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Note

Preparation and structure of $[PhPt(OCO_2H)(PEt_3)_2]$ and $[PhPt(OH_2)(PEt_3)_2]BF_4$

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Abstract

The reaction of $[PhPt(Cl)(PEt_3)_2]$ with $AgBF_4$ in aqueous methanol containing NEt_3 under CO_2 afforded *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ in a high yield. In the absence of the amine, the reaction gave *trans*-$[PhPt(OH_2)(PEt_3)_2]BF_4$. The Pt(II) bicarbonato complex was thermally stable. The bicarbonato complex crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with cell dimensions $a = 9.317(5)$, $b = 31.960(8)$, $c = 9.313(5)$ Å, $\beta = 122.50(4)°$, $U = 2338(2)$ Å^3, $Z = 4$. Residuals are $R = 0.029$ and $R_w = 0.024$ for 3466 observed data. The bicarbonato complex forms a doubly hydrogen-bonded dimer in the crystal. The aquo complex crystallizes in the orthorhombic space group *Pnma* (No. 62) with cell dimensions $a = 12.315(2)$, $b = 14.630(2)$, $c = 13.811(3)$ Å, $U = 2488.4(7)$ Å^3, $Z = 4$. Residuals are $R = 0.044$ and $R_w = 0.039$ for 1704 observed data.

Key words: Crystal structures; Platinum complexes; Bicarbonato complexes; Aquo complexes

Introduction

Coordination of CO_2 or CO_2-derived ligands to a transition metal center is of interest in connection with the utilization of CO_2 as carbon source and has been extensively studied in these two decades [1, 2]. Although bicarbonato complexes of Pd(II) have been well characterized [3, 4], studies on bicarbonato complexes of Pt(II) are quite rare. Only two platinum complexes with bicarbonato ligand have been reported on the basis of spectroscopic analyses [5, 6], and to our knowledge no X-ray structure determination of this class of complex has been reported. The reactions of $[(PBz_3)_2Pt(Ph)(OH)]$ ($Bz = C_6H_5CH_2$) with CO_2 have been reported to give an η^1,η^1,μ_2-CO_3 dinuclear complex and a bicarbonato complex was implied as an unstable intermediate [7]. We report here the formation and X-ray structure of *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ and *trans*-$[PhPt(OH_2)(PEt_3)_2]BF_4$.

Experimental

General

The starting complex, *trans*-$[PhPt(Cl)(PEt_3)_2]$, was prepared according to the literature procedure [8]. ^1H and ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer using tetramethylsilane as an internal reference. IR spectra were measured using a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

trans-$[PhPt(OCO_2H)(PEt_3)_2]$

Silver tetrafluoroborate (0.022 g, 0.11 mmol) in methanol (2 ml) was added dropwise over several minutes to a vigorously stirred solution of *trans*-$[PhPt(Cl)(PEt_3)_2]$ (0.060 g, 0.11 mmol) in methanol (10 ml) containing water (0.5 ml, 28 mmol) and triethylamine (0.5 ml, 3.6 mmol) in an ice-water bath under carbon dioxide. After 1.5 h of stirring, precipitates were filtered off and the filtrate was dried under a reduced pressure to give white solids, which were recrystallized from a methanol–water (1:1 vol.) mixture under a carbon dioxide atmosphere to yield analytically pure *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ as a white powder. Yield 0.050 g (80%), m.p. 78–80 °C. IR (KBr pellet, cm^{-1}): 3053(w), 2960(m), 2874(w), 2609(w, br), 1615(vs), 1572(s), 1462(s), 1417(s), 1394(s), 1335(vs), 1256(w), 1038(s), 1008(m), 769(s), 742(s), 730(s), 706(s). ^1H NMR ($CDCl_3$, −10 °C): δ 1.12 (methyl, m), 1.34 (methylene, m), 6.75–6.90 (phenyl, m), 7.15–7.45 (phenyl m), 11.2 (bicarbonato, vbr). ^{13}C NMR ($CDCl_3$): δ 7.5 (methyl), 12.8 (methylene, t, $J(CP) = 16.5$ Hz), 121.5 (phenyl, *para*), 124.8 (phenyl, *meta*), 127.4 (phenyl, *ortho*), 137.1 (phenyl, *ipso*), 161.4 (bicarbonato). *Anal.* Calc. for $C_{19}H_{36}O_3P_2Pt$: C, 40.07; H, 6.37. Found: C, 40.19; H, 6.40%.

trans-$[PhPt(OH_2)(PEt_3)_2]BF_4$

Silver tetrafluoroborate (0.072 g, 0.37 mmol) in methanol (8 ml) was added dropwise over several minutes to a vigorously stirred solution of *trans*-$[PhPt(Cl)(PEt_3)_2]$ (0.20 g, 0.37 mmol) in methanol (5 ml) containing water (0.5 ml, 28 mmol) in a ice-water bath under carbon

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dioxide. After 1.5 h of stirring, precipitates were filtered off and the filtrate was dried under a reduced pressure to give *trans*-$[PhPt(OH_2)(PEt_3)_2]BF_4$ as a white solid. Yield 0.20 g (90%). Recrystallization from a dichloromethane–hexane mixture under a carbon dioxide atmosphere yielded an analytically pure sample of colorless transparent microcrystals, m.p. 145–146 °C. Reaction and recrystallization under argon gave similar results. IR (KBr pellet, cm^{-1}): 3400(s, br), 2969(s), 1571 (s), 1465(s), 1421(s), 1385(m), 1259(m), 1036(s, br), 770(s), 708(m). ^1H NMR ($CDCl_3$): δ 1.14 (methyl, m), 1.57 (methylene, m), 4.54 (aquo, br, s), 6.8–7.4 (phenyl, m). ^{13}C NMR ($CDCl_3$): δ 7.3 (methyl), 12.5 (methylene), 122.6 (phenyl, *para*), 124.0 (phenyl, *meta*), 128.0 (phenyl, *ortho*), 135.2 (phenyl, *ipso*), 161.4 (bicarbonato). *Anal.* Calc. for $C_{18}H_{37}BF_4OP_2Pt$: C, 35.25; H, 6.08. Found: C, 35.33; H, 6.04%.

Thermolysis of trans-$[PhPt(OCO_2H)(PEt_3)_2]$

A few mg of *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ were sealed in a glass capillary under vacuum and heated at 120 °C for 30 min. The melting point and IR spectrum (KBr pellet) of the heated sample were identical with those of the starting complex.

X-ray data collection and structure refinement

Diffraction data were collected on a Rigaku AFC-7R diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, 50 kV, 280 mA) at 23 ± 1 °C. Structure analyses were performed by using a teXsan® crystallographic software package. Neutral atom scattering factors were taken from ref. 9. Abnormal dispersion effects were included in the calculations [10]. The weighting scheme for the refinements was $w = 1/\sigma^2(F_o)$.

trans-$[PhPt(OCO_2H)(PEt_3)_2]$

$C_{19}H_{36}O_3P_2Pt$, $M = 569.53$. A colorless single crystal of size 0.35 × 0.15 × 0.08 mm was cut off from a colorless needle grown from slow diffusion of hexane into a toluene solution of the complex. Monoclinic, $a = 9.317(5)$, $b = 31.960(8)$, $c = 9.313(5)$ Å, $\beta = 122.50(4)°$, $U = 2338(2)$ Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.617$ g cm^{-3}, $F(000) = 1128$, μ(Mo Kα) = 61.32 cm^{-1}, ω scan mode with ω scan width = 1.05 + 0.20 tan θ, scan speed 32° min^{-1}, 5085 reflections measured ($3 < 2\theta < 55°$, $h, k, \pm l$), 4772 unique (merging $R = 0.021$ after empirical absorption correction DIFABS [11] (max., min. transmission factors = 0.8473, 1.1292)) giving 3466 with $I > 3\sigma(I)$. No significant decay was observed. The position of the Pt atom was determined through automatic Patterson analysis (SHELXS-86 [12]) and the structure was expanded using Fourier technique. Full-matrix least-squares refinement with anisotropic thermal vibration model for the non-hydrogen atoms was used. The position of the bicarbonato hydrogen atom was determined from difference Fourier maps and others were from difference maps or calculations. The final least-squares cycle included fixed hydrogen atoms each isotropic thermal parameter of which is 1.2 times of that of the connecting atom. Final R and R_w values were 0.029 and 0.024.

trans-$[PhPt(OH_2)(PEt_3)_2]BF_4$

$C_{18}H_{37}BF_4OP_2Pt$, $M = 613.33$. A block-shaped colorless single crystal with size of 0.16 × 0.16 × 0.15 mm was grown from slow diffusion of n-hexane into a dichloromethane solution of the complex. Orthorhombic, $a = 12.315(2)$, $b = 14.630(2)$, $c = 13.811(3)$ Å, $U = 2488.4(7)$ Å^3, space group $Pnma$ (No. 62), $Z = 4$, $D_c = 1.64$ g cm^{-1}, $F(000) = 1208$, μ(Mo Kα) = 57.79 cm^{-1}. A total of 3218 reflections was measured ($3 < 2\theta < 55°$, h, k, l) with the ω–2θ mode with ω scan width = 1.37 + 0.20 tan θ, ω scan speed 16° min^{-1}, giving 1704 reflections with $I > 3\sigma(I)$. No significant decay was observed. An empirical absorption correction, ψ scan [13] (max., min. transmission factors = 0.227, 0.267), was applied. Patterson methods (SHELXS-86 [12]) were followed by normal heavy-atom procedures; full-matrix least-squares refinement with rigid group model for BF_4^- and all other non-hydrogen atoms anisotropic. The final R and R_w values were 0.044 and 0.039, respectively.

Results and discussion

When *trans*-$[PhPt(Cl)(PEt_3)_2]$ was reacted with $AgBF_4$ in aqueous methanol in the presence of triethylamine under carbon dioxide, *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ was formed in a high yield. Purification was accomplished by recrystallization from aqueous methanol, with X-ray quality crystals being obtained by slow diffusion of hexane into a toluene solution. The X-ray structure analysis of the crystal showed that the product is square-planar *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$. To our knowledge, this is the first X-ray structure analysis of a bicarbonato complex of Pt(II). The crystal structure of this complex is described in the following section. The IR spectrum (KBr) showed ν(OH) bands at 2609 and 2684 cm^{-1} and $-OCO_2-$ modes at 1615, 1334 and 1038 cm^{-1}. Their assignments are based on analogy to those of *trans*-$[PdMe(OCO_2H)(PEt_3)_2]$ [3] and *trans*-$[PtH(OCO_2Me)\{P(C_6H_{11})_3\}_2]$ [14]. The ^1H NMR of the Pt(II) bicarbonato complex in a $CDCl_3$ solution at −10 °C showed a very broad $-OCO_2H$ signal at δ 11.2.

When *trans*-$[PhPt(Cl)(PEt_3)_2]$ was reacted with $AgBF_4$ in aqueous methanol in the absence of triethylamine under carbon dioxide or argon, *trans*-$[PhPt(H_2O)$-

$(PEt_3)_2]BF_4$ was isolated in a high yield as confirmed by X-ray structure analysis (*vide infra*).

We suppose that the reaction of *trans*-$[PhPt(Cl)(PEt_3)_2]$ with Ag^+ in aqueous methanol gives the aquo complex, which then is deprotonated by triethylamine to give *trans*-$[PhPt(OH)(PEt_3)_2]$. Carbon dioxide inserts between the Pt atom and the hydroxo ligand to give the bicarbonato complex. A similar mechanism has been suggested for the formation of bicarbonato complexes [3, 4, 5, 15].

Since bicarbonato Pt(II) complexes have been postulated as intermediates for the formation of dinuclear Pt(II) complexes with an η^1,η^1,μ_2-CO_3 bridge [6, 7], we tried solid-state thermolysis of the present bicarbonato complex. Thermolysis at 120 °C under vacuum induced no reaction and the starting bicarbonato complex was recovered quantitatively.

Description of crystal structure

A perspective view of *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ is shown in Fig. 1, while selected dimensions are given in Table 1. This complex has a doubly hydrogen-bonded dimer structure in the crystal. A crystallographic inversion center is located between the H-bonded pair. The Pt1–O1 length of 2.118(4) Å is comparable with the corresponding length of 2.13(1) Å in *trans*-$[PtH(OCO_2Me)\{P(C_6H_{11})_3\}_2]$ [14]. The distance between the oxygen atoms which are intermolecularly H-bonded is 2.649(6) Å, which is similar to the corresponding distance of 2.60(2) Å in the crystal of *trans*-$[PdMe(OCO_2H)(PEt_3)_2]$ [3]. The dihedral angle between the PtP_2CO plane and the CO_3 plane is 73.6°.

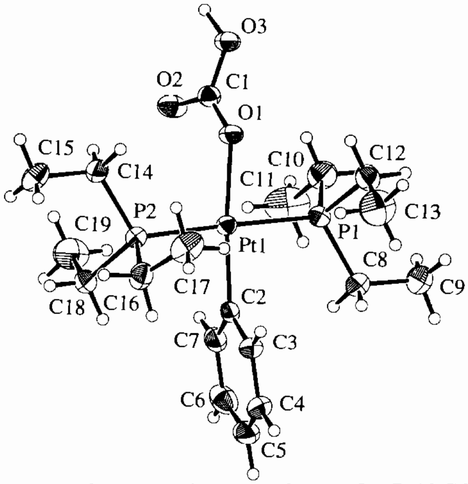

Fig 1. ORTEP diagram of *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ with ellipsoids scaled to 30% probability.

TABLE 1. Selected dimensions in *trans*-$[PhPt(OCO_2H)(PEt_3)_2]$ with e.s.d.s in parentheses

Bond lengths (Å)			
Pt1–P1	2.297(2)	Pt1–P2	2.294(2)
Pt1–O1	2.118(4)	Pt1–C2	1 985(6)
O1–C1	1.264(7)	C1–O2	1.249(7)
C1–O3	1.320(7)		
Bond angles (°)			
P1–Pt1–P2	176.16(6)	O1–Pt1–C2	174.4(2)
Pt1–O1–C1	125.7(4)	O1–C1–O2	125.0(6)
O2–C1–O3	119.9(6)	O1–C1–O3	115.2(6)
Dihedral angles between best planes (°)			
Pt1P1P2O1C2–O1C1O2O3		73.6	
Pt1P1P2O1C2–C2C3C4C5C6C7		86 9	

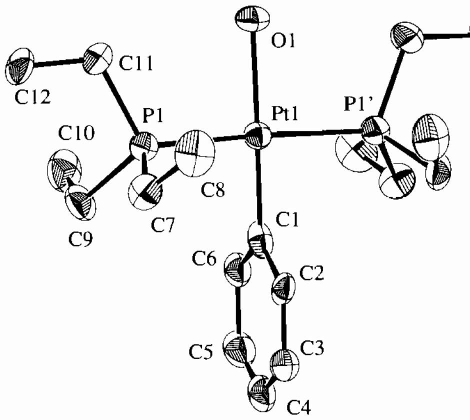

Fig. 2. ORTEP diagram of *trans*-$[PhPt(OH_2)(PEt_3)_2]^+$ in its tetrafluoroborate salt with ellipsoids scaled to 30% probability

TABLE 2 Selected dimensions in *trans*-$[PhPt(OH_2)(PEt_3)_2]^+$ in its BF_4^- salt with e s d.s in parentheses

Bond lengths (Å)			
Pt1–P1	2.309(3)	Pt1–O1	2.19(1)
Pt1–C1	1.97(2)		
Bond angles (°)			
P1–Pt1–P1'	175.0(2)	O1–Pt1–C1	177.6(7)
Dihedral angles between best planes (°)			
Pt1P1P1'O1C1–C1C2C3C4C5C6			90.0(0)

The molecular structure and the relevant bond lengths of *trans*-$[PhPt(OH_2)(PEt_3)_2]^+$ in the crystal of its BF_4^- salt are shown in Fig. 2 and Table 2, respectively. The oxygen and platinum atoms and the carbon atoms of the phenyl group are on a crystallographic mirror plane. The coordination geometry around the Pt atom is square-planar and the Pt1–O1 distance is 2.19(1) Å.

Supplementary material

Further crystallographic details can be obtained on request from the Director of the Cambridge Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, UK.

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