **3** (90 mg, 57% yield); m.p. 277 °C, ν(NH): 3475(m), 3358(m), 3140(vw) cm^{-1}. Anal. Found: C, 51.30; H, 3.50; N, 2.82. $C_{42}H_{35}IN_2O_2P_2Pt$ calcd.: C, 51.28; H, 3.58; N, 2.84%.

trans-[Pt($C_6H_3NH_2$-2,NO_2-5)(CO)(PPh_3)$_2$]ClO_4 (4)

The procedure used for **3** was followed but bubbling of CO through the solution for 1 h replaced the addition of NaI. The suspension was filtered, and the filtrate was concentrated (to 2 cm^3) and diethyl ether then added. The suspended solid was filtered off and recrystallized from dichloromethane/diethyl ether to give **4** (52 mg, 60% yield); m.p. 185 °C. ν(NH): 3410(w,br), 3330(w,br), 3210(w,br) cm^{-1}. Anal. Found: C, 52.56; H, 3.69; N, 2.78. $C_{43}H_{35}ClN_2O_7P_2Pt$ calcd.: C, 52.47; H, 3.58; N, 2.84%.

cis-[PtCl($C_6H_3NHC(O)CH_3$-2,NO_2-5)(COD)] (5)

A suspension of **1** (482 mg, 1 mmol) in acetic anhydride (50 cm^3) was kept at 90–95 °C for 2.5 h. The suspended solid was filtered off and recrystallized from dichloromethane/n-hexane then dried at 90 °C to give **5**. Concentration of the solution and addition of diethyl ether gave more of **5** (total yield: 432 mg, 81%); m.p. 208 °C dec. ν(NH): 3330(m) cm^{-1}; ν(CO) 1700(vs) cm^{-1}. Anal. Found: C, 36.51; H, 3.62; N, 5.08. $C_{16}H_{19}ClN_2O_3Pt$ calcd.: C, 37.11; H, 3.70; N, 5.41%.

trans-[PtCl($C_6H_3NHC(O)CH_3$-2,NO_2-5)(PPh_3)$_2$] (6)

A suspension of complex **2** (629 mg, 0.71 mmol) in acetic anhydride (15 cm^3) was refluxed for 1.5 h then cooled to 0 °C and filtered. The solid obtained was recrystallized from dichloromethane/hexane then dried at 80 °C for 24 h to give **6** (570 mg, 87% yield); m.p. 269 °C ν(NH): 3330 cm^{-1}; ν(CO) 1710(vs) cm^{-1}. Anal. Found: C, 57.02; H, 3.78; N, 2.57. $C_{44}H_{37}ClN_2O_3P_2Pt$ calcd.: C, 56.57; H, 3.99; N, 3.00%.

cis-[$\overline{Pt(C_6H_3NHC(O}$)$CH_3$-2,$NO_2$-5)(COD)]($ClO_4$) (7)

Solid $AgClO_4$ (130 mg, 0.63 mmol) was added to a suspension of **5** (325 mg, 0.63 mmol) in acetone (80 cm^3) protected from the light. After 6 h the suspension was filtered, the filtrate concentrated to ca. 2 cm^3, and diethyl ether added to give a precipitate of **7**. The precipitate filtered off from the original suspension was extracted with dichloromethane (200 cm^3) and the extract was filtered then concentrated. Addition of diethyl ether gave a further amount of **7** (Total yield: 242 mg, 66%) m.p. 235 °C dec. ν(NH): 3280(m) cm^{-1}; ν(CO) 1600(vs) cm^{-1}. Anal. Found: C, 33.05; H, 3.28; N, 4.73. $C_{16}H_{19}ClN_2O_7Pt$ calcd.: C, 33.03; H, 3.29; N, 4.81%.

cis-[$\overline{Pt(C_6H_3NHC(O}$)$CH_3$-2,$NO_2$-5)($PPh_3$)$_2$]($ClO_4$) (8)

Solid $AgClO_4$ (13 mg, 0.06 mmol) was added to a solution of **6** (60 mg, 0.06 mmol) in acetone (20 cm^3) protected from the light. After 15 h the suspension was filtered and the filtrate concentrated (to 2 cm^3). Addition of diethyl ether gave a precipitate of **8**, which was filtered off, recrystallized from dichloromethane/diethyl ether, and dried at 110 °C (52 mg, 81% yield); m.p. 232 °C dec. ν(NH): 3280(m) cm^{-1}; ν(CO) 1600(vs) cm^{-1}. Anal. Found: C, 52.34; H, 3.99; N, 2.49. $C_{44}H_{37}ClN_2O_7P_2Pt$ calcd.: C, 52.94; H, 3.74; N, 2.81.

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