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Concentration dependent switch from addition to substitution in the reaction between salicylaldoxime and a nitrile platinum(IV) complex

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Abstract

The nitrile complex $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ reacts with one equivalent of salicylaldoxime, $HON{=}CH(C_6H_4OH\text{-}o)$, in CH_2Cl_2 to afford mainly the addition product $[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON{=}CH(C_6H_4OH\text{-}o)\}]$ (**1**). In a diluted solution, i.e. if the same amount of the reagents is dissolved in 50-fold volume of dichloromethane, the four platinum-containing species, i.e. **1**, $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H){=}NOH\}]$ (**2**) $[Ph_3PCH_2Ph][PtCl_5(NH_3)]$ (**3**), and $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**), are formed and the substitution compound **2** is the major product at low concentrations. Addition of EtCN to the less concentrated solution suppresses the formation of the substitution product **2** and moves the reaction back towards formation of the addition product **1**. The complex **1** is unstable in non-dried solutions and decomposes to give **2** along with **3**, **4** and $EtCO_2H$. Compounds **1**, **2** and **4**·$1/2H_2O$ were characterized by elemental analyses, FAB mass-spectrometry, IR and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{195}Pt NMR spectroscopies. X-ray structure determinations have been performed for **2** and **4**·$1/2H_2O$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitrile complexes; Platinum(IV) complexes; Nucleophilic addition; Substitution; Hydrolysis; Metal-mediated reactions

1. Introduction

Metal-mediated transformations of organonitriles play an important role in both laboratory and industry due to their well-recognized chemical versatility and possibility to achieve products of vital significance such as, e.g. acrylamide or nicotineamide. In particular, addition of nucleophiles to the C≡N triple bond, electrophilically activated by ligation to a metal center, offers an attractive route for the creation of diverse C–C, C–N, C–O, C–P, and C–S bonds (for recent reviews see Ref. [1]). Owing to our general interest in ligand reactivity [2–5] shared with the particular focus on reactions of the metal-bound RCN [6–16], we carried out a search of potential nucleophiles for couplings with [M]–NCR group, giving new functionalities, and has been discovered fairly recently a remarkable addition of oximes $HON{=}CR^1R^2$, to coordinated nitriles in $[PtCl_4(RCN)_2]$ to give the iminoacylated products $[PtCl_4\{HN{=}C(R)ON{=}CR^1R^2\}_2]$ [6–10]. This reaction was later also found to occur in rhodium(III) [11], rhenium(IV) [12] and platinum(II) systems [13]; in the latter case the platinum(II)-assisted addition to dialkylcyanamides is catalyzed by Lewis acids. The useful coupling was then extended to nitrones $^-ON^+(R^3){=}CR^1R^2$ [14]—which can be viewed as the alkylated form of the other oxime tautomer—to achieve, as a result of [2+3] cycloaddition, the platinum(IV) complexes $[PtCl_4(\Delta^4\text{-}1,2,4\text{-oxadiazoline})_2]$ from which difficult-to-obtain Δ^4-1,2,4-oxadiazolines were liberated. Moreover, oxime–nitrile systems were used in the 3d metal-mediated processes to furnish amidines [15] and to obtain carboxamides by a catalytic and environmentally benign route [16].

Taking into account the high potential of the oxime–nitrile coupling, we focused our attention on the investigation of general features, restrictions and plau-

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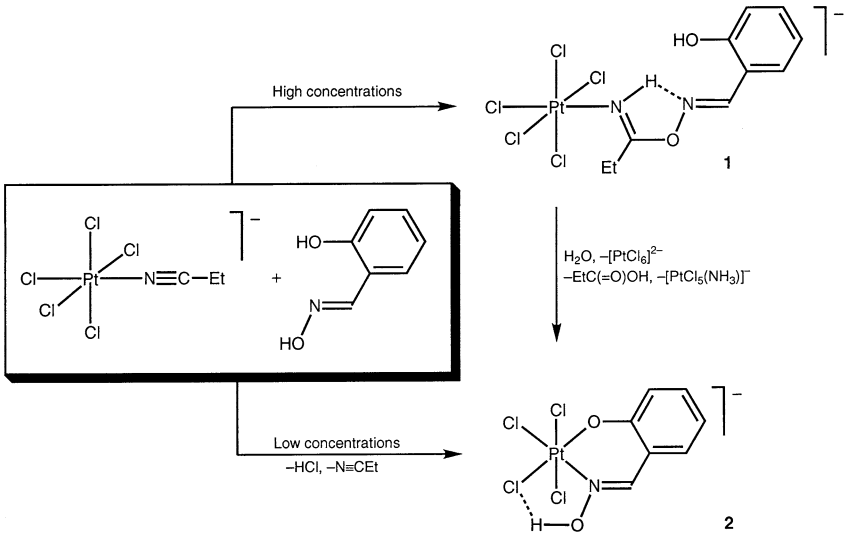
sible mechanism of the reaction—both experimentally [8] and theoretically [9]. In particular, it has been observed that the iminoacylation is dramatically inhibited by introducing acceptor groups to the oximes [8]. We have now found that the reaction can also be quite affected by the concentration of the reagents and we here report on the concentration dependent shift from addition to substitution in the reaction between the $[PtCl_5(EtCN)]^-$ complex and salicylaldoxime.

2. Results and discussion

For the current study we addressed, on one hand, the platinum(IV) complex $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ with the highly lipophilic cation and the Et radical at the nitrile group which provide good solubility of the compound in dichloromethane, and on the other hand, salicylaldoxime which can exhibit the dual reactivity in addition to platinum-bound nitrile [6] or in substitution around the platinum center [17]. It has been observed that $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ reacts with 1 equiv. of $HON{=}CH(C_6H_4OH\text{-}o)$ under mild conditions to afford the yellow addition product $[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON{=}CH(C_6H_4OH\text{-}o)\}]$ (**1**) (Scheme 1) along with some other products (see below). The former compound was purified by column chromatography. It gives satisfactory C, H and N elemental analyses and FAB^--MS and has been identified by: (i) IR spectroscopy showing no $\nu(C{\equiv}N)$ bands but displaying very strong $\nu(C{=}N)$ stretch and characteristic $\nu(N{-}H)$ stretching vibrations along with the strong bands due to the phosphonium counterion; (ii) measuring ^1H and $^{13}C\{^1H\}$ NMR spectra where the signals due to the HN=C moiety are in the same range as observed for the analogous neutral complexes $[PtCl_4\{NH{=}C(Et)ON{=}CH(C_6H_4OH\text{-}o)\}_2]$ containing iminoacylated salicylaldoxime [6] (the high field position of the imino H atom suggests its involvement in hydrogen bonding (Scheme 1), as in other iminoacylated oximes [6–9]); (iii) observation of a ^{195}Pt NMR chemical shift specific for similar type complexes [9].

If the same amount of the reagents is dissolved in the 50-fold volume of CH_2Cl_2 used in the previous experiment, the reaction mixture becomes *red*. ^1H and ^{195}Pt NMR and TLC monitoring of products formed in the reaction clearly indicate the formation of four platinum-containing species, i.e. $[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON{=}CH(C_6H_4OH\text{-}o)\}]$ (**1**), $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H){=}NOH\}]$ (**2**), $[Ph_3PCH_2Ph][PtCl_5(NH_3)]$ (**3**) and $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**), in variable quantities depending on the concentration of the reaction mixture. In the case of the more concentrated solution, the ratio between the addition and the substitution products, obtained by ^{195}Pt NMR peak integration, is approximately 9:1, while in the less concentrated solution it is almost reversed in favour of the substitution product (approximately 8:2) and, consequently, the amount of $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**) also increases. Moreover, addition of EtCN to the less concentrated solution suppresses the substitution and forwards the reaction again to the addition route. The complexes $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H){=}NOH\}]$ (**2**), $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**) (isolated as a hemihydrate) and well-known $[Ph_3PCH_2Ph][PtCl_5(NH_3)]$ (**3**) [9,18] were separated by column chromatography and characterized by physicochemical methods and the former two by X-ray crystallography.

In a separate experiment it has been shown that the addition product $[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON{=}CH(C_6H_4OH\text{-}o)\}]$ (**1**) is stable as solid but gradually decomposes in solution (for instance in dichloro-



Scheme 1.

methane) giving the substitution product $[Ph_3PCH_2Ph]$-$[PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**2**), the hexachloride $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**) as well as the two products arising from the hydrolysis [9,19], i.e. $[Ph_3PCH_2Ph]$-$[PtCl_5(NH_3)]$ (**3**) and $EtCO_2H$, the latter identified in ^1H NMR spectrum (Scheme 1). We believe that the conversion of **1**, initially involves hydrolysis of the C–O bond of the iminoacylated ligand giving the complex $[PtCl_5\{NH=C(Et)OH\}]^-$ (having ligated carboxamide in the iminol form [1]) and free salicylaldoxime. The former hydrolyses further to give **3** and $EtCO_2H$ [9], while the liberated oxime sequests the platinum(IV) center furnishing **2**.

The asymmetric unit of $[Ph_3PCH_2Ph][PtCl_4$-$\{C_6H_4(O)C(H)=NOH\}]$ (**2**) crystals contains a pair of both the anionic complex and the counterion whose bond lengths and angles are of typical values (Fig. 1, Table 2). The salicylaldoximato(1−) ligand is coordinated to the platinum(IV) center in its usual *N*,*O*-bidentate mode and all bonds are of normal values well comparable with those in the two previously reported (salicylaldoximato) Pt(IV) complexes [17]. The anion is additionally stabilized by hydrogen bonding between the oxime HO group and the Cl(2) atom [H(40)···Cl(2) distance is 2.21(6) Å, O(2)···Cl(2) is 2.982(6) Å, the angle O(2)–H(40)···Cl(2) is 160(5)°]. The data on $[Ph_3PCH_2Ph]_2[PtCl_6]\cdot 1/2H_2O$ (**4**) are coherent with many other structures of both the cation (see [20]) and the anion (see [21,22]), although previously determined in other combinations, and are included in Section 4.

The addition to the nitrile carbon requires strong electrophilic activation and occurs when EtCN is bound to the platinum(IV) center. The observed switch from the addition to the substitution can be probably explained on the basis of the increased amount of free EtCN upon dilution. Indeed, in diluted solutions dissociation of the nitrile, similar to that described for weak electrolytes by the Ostwald dilution law, increases and, consequently the amount of ligated EtCN decreases thus favoring the substitution via the expected dissociative mechanism. Another experimental observation supporting this assumption is that the addition of propanenitrile to the diluted solution suppresses the substitution and again forwards the reaction to the addition route.

3. Experimental

3.1. Materials and instrumentation

Solvents were obtained from commercial sources and used as received. $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ was obtained by the published method [9] and salicylaldoxime obtained from Aldrich. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. M.p.s were determined on a Kofler table. For TLC, Merck SiO_2-plates silica gel 60 F_{254} have been used. Positive-ion FAB-MS were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (approximately 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. IR spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{195}Pt NMR spectra were measured on Varian UNITY 300 and Bruker AMX 300 spectrometers at ambient temperature. ^{31}P chemical shifts are quoted relative to $H_3PO_4 = 0$ ppm, ^{195}Pt chemical shifts are given relative to aq. $K_2[PtCl_4] = -1630$ ppm, half height line width are given in parenthesis.

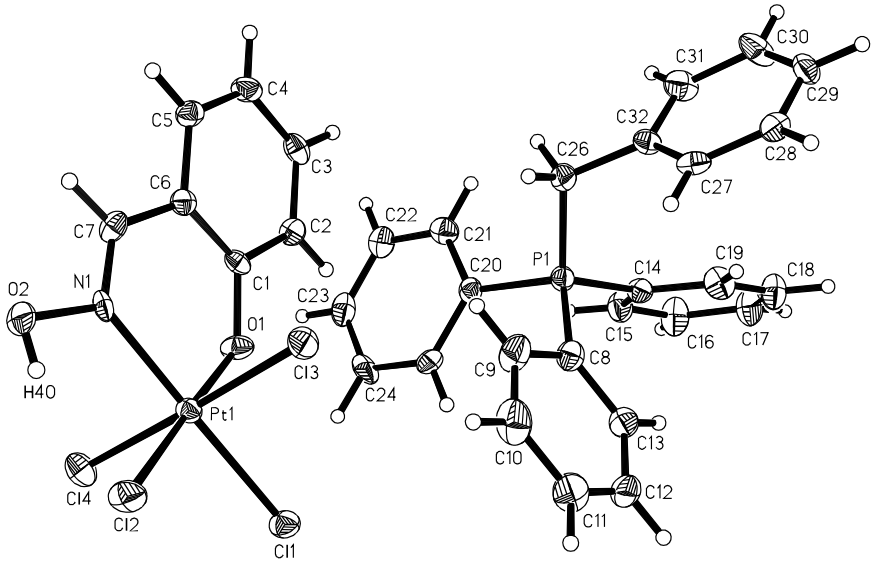


Fig. 1. ORTEP view of $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**1**). The thermal ellipsoids are drawn at the 50% probability level.

3.2. Synthetic work and characterization

3.2.1. Concentration dependence of the reaction between $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ and o-HOC_6H_4CH=NOH

$[Ph_3PCH_2Ph][PtCl_5(EtCN)]$ (28 mg, 0.036 mmol) is dissolved in dry CH_2Cl_2 (0.1 ml), salicylaldoxime (5 mg, 0.036 mmol) is added and the reaction mixture is left to stand at room temperature (r.t.) for 2 days. During that time the color of the solution gradually turns from yellow to orange. The complexes formed are separated by column chromatography on SiO_2 (Chemapol Silica gel L 40/100). The first fraction contains the dark-red substitution product $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**2**), the addition product $[Ph_3PCH_2Ph][PtCl_5\{NH=C(Et)ON=CH(C_6H_4OH\text{-}o)\}]$ (**1**) is in the second one and the last fraction contains the previously characterized $[Ph_3PCH_2Ph][PtCl_5(NH_3)]$ (**3**) [9,18]. Concurrently, $[Ph_3PCH_2Ph]_2[PtCl_6]$ (**4**) in the conditions applied retains on the silica gel but can be removed by eluation with C_3H_6O. If the same amount of the reagents is dissolved in the 50-fold volume (5 ml) of CH_2Cl_2 used above, the complex $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**2**) is mainly formed and it can be purified by column chromatography on SiO_2.

3.2.2. $[Ph_3PCH_2Ph][PtCl_5\{NH=C(Et)ON=CH(C_6H_4OH\text{-}o)\}]$ (1)

Anal. Calc. for $C_{35}H_{34}Cl_5N_2O_2PPt$: C, 45.79; H, 3.73; N, 3.05. Found: C, 44.69; H, 3.66; N, 2.61%. FAB^+-MS: *m/z* 353 [M_{cation}]. FAB^--MS: *m/z* 565 [M_{anion}], 373 [$PtCl_5$], 336 [$PtCl_4$], 301 [$PtCl_3$], 266 [$PtCl_2$]. m.p. = 105–108 °C. TLC, $R_f = 0.49$ (eluent C_3H_6O–$CHCl_3$ = 1:3). IR spectrum in KBr, selected bands (cm^{-1}): 3285 m ν(N–H), 1655 and 1609 s ν(C=N), 1435 s ν(C=C), 1109 s ν(P–C), 751 s δ(C–H). ^1H NMR in $CDCl_3$: δ 1.31 (t, 7.4 Hz, 3H) and 3.32 (q, 7.4 Hz, 2H) (Et), 4.88 (d, $^2J_{PH}$ 13.9 Hz, 2H, CH_2Ph), 6.98 (m, 1H), 7.07 (d, 8.4 Hz, 1H), 7.40 (t, 8.5 Hz, 1H) and 7.55 (m, 1H) (C_6H_4OH), 7.02 (m, 2H, *ortho*), 7.15 (m, 2H, *meta*) and 7.24 (m, 1H, *para*) (CH_2Ph), 7.67 (m, 12H, *ortho*+*meta*) and 7.78 (m, 3H, *para*) (Ph), 8.38 (s, broad, 1H, NH), 8.62 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR in $CDCl_3$: δ 10.7 (CH_3) and 24.7 (CH_2) (Et), 31.5 (CH_2, $^1J_{PC}$ 47.6 Hz, CH_2Ph), 117.2 (C_{ipso}, $^1J_{PC}$ 86.0 Hz, Ph), 126.7 (C_{ipso}, $^2J_{PC}$ 8.3 Hz, CH_2Ph), 128.6 (CH_p, CH_2Ph), 129.0 (CH_m, CH_2Ph), 130.3 (CH, J_{PC} 12.8 Hz, Ph), 131.5 (CH_o, J_{PC} 5.5 Hz, CH_2Ph), 134.4 (CH, J_{PC} 9.1 Hz, Ph), 135.2 (CH_p, Ph), 114.2, 117.7, 120.5, 132.0, 134.6 and 157.7 (C_6H_4OH), 158.7 (CH=N), 176.1 (HN=C). $^{31}P\{^1H\}$ NMR in $CDCl_3$: δ 23.3. ^{195}Pt NMR in $CDCl_3$: δ −32.5 (400 Hz).

3.2.3. $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (2)

Anal. Calc. for $C_{32}H_{27}Cl_4NO_2PPt$: C, 46.56; H, 3.30; N, 1.70. Found: C, 46.82; H, 3.37; N, 1.75%. FAB^+-MS: *m/z* 353 [M_{cation}]. FAB^--MS: *m/z* 472 [M_{anion}]. m.p. = 123 °C (dec.). TLC, $R_f = 0.52$ (eluent C_3H_6O–$CHCl_3$ = 1:3). IR spectrum in KBr, selected bands (cm^{-1}): 3261 m ν(N–H), 2923 m-w ν(C–H), 1647 s ν(C=N), 1479 and 1433 s ν(C=C), 1107 s ν(P–C), 754 s δ(C–H). ^1H NMR in DMSO-d_6: δ 7.7 (m, Ph), 7.42 (d, H(6) from C_6H_4(O)C=), 7.30 (t, H(4) from C_6H_4(O)C=), 6.85 (d, H(3) from C_6H_4(O)C=) and 6.67 (t, H(5) from C_6H_4(O)C=), 5.27 (d, J_{PH} 15.6 Hz, CH_2Ph), 6.95–7.29 (m, CH_2Ph), 8.54 (s+d, J_{PtH} 36.2 Hz, =CH), 10.91 and 10.39 (s, b, OH). $^{31}P\{H\}$ NMR in DMSO-d_6: δ 28.3. ^{195}Pt NMR in DMSO-d_6: δ 682 (145 Hz).

3.2.4. $[Ph_3PCH_2Ph]_2[PtCl_6]\cdot 1/2H_2O$ (4)

Anal. Calc. for $C_{50}H_{44}Cl_6P_2Pt\cdot 1/2H_2O$: C, 53.45; H, 4.04. Found: C, 53.61; H, 3.89%. FAB^+-MS: *m/z* 353 [M_{cation}]. FAB^--MS: *m/z* 408 [M_{anion}]. m.p. = 240 °C. TLC, $R_f = 0.70$ (eluent C_3H_6O–$CHCl_3$ = 1:1). IR spectrum in KBr, selected bands (cm^{-1}): 1110 s ν(P–C), 745 s δ(C–H). $^{31}P\{^1H\}$ NMR in $CDCl_3$: δ 23.3. ^{195}Pt NMR in CD_2Cl_2: δ 230.1 (211 Hz).

Table 1
Crystal data and structure refinement for $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**2**) and $[Ph_3PCH_2Ph]_2[PtCl_6]\cdot 1/2H_2O$ (**4**)

	2	**4**
Empirical formula	$C_{32}H_{28}Cl_4NO_2PPt$	$C_{50}H_{45}Cl_6O_{0.50}P_2Pt$
Formula weight	826.41	1123.59
Temperature (K)	120(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.6395(3)	21.4101(5)
b (Å)	10.6981(4)	12.8386(3)
c (Å)	14.4015(6)	18.5806(3)
α (°)	97.087(2)	90
β (°)	104.626(2)	114.1798(8)
γ (°)	97.050(2)	90
V (Å^3)	1553.63(10)	4659.3(2)
Z	2	4
ρ_{calc} (g cm^{-3})	1.767	1.602
μ (mm^{-1})	4.942	3.460
F(000)	808	2236
θ Range	2.84–26.01	2.45–25.00
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-17 \le l \le 17$	$-24 \le h \le 25$, $-15 \le k \le 15$, $-22 \le l \le 21$
Reflections collected	19 163	34 423
Independent reflections	5692	8195
R_{int}	0.0555	0.0794
R_1 [$I > 2\sigma(I)$]	0.0307	0.0502
wR_2 [$I > 2\sigma(I)$]	0.0637	0.1048
wR_2 (all data)	0.0677	0.1132
Goodness-of-fit (F^2)	1.039	1.026
Largest difference peak and hole (e Å^{-3})	0.938 and −0.943	1.209 and −1.254

Table 2
Bond lengths (Å) and angles (°) for the anion in $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**1**)

Bond lengths	
Pt(1)–O(1)	1.996(3)
Pt(1)–N(1)	2.018(4)
Pt(1)–Cl(1)	2.3073(12)
Pt(1)–Cl(4)	2.3190(12)
Pt(1)–Cl(3)	2.3196(12)
Pt(1)–Cl(2)	2.3227(11)
C(1)–O(1)	1.334(5)
O(2)–N(1)	1.380(5)
N(1)–C(7)	1.278(6)
C(6)–C(7)	1.445(7)
Bond angles	
Cl(1)–Pt(1)–N(1)	178.50(11)
Cl(2)–Pt(1)–O(1)	178.50(10)
N(1)–Pt(1)–O(1)	91.64(14)
Pt(1)–N(1)–O(2)	120.1(3)
Pt(1)–N(1)–C(7)	125.0(3)
Pt(1)–O(1)–C(1)	121.7(3)
Cl(1)–Pt(1)–Cl(2)	91.72(4)
Cl(1)–Pt(1)–Cl(3)	90.65(4)
Cl(1)–Pt(1)–Cl(4)	90.68(4)
Cl(3)–Pt(1)–Cl(4)	178.38(4)

3.2.5. X-ray structure determinations of $[Ph_3PCH_2Ph][PtCl_4\{C_6H_4(O)C(H)=NOH\}]$ (**2**) and $[Ph_3PCH_2Ph]_2[PtCl_6]\cdot 1/2H_2O$ (**4**)

The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and the Collect [23] data collection program. The DENZO-SCALEPACK [24] program package was used for cell refinements and data reduction. Structures of **2** and **4** were solved by direct methods using the SIR-97 or SHELXS-97 programs [25,26], respectively. An empirical absorption correction based on equivalent reflections [27] was applied to all data (T_{max}/T_{min} was 0.33164/0.25400 and 0.28204/0.20531, respectively for **1** and **2**). Both structures were refined with the SHELXL-97 [28] program and the WinGX graphical user interface [29]. In **2**, hydrogen of the OH group and in **4** hydrogens of the crystal water were located from the difference Fourier map. In **4**, only half a molecule of water was found in the asymmetric unit. OH hydrogen was refined isotropically while the positions of the water hydrogens were fix. All other hydrogens were constrained to ride on their parent atom. Crystallographic data for all complexes is summarized in Table 1 and selected bond lengths and angles for **2** in Table 2, while for **4** in Section 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176721 and 176722 for compounds **2** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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