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Note

Reaction of platinum acetate with phosphines and molecular structure of *trans*-[$Pt(OAc)_2(PPh_3)_2$]

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Abstract

An improved synthesis of platinum acetate is reported in detail. This tetrameric complex reacts with PPh_3 or P–n-Bu_3 at room temperature to give the thermodynamically unstable bis-substituted *trans*-[$Pt(OAc)_2L_2$] complexes, which are not easily accessible via other routes. The structure of the new compound *trans*-[$Pt(OAc)_2(PPh_3)_2$] has been determined by X-ray analysis.

Keywords: Platinum acetate; Platinum(II) complexes; Phosphino complexes; Acetato complexes; *trans* Complexes

1. Introduction

The chemistry of Pt(II) complexes with carboxylate ligands is rather limited. This is not surprising if one considers that the logical starting reagent, platinum acetate, is not commercially available; furthermore, its reported synthesis can produce explosive mixtures and is characterized by low irreproducible yields [1–3]. The known carboxylate complexes mainly contain mono- and bidentate phosphines as additional ligands: in fact, they are synthesized by oxidation of PtL_4 phosphino complexes [4–6], or via a Cl^-/O_2CR^- exchange by treating the corresponding chloro-complexes with silver carboxylate [7]. The more straightforward synthesis for this type of complexes, i.e. the reaction of platinum acetate with phosphines, requires the availability of a convenient synthetic procedure for the platinum salt.

An alternative method is described in an ICI Patent and is based on treatment of $PtCl_4$ with silver acetate in acetic acid at reflux [8]. In our experience, the isolated solid was always a mixture, as indicated by its ^1H and ^{195}Pt NMR spectra in $CDCl_3$; however, a pure sample of $[Pt_4(OAc)_8]$ was obtained, albeit in low yield (20%), by chromatography on Sephadex LH-20 using acetic acid as the eluent. ^1H and ^{195}Pt NMR spectra of the product in $CDCl_3$ show the expected signals of the methyl protons out (2.01 ppm) and in (2.44 ppm) the plane of the four platinum centers [9], and a unique ^{195}Pt signal at -589 ppm [10]. The ^{13}C resonances, which are not detectable in the 1D spectrum, are clearly observed in the $^1H-^{13}C$ 2D heterocorrelated experiments [11][1] [$^1H-^{13}C$, δ (ppm): 2.01–21.57 (CH_3COO^- out of plane, $^3J_{PtC} = 131$ Hz), 2.44–22.35 (CH_3COO^- in plane, $^3J_{PtC} = 131$ Hz), 2.44–188.12 (CH_3COO^- in plane $^2J_{PtC} = 650$ Hz), 2.01–193.71 (CH_3COO^- out of plane $^2J_{PtC} = 740$ Hz).

2. Results and discussion

We have developed a more convenient synthesis in which $PtCl_4$ is replaced by $PtCl_2$ [12]. Treatment of $PtCl_2$ with 2 equiv. of Ag(OAc) in acetic acid at reflux for 45 min gives a pure sample of platinum acetate in

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[1] HMQC with bird sequence and quadrature along F1 was achieved using the TPPI method for the H-bonded atoms, HBBC for the carbonyl ones.

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fair yield (45–55%), with Pt metal as the main by-product. Under the adopted experimental conditions $[Pt_4(OAc)_8]$ is solvated by 2 mol of acetic acid, whose presence strongly affects the ^1H NMR spectrum of the compound. In $CDCl_3$ solution the two peaks of the methyl protons at 2.01 and 2.44 ppm appear actually superimposed to a broad large band centered at 2.25 ppm; however, only the expected signal at -589 ppm is observed in the ^{195}Pt spectrum (investigated range from 100 to -4600 ppm).

$[Pt_4(OAc)_8]$ reacts quickly in chloroform at room temperature with phosphines having different steric and electronic properties. The reaction involves the degradation of the tetrameric structure and yields the mononuclear $[Pt(OAc)_2L_2]$ complexes ($L = PPh_3$, P–n-Bu_3, 1/2 $Ph_2PCH_2PPh_2$) when the ligand is used in a Pt/L 1/2 molar ratio. NMR data indicate that the isolated bis-substituted complexes with monophosphines are *trans* isomers; the $^1J_{PtP}$ constants (3080 Hz for PPh_3 and 2760 Hz for P–n-Bu_3) are in the typical range for *trans* phosphino complexes (2500–3000 Hz) and, in addition, the resonances of *ortho* and *meta* phenyl carbons appear as triplets. This behavior is characteristic of a *trans* arrangement of the two phosphines; in fact, the coupling constant $^2J_{PP\,trans}$ is so high that the carbon nuclei experience the effect of both phosphorus atoms (virtual coupling). The *cis* geometry observed with $Ph_2PCH_2PPh_2$ is imposed by the chelating properties of this diphosphine.

The molecular structure of $[Pt(OAc)_2(PPh_3)_2]$ is shown in Fig. 1 with the atom-labeling scheme used. X-ray structure analysis of *trans*-$[Pt(OAc)_2(PPh_3)_2]$: $C_{40}H_{36}O_4P_2Pt$, $M_r = 837.76$, monoclinic, space group $P2_1/c$, $a = 11.830(3)$ Å, $b = 15.158(3)$ Å, $c = 19.632(4)$ Å, $\beta = 94.69(3)^\circ$, $Z = 4$, $V = 3509(1)$ Å^3, $\rho_{calc} = 1.586$ g cm^{-3}, $\mu = 4.130$ mm^{-1}, Mo Kα ($\lambda = 0.71073$ Å), T = 293(2) K. Philips PW1100 (Febo System); structure solved by heavy atoms methods and refined with SHELXL-97. Reflections collected = 6948; reflections observed = 6422 [$I > 2\sigma(I)$]; $R_1 = 0.048$ ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$); $wR_2 = 0.104$ ($wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$). All the bond lengths and angles are in ranges typical for comparable molecular groupings.

The coordination around Pt is only slightly distorted four-planar, the highest deviations being P(2)–Pt–P(1) 167.8(2)° and P(2)–Pt–O(4) 84.9(2)°. The triphenylphosphine groups in *trans* position assume an intrinsically asymmetric propeller-shaped geometry. They exhibit the same configuration and are apparently related by a local pseudo C_2 symmetry with the twofold axis almost orthogonal to the coordination plane of Pt. Intramolecular non bonded distances (Å): O(1)···H(14) 2.28, O(3)···H(8) 2.72, O(1)···H(36) 2.72, O(3)···H(30) 3.04, O(2)···H(8) = 2.93, O(4)···H(24) 2.38. Intermolecular non bonded distances (Å): O(2)···H(22) 2.61, O(2)···H(23)′ 2.71, O(3)···H(22)′ 2.88 (′ at x, $1/2 - y$, $1/2 - z$); O(2)···H(33)″ 2.71 (″ at $1 - x$, $1 - x$, $1 - z$). Torsion angles (°): Pt–P(1)–C(1)–C(6)–62.7(7), Pt–P(2)–C(31)–C(36)–59.0(7), Pt–P(1)–C(7)–C(8)–16.7(7), Pt–P(2)–C(25)–C(30)–55.4(7), Pt–P(1)–C(13)–C(14)–45.7(7), Pt–P(2)–C(19)–C(24)–42.0(7), P(1)–Pt–O(4)–C(39)–80.8(5), P(2)–Pt–O(1)–C(37)–84.2(6), P(1)–Pt–O(1)–C(37)–106.9(5), P(2)–Pt–O(4)–C(39) 110.4(5); the reciprocal orientation of the two phosphines corresponds almost exactly to a staggered conformation. In this way, the contact interactions between faced phenyl groups are minimized [13]. In agreement with the observed molecular pseudo-symmetry C_2, the two acetato groups are disposed in a *cisoid* arrangement with respect to the coordination plane of Pt. A rough, yet reliable conformational analysis of the complex has shown that any different reciprocal arrangement of the two acetato groups and/or of the two PPh_3 groups would lead to highly repulsive intramolecular contact distances, namely: O···H < 2.00 Å, C···H < 2.10 Å and C···C < 2.8 Å. Nonetheless, even in the observed molecular structure very short contact distances are present. However, they appear to be of quite different nature. In fact, values such as O(3)···H(8) 2.72 Å and O(1)···H(36) 2.72 Å, but also H(30)···O(3) 3.04 Å and H(8)···O(2) 2.93 Å, fall in the range of now generally accepted weak bond interactions of type C–H···X (X acceptor = O, N); the bond angles C–H···X (110–140°) are in agreement with this as-

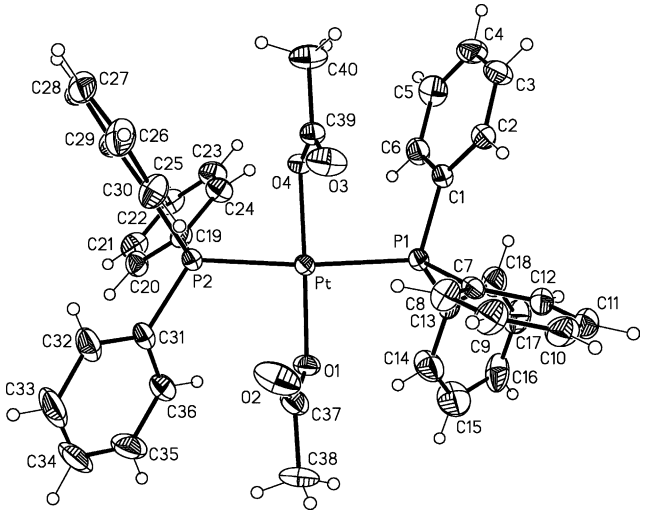


Fig. 1. ORTEP plot of $[Pt(OAc)_2(PPh_3)_2]$ with atom labeling. Selected bond distances (Å) and bond angles (°): Pt–P(1) = 2.327(2), P(2)–C(25) = 1.836(8), Pt–P(2) = 2.313(2), P(2)–C(31) = 1.829(8), Pt–O(1) = 2.032(5), O(1)–C(37) = 1.31(1), Pt–O(4) = 2.044(5), C(37)–O(2) = 1.22(1), P(1)–C(1) = 1.823(8), C(37)–C(38) = 1.51(1), P(1)–C(7) = 1.835(8), O(4)–C(39) = 1.31(1), P(1)–C(13) = 1.839(9), C(39)–O(3) = 1.21(1), P(2)–C(19) = 1.819(8), C(39)–C(40) = 1.50(1); P(1)–Pt–P(2) = 167.8(7), P(2)–Pt–O(1) = 93.5(2), P(1)–Pt–O(1) = 91.3(2), P(2)–Pt–O(4) = 84.9(2), P(1)–Pt–O(4) = 90.1(2), O(1)–Pt–O(4) = 178.3(2), O(1)–C(37)–O(2) = 124.0(9), O(4)–C(39)–O(3) = 126.0(8), O(1)–C(37)–C(38) = 113.1(8), O(4)–C(39)–C(40) = 112.3(7), O(2)–C(37)–C(38) = 122.8(9), O(3)–C(39)–C(40) = 121.8(8).

sumption as well [14]. In contrast, the distances and angles O(1)···H(14) 2.28 Å (O(1)···H(14)–C(14) 144°) and O(4)···H(24) 2.36 Å (O(4)vH(24)–C(24) 144°), are close to the expected values for typical hydrogen-bonds [15]. All of these bond interactions play a significant role in the stabilization of the observed molecular structure.

The complex undergoes an easy rearrangement to a *cis* configuration by moderate heating in polar solvents. In fact, the platinum *cis*-bisphosphino complexes are stabilized, compared with the *trans* ones, by stronger Pt–P bonds and better solvent effects, which may overcome the less favourable electrostatic interactions between the metal and the ligand set [16].

The reactivity of platinum acetate toward phosphines has been checked also with the smaller phosphine PMe_2Ph at different molar ratios in deuterated acetic acid, at room temperature and at 90 °C (Scheme 1).

It is interesting to note that: (i) reaction at room temperature gives the kinetically favored tris–phosphino complex $[Pt(OAc)L_3](OAc)$ even at low L/Pt molar ratios (0.5–1.0) together with unreacted platinum acetate; (ii) heating of these mixtures at 90 °C affords the thermodynamically stable monosubstituted complexes $[Pt(OAc)_2L]_{1,2}$ and the bis-substituted *cis*-$[Pt(OAc)_2L_2]$, in relative amounts dependent on the total phosphine content; (iii) heating induces conversion of the *trans* into the *cis* isomer; (iv) at a Pt/L 1/2 molar ratio the mixture of platinum acetate, bis- and tris-substituted complexes formed at room temperature is converted upon heating into the expected *trans*- and *cis*-$[Pt(OAc)_2L_2]$; (v) the small PMe_2Ph (Tolman's cone angle 122° compared to 132° for P–n-Bu_3 and 145° for PPh_3) easily forms the dicationic tetraphosphino complex $[Pt(PMe_2Ph)_4]^{2+}$, whereas with the more hindering PPh_3 only two phosphines can be coordinated to the platinum centre.

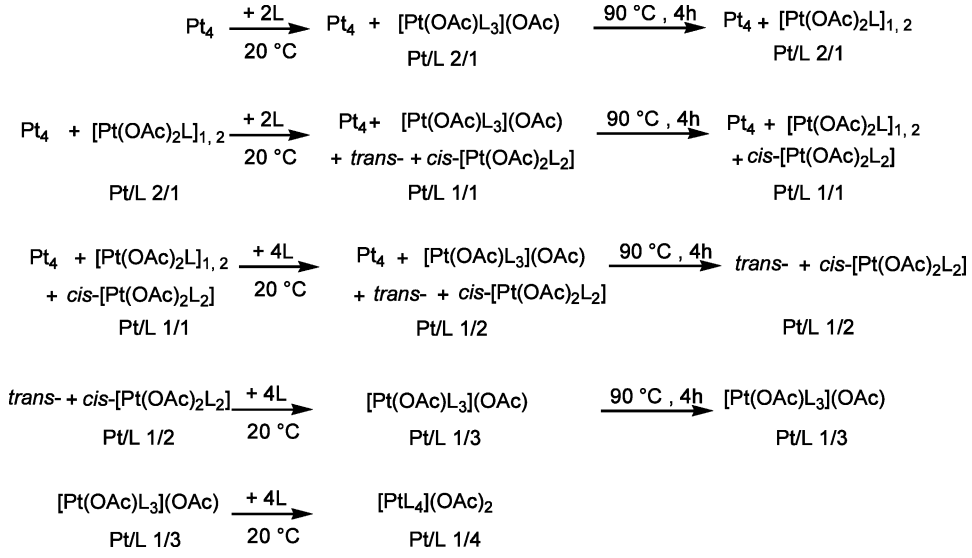
The results obtained indicate that platinum acetate is a very convenient reagent for the room temperature synthesis of *trans* bis-phosphine complexes. The high *trans* effect of the phosphine ligand appears responsible for the observed geometry and for the degradation of the tetrameric structure of the platinum salt. Heating of the *trans* complexes in deuteroacetic acid at 90 °C induces *trans*–*cis* isomerization without any evidence of the formation of reduction products. This last aspect confirms the difference of reactivity between platinum and palladium complexes; in fact, bis-carboxylato bis-phosphine palladium complexes are good catalysts for the Heck reaction, due to their ability to give on heating catalytically active palladium zero species [17].

3. Experimental

3.1. Synthesis

3.1.1. Platinum acetate

A mixture of $PtCl_2$ (1.02 g, 3.85 mmol) and Ag(OAc) (1.35 g, 8.10 mmol) in acetic acid (60 ml) was maintained at reflux under stirring for 45 min. The precipitated AgCl was filtered off at room temperature (r.t.) and the resulting blue solution was evaporated at reduced pressure. The solid was dissolved with dichloromethane (20 ml) and filtered over celite to eliminate traces of residual silver chloride and some metallic platinum. The blue solid obtained after solvent removal was treated with diethyl ether, filtered and dried under vacuum (0.65 g, 47% yield calculated on $[Pt_4(OAc)_8]\cdot 2HOAc$). *Anal.* Calc. for $C_{20}H_{32}O_{20}Pt_4$: C, 17.50; H, 2.34. Found: C, 17.20; H, 2.16%.



Scheme 1. Major products of the reaction between $[Pt_4(OAc)_8]$ (Pt_4) and PMe_2Ph (L) at different Pt/L ratios, in CD_3COOD. In this solvent OAc indicates deutero acetate.

3.1.2. *trans*-[Pt(OAc)$_2$(PPh$_3$)$_2$]

A solution of [Pt$_4$(OAc)$_8$]·2HOAc (75 mg, 0.054 mmol) and PPh_3 (130 mg, 0.48 mmol) in chloroform (30 mL) was stirred at r.t. for 3 h, during which time the color changed from deep blue to orange. The solvent was evaporated at reduced pressure; the resulting yellow solid was treated with diethyl ether and filtered (120 mg, 66% yield). *Anal.* Calc. for $C_{40}H_{36}O_4P_2Pt$: C, 57.36; H, 4.30. Found: C, 57.32; H, 4.22%. NMR data; ^{1}H, δ (ppm): 0.89 (s, 3H, CH_3COO^-), 7.19–7.77 (m, 15H, Ph); ^{13}C: 21.12 (s, CH_3COO^-), 128.11–134.79 (Ph), 175.92 (s, CH_3COO^-); ^{31}P: 14.55 (s, $^1J_{PtP} = 3080$ Hz); ^{195}Pt (vs. $[PtCl_6]^{2-} = 0$): -2910 (t, $^1J_{PtP} = 3080$ Hz). Crystals for X-ray analysis were obtained by slow evaporation of an acetonitrile solution. Further NMR data in $CDCl_3$: ^{13}C, δ (ppm): 21.12 (s, CH_3COO^-), 128.1 (t, *m*-C_6H_5, $^3J_{PC} = 5.3$ Hz), 130.4 (s, *p*-C_6H_5), 134.8 (t, *o*-C_6H_5, $^2J_{PC} = 6.5$ Hz), 175.9 (s, CH_3COO^-). FTIR (KBr, cm^{-1}): 3047 [ν(C–H)], 1660 and 1435 [$\nu(CO_2^-)$], 1481, 1284, 1097, 744, 692. MS (ESI, capillary voltage 4.5 kV, capillary temp. 200 °C): *m*/*z* 778 ($[Pt(OAc)(PPh_3)_2]^+$).

3.1.3. *trans*-[Pt(OAc)$_2$(P–*n*-Bu$_3$)$_2$]

n-Butylphosphine (0.115 g, 0.57 mmol) was added to a solution of [Pt$_4$(OAc)$_8$]·2HOAc (0.095 g, 0.07 mmol) in chloroform (25 ml); the mixture was left under stirring at r.t. for 3 h, during which time the color changed from deep blue to yellow. The solution was then evaporated to dryness, to give an orange oil. *Anal.* Calc. for $C_{28}H_{60}O_4P_2Pt$: C, 46.88; H, 8.36. Found: C, 47.57; H, 9.07%. NMR data in $CDCl_3$: ^{1}H, δ (ppm): 0.7–2.1 (cm, butyl and acetoxy protons); ^{13}C: 13.7 (s), 21.0 (t), 24.4 (t), 25.6 (s), 27.6 (s), 176.9 (CH_3COO^-); ^{31}P: 8.12 (s, $^1J_{PtP} = 2760$ Hz); ^{195}Pt (vs.$[PtCl_6]^{2-} = 0$ ppm): -2932 (t, $^1J_{PtP} = 2760$ Hz).

3.1.4. [Pt(OAc)$_2$(Ph$_2$PCH$_2$PPh$_2$)]

The reaction between platinum acetate and $Ph_2PCH_2PPh_2$ was studied in $CDCl_3$, recording the ^{31}P and ^{1}H NMR spectra. The diphosphine (0.016 g, 0.04 mmol) was added to a solution of [Pt$_4$(OAc)$_8$]·2HOAc (0.015 g, 0.01 mmol) in deuterated chloroform. The color of the solution changed immediately from deep blue to orange. NMR data in $CDCl_3$: ^{1}H, δ (ppm): 1.96 (s, 3H, CH_3COO^-), 4.18 (t, 1H, CH_2, $^2J_{PH} = 9$ Hz), 7.00–7.82 (m, 10H, Ph); ^{31}P: -68.6 (s, $^1J_{PtP} = 3460$ Hz). These data were in agreement with those reported in Ref. [5].

3.2. Reaction of [Pt$_4$(OAc)$_8$] (Pt$_4$) with PMe$_2$Ph (L) at different Pt/L ratios

The reaction between [Pt$_4$(OAc)$_8$]·2HOAc and PMe_2Ph was followed in deuterated acetic acid at different Pt/L molar ratios, in a NMR tube. The phosphine was added directly, in successive steps, to a solution of [Pt$_4$(OAc)$_8$]·2HOAc (ca. 10^{-2} mol dm^{-3}) to reach the following Pt/L ratios 2/1, 1/1, 1/2, 1/3, and 1/4. The ^{1}H and ^{31}P NMR spectra were recorded at r.t. immediately after the addition of the phosphine and after heating of the resulting solution at 90 °C for 4 h. The major products for each investigated Pt/L molar ratios were summarised in Scheme 1.

The tris-substituted complex [Pt(OAc)($PMe_2Ph)_3$](OAc) possesses two equivalent phosphorous donor atoms in *trans* to each other and a 'middle' phosphorous coupled to those in *cis* positions. The ^{31}P peak at -25.4 ppm (t, $^2J_{PP} = 22.8$ Hz, $^1J_{PtP} = 3420$ Hz) can be assigned to the central phosphorous (P_a) and that at -0.1 ppm (d, $^2J_{PP} = 22.8$ Hz, $^1J_{PtP} = 2480$ Hz) to the remaining two phosphorous atoms (P_b), on the basis of multiplicity, integration (1:2) and $^1J_{PtP}$ coupling constants. The pattern of these signals is characteristic of tris–phosphino complexes [18]. NMR data in CD_3COOD: ^{1}H, δ (ppm): 1.78 (t, $^2J_{PH} = 3.5$ Hz, P_aCH_3), 1.53 (d, $^2J_{PH} = 11$ Hz, P_bCH_3), 7.4–8 (PPh); ^{13}C, 12.1 (t, $^1J_{PC} = 19.7$ Hz, P_aCH_3), 15.8 (d, $^1J_{PC} = 72.0$ Hz, P_bCH_3), 128.7 (d, $^2J_{PC} = 12$ Hz, P_b(*o*-Ph)), 129.4 (t, $^3J_{PC} = 5.3$ Hz, P_a(*m*-Ph)), 129.6 (d, $^3J_{PC} = 10.4$ Hz, P_b(*m*-Ph)), 131.2 (t, $^2J_{PC} = 6.2$ Hz, P_a(*o*-Ph)), 131.8 (s, *p*-Ph), 132.1 (d, $^4J_{PC} = 2.9$ Hz, *p*-Ph); ^{195}Pt (vs.$[PtCl_6]^{2-} = 0$ ppm), -4910 (dt, $^1J_{PtP} = 3420$ Hz, $^1J_{PtP} = 2480$ Hz).

Two singlets in the ^{31}P NMR spectra at –24.7 ($^1J_{PtP} = 4080$ Hz) and –26.2 ($^1J_{PtP} = 4400$ Hz), observed in the heated solution with Pt/L 2/1, are attributed to the mono-substituted complexes $[Pt(OAc)_2L]_{1,2}$ on the basis of the ESI MS spectrum, which shows two peaks at *m*/*z* 937 ($[Pt(CD_3COO)_2(PMe_2Ph)]_2(Na^+)$) and 480 ($[Pt(CD_3COO)_2(PMe_2Ph)](Na^+)$). The different nuclearity of the fragments was confirmed also by the analysis of the isotopic pattern of the two metal clusters.

The *trans*- and *cis*-[Pt(OAc)$_2$($PMe_2Ph)_2$] were identified on the basis of the $^1J_{PtP}$ constants and of the resonances of the phosphine methyl protons, which appeared as triplets or doublets in the *trans* or *cis* geometry respectively. *cis*-[Pt(OAc)$_2$($PMe_2Ph)_2$]; NMR data in CD_3COOD: ^{1}H, δ (ppm): 1.67 (d, $^2J_{PH} = 11.3$ Hz, PCH_3), 7.4–8.0 (PPh); ^{31}P, -20.8(s, $^1J_{PtP} = 3700$ Hz). *trans*-[Pt(OAc)$_2$($PMe_2Ph)_2$]; NMR data in CD_3COOD: ^{1}H, δ (ppm): 1.73 (t, $^2J_{PH} = 3.6$ Hz, PCH_3), 7.4–8 (PPh); ^{31}P, -3.8 (s, $^1J_{PtP} = 2680$ Hz).

The dicationic tetra-phosphino complex [Pt($PMe_2Ph)_4$](OAc)$_2$ presents a singlet at -12.8 (s, $^1J_{PtP} = 2320$ Hz); these values are in agreement with those reported in literature for the same cation [19].

The acetato groups rapidly exchange with deuterated acetic acid, so that the resonances of their methyl protons can not be detected.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 203517. 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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