

4-Chloro-5-methyl-3-diphenylphosphino-1-phenyl-1,2,3,6-tetrahydrophosphinine as a bidentate P-ligand in a *cis* chelate Pt(II) complex

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Abstract

Double deoxygenation of a 3-phosphinoxido-1,2,3,6-tetrahydrophosphine oxide (**2**) led to bisphosphine **3–2** with an inverted ring P atom. The reaction of bidentate P-ligand **3–2** with dichlorodibenzonitrilo platinum(II) yielded the mixture of a novel *cis* chelate complex (**7** = PtCl₂(**3–2**)) and a *cis* bis(3-diphenylphosphino-1,2,3,6-tetrahydrophosphinyl) complex (**8** = PtCl₂(η^1 -**5**)₂) containing two units of monodentate P-ligand **5**.

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1. Introduction

The phosphines are important ligands in transition metal complexes that can be catalysts in a great variety of homogeneous catalytic reactions among them hydrogenation and hydroformylation [1]. Especially the chiral homo- and heterobidentate P-ligands, such as BINAP, DIOP, DIPAMP and BINAPHOS are of practical interest [2]. In this paper, the preparation and the coordination properties of a novel bidentate P-ligand containing one of the phosphine moieties in an unsaturated six-membered hetero ring, while the other one as an exocyclic diphenylphosphino substituent in position 3 is described.

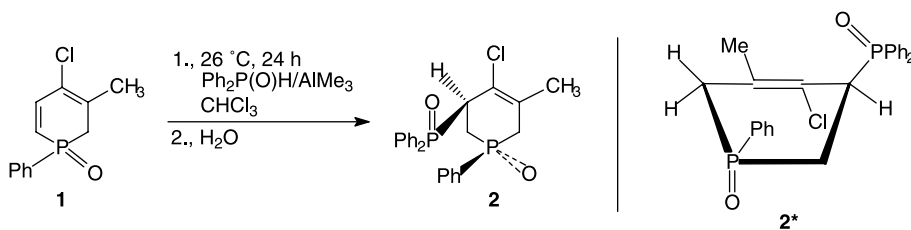
The parent bis(phosphine oxide), 3-diphenylphosphinoxido-1-phenyl-1,2,3,6-tetrahydrophosphinine oxide (**2**) was obtained by the diastereoselective Michael addition of diphenylphosphine oxide at the α,β -double bond of 1,2-dihydrophosphinine oxide (**1**) [3], as it was described (Scheme 1) [4].

The preferred conformer, a *twist-boat* containing the Ph₂P(O) moiety and the oxygen atom of the ring P=O in the *trans* disposition (**2***) was established by DFT calculations. A novel intramolecular H-bonding between the oxygen atom of the Ph₂P(O) moiety and the suitable hydrogen atom of the C(6)H₂ unit was found to stabilise the *twist-boat* form [5].

The bis(phosphine oxide) (**2**) was deoxygenated by a standard procedure applying trichlorosilane–pyridine in boiling benzene [6] to give a diphosphine (**3**). According to DFT ab initio calculations [7], the isomer with inverted P₁-atom (**3–2**) containing the Ph₂P group and the

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Scheme 1.

lone electron pair of the ring phosphorus in the *cis* position is more favourable than the diphosphine with preserved P_1 -configuration (**3-1**). Twist-boat conformer **3-2*** is by 0.58 kcal/mol more favourable than the most stable conformer of **3-1** (Scheme 2).

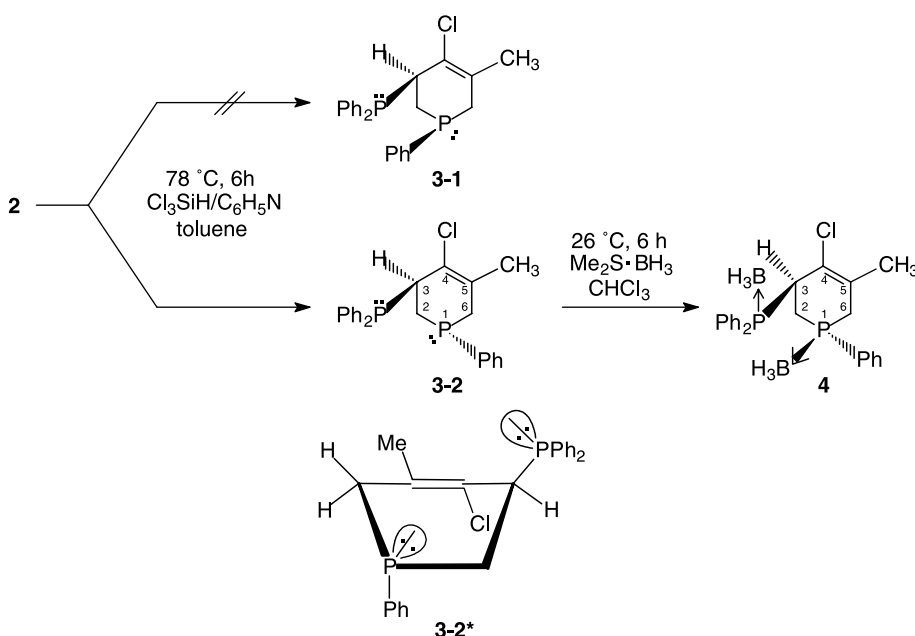
Due to the high inversion barrier of 35.4 kcal/mol obtained by DFT ab initio calculations for the **3-1** \rightarrow **3-2** transformation, that is in accord with the usual activation enthalpy of 29–36 kcal/mol for phosphines [8], it had to be assumed that the phosphine with inverted P-configuration (**3-2**) was formed directly on deoxygenation. Although the silane reductions are known to proceed mostly with retention of configuration [9], inversion of the P-pyramid was reported in a few cases, especially in the sphere of P-heterocycles [10]. Silane reductions carried out in the presence of tertiary amines were also observed to result in inversion of the P-center in certain cases [11]. A possible mechanism starting with the protonation of the $\text{P}=\text{O}$ moiety by $\text{R}_3\text{HN}^+ \text{SiCl}_3^-$ followed by a $\text{Cl}_3\text{Si}^-\text{HO}^-$ exchange, and finally by the loss of Cl_3SiOH is shown in Scheme 3.

The diphosphine (**3-2**) was stored as its diborane complex (**4**) from which it could be regenerated by treatment with diethylamine at 78°C [12] (Scheme 2).

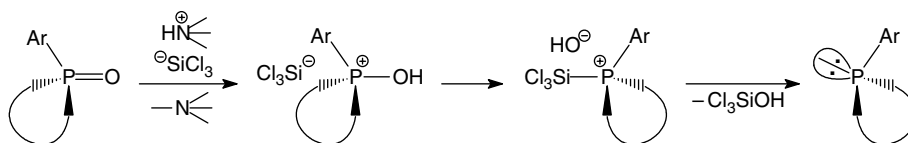
The exocyclic P-moiety of the diphosphine (**3-2**), however, extremely sensitive towards oxidation. After a several minutes exposure to air, **3-2** was converted to hemioxide **5** ($\delta_{\text{P}} -32.1$ and 35.6 , $(\text{M} + \text{H})^+ = 425$) that was identified as the corresponding monoborane complex (**6**) (Scheme 4).

It was assumed that the stereochemistry of the starting phosphine (**3-2**) was preserved in phosphine-boranes **4** and **6**.

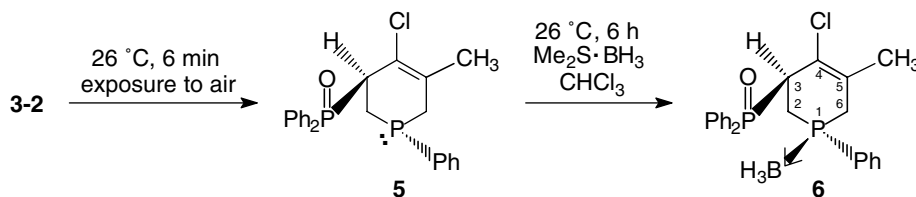
Diphosphine **3-2** was reacted with one molar equivalent of dichlorodibenzonitrilo platinum(II) at benzene reflux. ^{31}P NMR analysis of the crystal fractions, obtained by fractional crystallisation on cooling, suggested that two complexes were formed, *cis* chelate complex **7** represented as *cis*- $\text{PtCl}_2(\text{3-2})$ and *cis* bis(3-diphenylphosphino-1,2,3,6-tetrahydrophosphinyl) platinum complex **8** formulated as *cis*- $\text{PtCl}_2(\eta^1\text{-5})_2$. In the latter complex, hemioxide **5** coordinates as a monodentate ligand. The ratio of **7** and **8** was ca. 3:7 (Scheme 5).



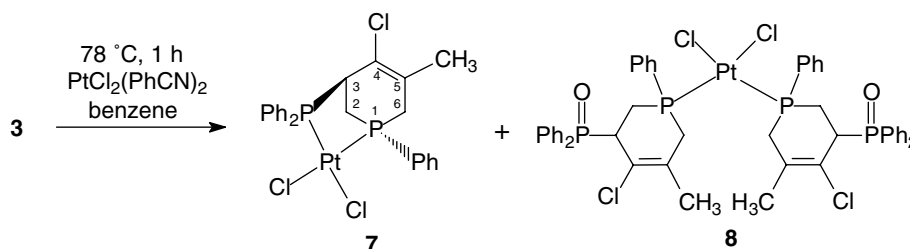
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

cis Chelate complex **7** can be regarded as a proof for the stereostructure of diphosphine **3–2**, containing the two P lone pairs on the same side. Bis(tetrahydrophosphinyl) monodentate complex **8** was the major component containing the 3-substituent in the phosphine oxide form. The ring phosphine unit seems to be more reactive towards the platinum(II) center than the diphenylphosphine moiety, which is, in turn, highly sensitive towards oxidation. The phosphine oxide functions in the major component were formed by oxidation during the work-up procedure.

Complexes **7** and **8** were purified by repeated recrystallisations to afford the products in an almost pure form, whose structures were confirmed by ^{31}P NMR spectral data. The ^{31}P NMR spectrum of *cis* chelate **7** contained doublets at 17.7 and at 50.3 ($J_{\text{P-P}} = 6.7$ Hz) justifying that the two phosphorus atoms are bound to the same metal center. Moreover, both doublets were accompanied by satellites due to the $^{195}\text{Pt}-^{31}\text{P}$ coupling ($J_{\text{Pt-P}}$ coupling constants were 3496 and 3681 Hz, respectively). At the same time, the ^{31}P NMR spectrum of complex **8** contained singlets at $\delta_{\text{P}} -8.2$ and at 42.3, and only the first one was associated with a $J_{\text{Pt-P}}$ satellite of 3566 Hz. In both cases (**7** and **8**), the *cis* relationship of the P-moieties was proved by the $J_{\text{Pt-P}}$ couplings of diagnostic value (ca. 3600 Hz) referring to the *trans* position of the P-unit and the chloro ligand [13].

The assignment of the ^1H and ^{13}C NMR of **7** was carried out by using various 2D techniques including COSY and HSQC. The methine proton adjacent to the exocyclic PPh_2 group shows a clear $J_{\text{P-H}} = 48$ Hz coupling to P. Interestingly, one of the two methylene groups (CH_2 adjacent to CH) shows a large separation of the two protons (2.03 and 2.42 ppm) and only one of them gives a $^{31}\text{P}-^1\text{H}$ coupling of similar magnitude ($J_{\text{P-H}} = 55$ Hz). The other methylene group (bound to the olefinic moiety) shows an AB pattern centered at 3.5 ppm due to the close chemical shifts of the two geminal protons.

Stereostructure and geometrical data of the *cis* chelate complex (**7**) was determined by DFT ab initio calculations [7]. It can be seen from Fig. 1 that the tetrahydrophosphinine ring adopts a *half-chair* conformation in complex **7**. It means that the complexation also affects the conformation of the six-membered hetero ring, i.e., the *twist-boat* form is converted to a *half-chair*. The change in the conformation may be the consequence of the steric hindrance due to the coordinating platinum.

It can be concluded that the double deoxygenation of 3-diphenylphosphinoxido-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-oxide (**2**) made available a novel bidentate P-ligand (**3–2**) that was useful in the preparation of a *cis* chelate platinum(II) complex (**7**). The other

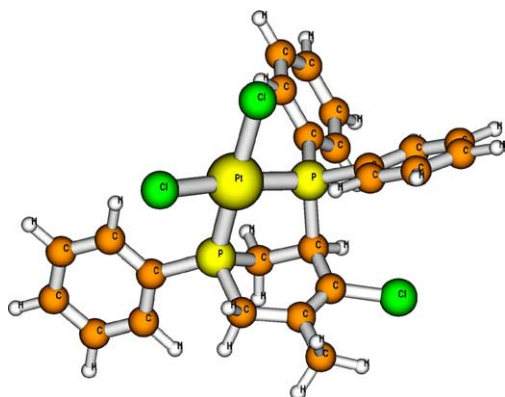


Fig. 1. Perspective view of *cis* chelate complex **7** with bond lengths (Å), bond angles (°) and torsion angles (°) obtained by B3LYP calculations. P(1)–C(2) 1.844, C(2)–C(3) 1.542, C(3)–C(4) 1.521, C(4)–C(5) 1.352, C(5)–C(6) 1.527, C(6)–P(1) 1.840, P(1)–C(1') 1.823, C(3)–PPh₂ 1.902, P(1)–Pt 2.264, Pt–PPh₂ 2.277, P(1)–C(2)–C(3) 105.3, C(2)–C(3)–C(4) 111.1, C(3)–C(4)–C(5) 127.3, C(4)–C(5)–C(6) 123.5, C(5)–C(6)–P(1) 114.0, C(6)–P(1)–C(2) 98.7, C(2)–C(3)–PPh₂ 106.0, C(4)–C(3)–PPh₂ 112.6, C(2)–P(1)–C(1') 106.0, C(6)–P(1)–C(1') 108.3, P(1)–C(2)–C(3)–C(4) 62.7, P(1)–C(6)–C(5)–C(4) –10.6, P(1)–C(2)–C(3)–PPh₂ –59.9, C(5)–C(4)–C(3)–C(2) –29.4, C(5)–C(6)–P–C(1') 150.8, P(1)–C(6)–C(5)–CH₃ 169.7.

product of the complex formation was a bis(3-diphenylphosphino-1,2,3,6-tetrahydrophosphinyl) platinum(II) complex (**8**) containing hemioxide **5** as a monodentate P-ligand.

2. Experimental

³¹P, ¹³C and ¹H NMR spectra were recorded in CDCl₃ on a Varian Inova 400 spectrometer at 161.89, 100.62 and 400.13 MHz, respectively. Chemical shifts are given relative to CHCl₃ (7.26 and 77.00 ppm for ¹H and ¹³C) or relative to H₃PO₄ (³¹P). The couplings are listed in Hertz. The starting 3-phosphinoxido-tetrahydrophosphinine oxide derivative (**2**) was synthesized as described earlier [4]. PtCl₂(PhCN)₂ was prepared by a known procedure [14].

2.1. Deoxygenation of the bis(phosphine oxide) precursor (**2**) – preparation of diborane-diphosphine **4**

0.09 ml (0.9 mmol) of trichlorosilane and 0.20 ml (2.5 mmol) of pyridine were added to 0.18 g (0.41 mmol) of **2** [3] in 25 ml of degassed toluene and the mixture was stirred at the boiling point for 6 h under nitrogen. The precipitated silane was removed by filtration under nitrogen and the filtrate was evaporated to give the diphosphine (**3**) quantitatively ($\delta_{\text{P}}(\text{CDCl}_3)$ –32.1 and –3.1, (M + H)⁺ = 409). The diphosphine (**3**) that was highly sensitive towards oxygen was identified as its bis(phosphine borane) complex (**4**).

0.16 g (0.40 mmol) of diphosphine in 25 ml of degassed dichloromethane was treated with 0.47 ml of 2M dimethylsulfide borane in THF solution (0.93 mmol) at room temperature. After a 4 h reaction time, 0.50 ml of water was added and the mixture stirred for 10 min. The precipitated material was removed by filtration and the organic phase was dried (Na₂SO₄). Concentration in vacuo left 0.17 g (98%) of bis(phosphine borane) **4**. $\delta_{\text{P}}(\text{CDCl}_3)$ 7.7 (broad signal) and 30.8 (broad signal), $\delta_{\text{C}}(\text{CDCl}_3)$ 22.8 (¹J = 34.9, C(6)), 23.7 (C(5)–CH₃), 28.8 (¹J = 30.7, C(2)), 44.4 (²J = 38.9, C(3)), 124.5 (¹J = 5.7, ²J = 12.2, C(5)), 128.5 (¹J = 12.1, C(3''))^a, 128.9 (²J = 9.5, C(3''))^a, 129.2 (²J = 10.0, C(3''))^a, 130.4 (C(4)), 131.3 (²J = 9.6, C(2''))^a, 131.4 (²J = 8.7, C(2''))^a, 131.7 (¹J = 8.9, C(2''))^a, 132.3 (²J = 2.2, C(4''))^b, 132.5 (²J = 2.9, C(4''))^b, ^{a,b}tentative assignment; (M – H)⁺_{found} = 435.1468, C₂₄H₂₈B₂ClP₂ requires 435.1541 for the ¹¹B and ³⁵Cl isotopes.

On exposure to air, **3** was rapidly converted to hemioxide **5** that was identified as the corresponding phosphine borane (**6**) $\delta_{\text{P}}(\text{CDCl}_3)$ 10.9 (broad signal) and 34.9; $\delta_{\text{C}}(\text{CDCl}_3)$ 22.0 (¹J = 34.8, C(6)), 24.2 (C(5)–CH₃), 29.9 (¹J = 29.9, ²J = 2.4, C(2)), 43.9 (¹J = 7.8, ²J = 67.0, C(3)), 123.1 (¹J = 8.5, ²J = 13.5, C(5)), 128.6 (¹J = 11.9, C(3''))^a, 129.0 (²J = 9.7, C(3''))^a, 129.3 (²J = 9.8, C(3''))^a, C(4') overlapped, 130.3 (¹J = 1.7, C(4)), 131.4 (²J = 7.0, C(2''))^a, 131.5 (²J = 6.5, C(2''))^a, 131.8 (¹J = 9.2, C(2''))^a, 132.4 (²J = 2.8, C(4''))^b, 132.6 (²J = 2.8, C(4''))^b, ^{a,b}tentative assignment; (M – H)⁺_{found} = 437.1077, C₂₄H₂₅BClOP₂ requires 437.1162 for the ¹¹B and ³⁵Cl isotopes.

2.2. Complexation of the bisphosphine (**3**) by PtCl₂(PhCN)₂

To 0.40 mmol of diphosphine **3** in 40 ml of benzene 0.20 g (0.42 mmol) of dichlorodibenzonitrilo platinum(II) was added and the mixture was stirred at reflux for 1 h under nitrogen. Fractional crystallisation from the benzene solution (repeated with both fractions obtained in the first run) furnished **7** as pale yellow powder-like crystal in pure form and **8** as an off-white powder-like material in ca. 85% purity (containing **7** as an impurity).

Complex **7**: $\delta_{\text{P}}(\text{CDCl}_3)$ 17.7 ($J_{\text{Pt-P}} = 3496$, $J_{\text{P-P}} = 6.7$, P(1)), 50.3 ($J_{\text{Pt-P}} = 3681$, $J_{\text{P-P}} = 6.7$, C(3)–P); $\delta_{\text{C}}(\text{CDCl}_3)$ 23.2 (CH₃), 30.5 (C(6)), 31.1 (C(2)), 45.2 (C(3)), 124.0 (C(5)), 130.3 (C(4)), $\delta_{\text{H}}(\text{CDCl}_3)$ 1.92 (d, $J_{\text{H-H}} = 4.0$, 3H, CH₃), 2.03 (m, 1H, C(2)H_aH_b), 2.42 (ddd, $J_{\text{H-H}} = 11.4$, $J_{\text{H-H}} = 11.0$, $J_{\text{P-H}} = 55$, 1H, C(2)H_aH_b), 3.47 (d, $J_{\text{H-H}} = 19$, 1H, C(6)H_aH_b), 3.52 (d, $J_{\text{H-H}} = 19$, 1H, C(6)H_aH_b), 3.78 (dd, $J_{\text{H-H}} = 9$, $J_{\text{P-H}} = 48$, 1H, C(3)H), 7.2–7.8 (m, 15H, Ph); Anal. calc. for C₂₄H₂₃P₂Cl₃Pt (674.83): C, 42.72; H, 3.44; Found: C, 43.05; H, 3.73%.

Complex 8: $\delta_{\text{P}}(\text{CDCl}_3) -8.2$ ($J_{\text{Pt-P}} = 3566$, P(1)), 42.3 (C(3)-P); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.35 (d, $J = 3.7$, 3H, CH₃), 2.50 (m, 2H, CH₂), 3.05 (m, 1H, CH_aH_b), 3.2 (m, 1H, CH_aH_b), 3.7 (m, 1H, C(3)H), 7.2–7.9 (m, 15H, Ph).

2.3. Quantum chemical calculations

Quantum chemical calculations were carried out using the GAUSSIAN 98 program package [7]. Geometries of all conformers of **3** were optimised at the B3LYP/3-21G* level of theory. Energies were further refined with the help of B3LYP/6-31 + G* single point calculations. In case of **7** the determination of geometries and energies were carried out using the B3LYP functional with the LANL2DZ ECP basis set augmented with polarisation functions.

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