Pamela Moyo, Leah Matsinha and C.E. Makhubela Banothile*

The crystal structure of bis{3-(diphenylphosphaneyl)propanoato- $\kappa^2 O,P$ }platinum(II) dihydrate, $C_{30}H_{28}O_6P_2Pt$

Table 1: Data collection and handling.

Crystal:	Brown needle
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.45 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, ω
$\theta_{\max}$, completeness:	26.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18368, 2675, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2653
$N(\text{param})_{\text{refined}}$:	183
Programs:	Bruker [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.44711(12)	0.5225(2)	0.63025(11)	0.0133(4)
C2	0.37156(12)	0.4801(2)	0.58769(12)	0.0155(4)
H2	0.36282(12)	0.3851(2)	0.57082(12)	0.0186(5)*
C3	0.30961(12)	0.5772(2)	0.57029(13)	0.0184(4)
H3	0.25859(12)	0.5490(2)	0.54067(13)	0.0220(5)*
C4	0.32192(13)	0.7156(2)	0.59605(13)	0.0185(4)
H4	0.27880(13)	0.7811(2)	0.58555(13)	0.0222(5)*
C5	0.39700(13)	0.7584(2)	0.63702(13)	0.0173(4)
H5	0.40539(13)	0.8534(2)	0.65395(13)	0.0208(5)*
C6	0.46002(12)	0.6626(2)	0.65337(12)	0.0147(4)
H6	0.51178(12)	0.6925(2)	0.68026(12)	0.0176(5)*
C7	0.62125(12)	0.4721(2)	0.68086(12)	0.0146(4)
C8	0.64127(12)	0.5775(2)	0.62994(13)	0.0177(4)
H8	0.60066(12)	0.6188(2)	0.59002(13)	0.0212(5)*
C9	0.72043(13)	0.6213(2)	0.63794(14)	0.0205(4)
H9	0.73415(13)	0.6930(2)	0.60361(14)	0.0246(5)*
C11	0.76032(12)	0.4574(2)	0.74725(13)	0.0200(4)
H11	0.80102(12)	0.4170(2)	0.78744(13)	0.0240(5)*
C12	0.68106(12)	0.4134(2)	0.73956(12)	0.0164(4)
H12	0.66757(12)	0.3426(2)	0.77462(12)	0.0196(5)*
C13	0.52914(13)	0.2961(2)	0.56534(12)	0.0167(4)
H13a	0.47483(13)	0.2624(2)	0.54003(12)	0.0201(5)*
H13b	0.54777(13)	0.3617(2)	0.52699(12)	0.0201(5)*
C15	0.55317(12)	0.0447(2)	0.61826(12)	0.0146(4)
C16	0.77982(13)	0.5604(2)	0.69612(14)	0.0209(4)
H16	0.83419(13)	0.5898(2)	0.70084(14)	0.0251(5)*
C17	0.58688(12)	0.1706(2)	0.58063(13)	0.0171(4)
H17a	0.60102(12)	0.1416(2)	0.52844(13)	0.0205(5)*
H17b	0.63708(12)	0.2010(2)	0.61684(13)	0.0205(5)*
O1	0.51177(9)	0.06433(15)	0.67441(9)	0.0182(3)
O2	0.56517(9)	-0.07417(16)	0.59461(9)	0.0217(3)

<https://doi.org/10.1515/ncrs-2020-0167>

Received March 31, 2020; accepted April 30, 2020; available online May 12, 2020

Abstract

$C_{30}H_{28}O_6P_2Pt$, monoclinic, $C2/c$ (no. 15), $a = 16.911(3)$ Å, $b = 9.516(2)$ Å, $c = 16.790(3)$ Å, $\beta = 100.830(4)^\circ$, $V = 2653.8(9)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0126$, $wR_{\text{ref}}(F^2) = 0.0310$, $T = 293$ K.

CCDC no.: 1984887

The complex title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: C.E. Makhubela Banothile, University of Johannesburg, Department of Chemical Sciences, P.O.Box 524, Auckland Park Kingsway Avenue, 2006 Johannesburg, South Africa, e-mail: bmakhubela@uj.ac.za. <https://orcid.org/0000-0002-7075-4858>

Pamela Moyo and Leah Matsinha: University of Johannesburg, Department of Chemical Sciences, P.O.Box 524, Auckland Park Kingsway Avenue, 2006 Johannesburg, South Africa

Table 2 (continued)

Atom	x	y	z	U _{iso} [*] /U _{eq}
O3	0.64613(11)	−0.1206(2)	0.47227(12)	0.0365(4)
H3a	0.6097(17)	−0.088(4)	0.4284(14)	0.0548(6)*
H3b	0.6201(18)	−0.098(4)	0.5148(14)	0.0548(6)*
P1	0.52316(3)	0.38910(5)	0.65876(3)	0.01164(10)
Pt1	0.5	0.232461(10)	0.75	0.01130(4)

Source of material

Treatment of 4-formyl-3-hydroxybenzoic acid (0.401 g, 2.41 mmol) with one equivalent of 4-amino-3-hydroxybenzoic acid (0.396 g, 2.41 mmol) in ethanol yielded a mixture, which was refluxed for 10 h. This procedure resulted in the formation of (*E*)-4-(4-carboxy-2-hydroxybenzylidene)amino-3-hydroxybenzoic acid [3]. This educt (0.100 g, 0.332 mmol) was further treated with (0.115 g, 0.166 mmol) [PtCl₂(C₁₅H₁₅O₂P)₂] salt precursor to isolate a tridentate O–N–O Pt(II) Schiff base complex for 24 h as an orange solid in good yield (75%). Upon growing crystals of this complex, ligand substitution of the imine resulted in a second mole of the propionic acid ligand coordinating to the metal. This resulted in simultaneous deprotonation of the propionic acid resulting in a bis coordination fashion.

Brown crystals suitable for single X-ray diffraction were obtained by slow evaporation from dimethylsulfoxide and methanol from a solution of the complex for 3 weeks at room temperature.

Experimental details

Crystal data was collected on a Bruker APEXII diffractometer with detector to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in approximately a 6° range with an exposure time of 10 s per frame. Structure solution was achieved by direct methods (program SHELX) within the XSEED interface and all non-hydrogen atoms from F-map. All hydrogen atoms were included at idealized positions and were allowed to ride on the parent atoms with relative isotropic displacement coefficients.

Comment

Phosphine ligands have a general formula PR₃ (where R = alkyl, halide, aryl, hydrogen etc.) [4]. These ligands play an important role in stabilizing many transition metal catalysts and can activate the metal centre while also assist in fine-tuning the selectivity of products in catalytic transformations. This is done by modifying the steric and electronic

environment around the phosphine by simply varying the substituents on the phosphorus atom [5, 6]. These ligands are well known for their versatility to perform various applications [7, 8]. Phosphine ligands can be coordinated to various transition metals (Pt, Pd, Rh, Ru etc.) for various applications such as hydroformylation, hydrogenation, Mizoroki-Heck and Suzuki cross-coupling reactions [9–13]. Our interests in phosphine ligands includes application of platinum complexes in catalytic as well as biological studies. Trettenbrein and co-workers reported the synthesis of an electron rich, highly stable new phosphanyl-carboxylate ligand and its coordination to Pt(II). These organometallic compounds with functionalised phosphanes have revealed a great in homogenous catalysis [14]. However, the synthesis procedure of this Pt-based phosphanyl-carboxylate ligand involves several steps. Our work, reports the synthesis and characterisation of bis (3-diphenylphosphinopropanoate)platinum(II), following a single-step process under ambient conditions. Single crystal X-ray diffraction showed that the title structure is best described in the space group C2/c. The central Pt(II) has a square planar coordination geometry which is found in d⁸ complexes reported in the literature [15, 16]. The crystal structure shows coordination of Pt metal to two oxygen atoms and two phosphorus atoms in a bis fashion with a pendant carboxylate group forming the oxygen donor ligands. The connectivity in the title compound together with the bond lengths and bond angles are in expected ranges. The Pt–O and Pt–P bond lengths are 2.0744 Å and 2.2242 Å, respectively which is similar to what has been reported in literature [17–20].

Acknowledgements: This work was supported by the South African National Research Foundation (Grant Numbers: 117989), UJ Centre for Synthesis and Catalysis and SASOL (under the Sasol University Collaboration Programme).

References

1. Bruker. ApexII. Bruker Axs Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sathyadevi, P.; Krishnamoorthy, P.; Butorac, R. R.; Cowley, A. H.; Bhuvanesh, N. S. P.; Dharmaraj, N.: Effect of substitution and planarity of the ligand on dna/bsa interaction, free radical scavenging and cytotoxicity of diamagnetic Ni(II) complexes: a systematic investigation. *Dalton Trans.* **40** (2011) 9690–9702.
4. Gharamaleki, J. A.; Akbari, F.; Karbalaee, A.; Ghiassi, K. B.; Olmstead, M. M.: Synthesis, characterization and crystal structure of a new schiff base ligand from a bis (thiazoline) template and hydrolytic cleavage of the imine bond induced by a Co(II) cation. *Open J. Inorg. Chem.* **6** (2016) 76–88.
5. Twigg, M. V.: Vol. 6: Substitution reactions of inert-metal complexes. In *Mechanisms of inorganic and organometallic*

- reaction. (Ed. M. V. Twigg), Springer, Boston (1989), pp. 129–151.
6. Mazuela, J.; Norrby, P. O.; Andersson, P. G.; Pàmies, O.; Diéguez, M.: Pyranoside phosphite–oxazoline ligands for the highly versatile and enantioselective Ir-catalyzed hydrogenation of minimally functionalized olefins. a combined theoretical and experimental study. *J. Am. Chem. Soc.* **133** (2011) 13634–13645.
 7. Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J.; García-Granda, S.; Rodríguez, M. A.: Ruthenium(II) and ruthenium(IV) complexes containing $\kappa^1\text{-P}$ -, $\kappa^2\text{-P,O}$ -, and $\kappa^3\text{-P,N,O}$ -iminophosphorane-phosphine ligands $\text{Ph}_2\text{PCH}_2\text{P}\{\text{NP}(\text{O})(\text{OR})_2\}\text{Ph}_2$ (R = Et, Ph): synthesis, reactivity, theoretical studies, and catalytic activity in transfer hydrogenation of cyclohexanone. *Inorg. Chem.* **42** (2003) 3293–3307.
 8. Fernández-Pérez, H.; Etayo, P.; Panossian, A.; Vidal-Ferran, A.: Phosphine–phosphinite and phosphine–phosphite ligands: preparation and applications in asymmetric catalysis. *Chem. Rev.* **111** (2011) 2119–2176.
 9. Matsinha, L. C.; Siangwata, S.; Makhubela, B. C. E.; Smith, G. S.: Aqueous biphasic hydroformylation of olefins: from classical phosphine-containing systems to emerging strategies based on water-soluble nonphosphine ligands. *Cat. Rev. Sci. Eng.* **61** (2019) 111–133.
 10. Govender, P.; Renfrew, A. K.; Clavel, C. M.; Dyson, P. J.; Smith, G. S.: Phosphorus dendrimers functionalised with nitrogen ligands, for catalysis and biology. *Dalton Trans.* **40** (2011) 1158–1167.
 11. Amenuvor, G.; Makhubela, B. C. E.; Dhakwa, J.: Homogeneous polymetallic ruthenium(II) zinc(II) complexes: robust catalysts for the efficient hydrogenation of levulinic acid to γ -valerolactone. *Catal. Sci. Technol.* **8** (2018) 2370–2380.
 12. Liu, Y.; Zhao, J.; Liu, H.; Fu, H.; Zheng, X.; Yuan, M.; Li, R.; Chen, H.: Homogeneous hydroformylation of long chain alkenes catalyzed by water phosphine rhodium complex in methanol and efficient catalyst cycling. *RSC Adv.* **9** (2019) 7382–7387.
 13. Stringer, T.; Hendricks, D. T.; Guzgay, H.; Smith, G. S.: Synthesis and characterization of multimeric salicylaldehyde thiosemicarbazones and their Pd(II) and Pt(II) complexes. *Polyhedron* **31** (2012) 486–493.
 14. Maulana, I.; Peter, L.; Hey-Hawkins, E.: Synthesis and reactivity of ortho-carbaborane-containing chiral aminohalophosphines. *Inorg. Chem.* **11** (2009) 8638–8645.
 15. Alsalahi, W.; Trzeciak, A. M.: Hydroformylation of unsaturated esters and 2,3-dihydrofuran under solventless conditions at room temperature catalysed by rhodium *N*-pyrrolyl phosphine catalysts. *New J. Chem.* **43** (2019) 16990–16999.
 16. Trettenbrein, B.; Fessler, M.; Ruggenthaler, M.; Haringer, S.; Oberhuber, D.; Czermak, G.; Brüggeller, P.; Oberhauser, W.: First microwave-assisted synthesis of an electron-rich phosphine and its coordination chemistry with platinum(II) and palladium(II). *Inorg. Chim. Acta* **375** (2011) 324–328.
 17. Kořenková, M.; Hejda, M.; Štěpnička, P.; Uhlík, F.; Jambor, R.; Růžička, A.; Dost'ál, L.: Synthesis and non-conventional structure of square-planar Pd(II) and Pt(II) complexes with an *N,C,N*-chelated stibinidene ligand. *Dalton Trans.* **47** (2018) 5812–5822.
 18. Chiririwa, H.; Moss, J. R.; Hendricks, D.; Smith, G. S.; Meijboom, R.: Synthesis, characterisation and *in vitro* evaluation of platinum(II) and gold(I) iminophosphine complexes for anticancer activity. *Polyhedron* **49** (2013) 29–35.
 19. Maulana, I.; Lonnecke, P.; Hey-Hawkins, E.: Platinum(II) and palladium(II) complexes of chiral P-Cl functionalized bis-phosphino ortho-carbaboranes. *Inorg. Chem.* **48** (2009) 8638–8645.
 20. Xu, X.; Kua, J.; Periana, R. A.; Goddard, W. A.: Structure, bonding, and stability of a catalytical platinum(II) catalyst: a computational study. *Organometallics* **22** (2003) 2057–2068.