

## Structural Characterization of *N,N*-Bis(diphenylphosphanyl)propylamine

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*Dedicated to Professor Joachim Heinicke on the occasion of his 65<sup>th</sup> birthday*

The synthesis and structural characterization of the *N*-substituted bis(diphenylphosphanyl)amine  $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$  ( $\text{R} = n$ -propyl, **1**) is reported. Single crystals of **1** grown from dichloromethane/acetonitrile have been analyzed by X-ray crystallography. The crystallographic study revealed that the diphenylphosphanyl groups in **1** are staggered relative to the PNP backbone as observed for other closely related molecules.

**Key words:** Phosphorus, Organophosphorus Ligands, Diphosphanes, *N*-Substituted Bis(phosphanyl)amines, X-Ray Diffraction

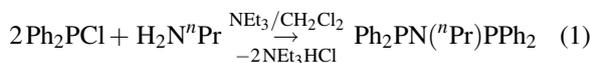
### Introduction

Recently we reported some new coordinatively unsaturated diruthenium complexes of the general formula  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-P}^j\text{P})]$  ( $\text{P}^i\text{P} =$  diphosphanes and *N*-substituted bis(diphenylphosphanyl)amines) [1]. These compounds represent good candidates for the synthesis of some new complexes bearing *trans*-hyponitrito ligands [2]. During these studies we used among others the *N*-substituted bis(diphenylphosphanyl)amine  $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$  ( $\text{R} = n$ -propyl, **1**) as the bridging ligand in the diruthenium metal core. The syntheses of amino compounds of the latter type have been described in the literature [3–6], however there was no crystal structure report of the title compound till now. In this paper we describe some modifications in the synthesis of compound **1** as well as the result of its characterization by X-ray crystallography.

### Results and Discussion

We found that the reaction of two equivalents of chlorodiphenylphosphane with one equivalent of the

corresponding amine in the presence of the base triethylamine as the hydrogen chloride acceptor in one step, *cf. e. g.* ref. [6], resulted in our hands often in a mixture of compounds. To realize an efficient synthesis according to Eq. 1, we divided the synthetic procedure in two steps.



At first equimolar amounts of the amine and the chlorophosphane were reacted in dichloromethane at room temperature. After about 30 min a second equivalent of the chlorophosphane was added. This resulted in a clean synthesis of the desired *N*-substituted bis(diphenylphosphanyl)amine without side products. After workup, compound **1** was isolated as colorless crystals in yields of about 63%. This procedure was also used in the preparation of some other *N,N*-bis(diphenylphosphanyl)amines affording these compounds in similar yields [1]. The title compound **1** was characterized by elemental analysis, NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ; see Experimental Section), and single-crystal X-ray diffraction.

Crystals of **1** belong to the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. A selected view of the molecule is shown in Fig. 1, appropriate bond lengths and angles are given in the caption. The molecular structure of **1** is comparable to those of the reported ones of the type  $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$  ( $\text{R} =$  benzyl [6],  $\text{R} = 1,2$ -dimethylpropyl [7]). As found for the latter compounds, the diphenylphosphanyl groups are staggered relative to the PNP backbone. The angles around the central nitrogen atom (see caption of Fig. 1) are comparable *e. g.* with those in *N,N*-bis(diphenylphosphanyl)benzylamine:  $\text{P1-N1-P2}$ , 120.6(1),  $\text{P2-N1-C25}$ , 120.8(2) and  $\text{P1-N1-C25}$ , 113.3(2) $^\circ$  [6]. These structural parameters indicate that the phosphorus atoms exhibit a distorted trigonal-pyramidal geometry, whereas the nitrogen atom in **1** is surrounded in a nearly trigonal-planar array by the carbon and the two phosphorus atoms.

In the literature, the *N,N*-bis(diphenylphosphanyl)propylamine unit was characterized by X-ray crystallography as the ligand in the complex  $[\text{ReBr}(\text{CO})_3\{\text{Ph}_2\text{PN}^i(\text{Pr})\text{PPh}_2\}]$  [9]. The bonding characteristics of the latter agree well with the corresponding ones of compound **1**. Thus in the rhenium

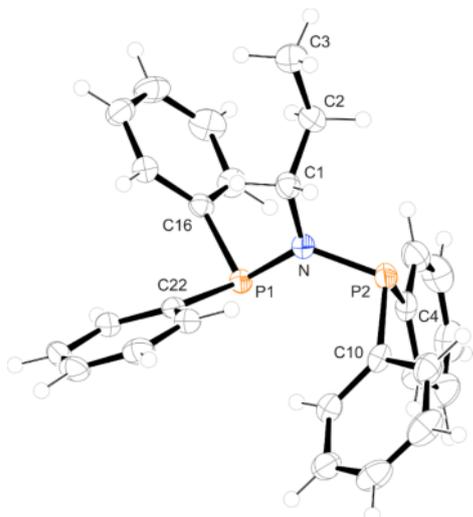


Fig. 1 (color online). Molecular structure of **1** in the crystal. Displacement ellipsoids are at the 50% probability level, H atoms as spheres with arbitrary radii. Selected bond lengths (Å) and angles (deg): N–P1 1.705(1), N–P2 1.720(1), N–C1 1.486(2); P1–C16 1.838(2), P1–C22 1.835(2), P2–C4 1.833(2), P2–C10 1.834(2); P1–N–P2 124.8(1), P1–N–C1 120.6(1), P2–N–C1 114.5(1). The largest deviation from the least-square plane P1–P2–N–C1 [8] was found to be 0.008(1) Å for N.

complex the following observed bonding characteristics are comparable to the corresponding ones in the free ligand **1** (compare caption in Fig. 1): N1–C4 1.478(9), N1–P1 1.713(4), N1–P2 1.702(5), P1–C11 1.824(5), P1–C21 1.804(5), P2–C31 1.820(5), P2–C41 1.828(5) Å. Because of the chelation of the rhenium atom, the bite angle P1–N1–P2 103.9(2)° is remarkably smaller than in the free ligand, whereas the angles P1–N1–C4 and P2–N1–C4 were found to be 122.9(4) and 130.1(4)°, respectively. It should be noted that the P–N–P angle is only little influenced by coordination as a bridging ligand in a bidentate fashion across a metal–metal bond. The corresponding P–N–P angle in [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-P'Bu<sub>2</sub>){μ-Ph<sub>2</sub>PN(<sup>m</sup>Pr)PPh<sub>2</sub>}] was found to be 119.4(1)° [1] and lies therefore closer to that of the free ligand **1**.

## Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under nitrogen. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded

Table 1. Crystal data and structure refinement details for **1**.

Formula	C <sub>27</sub> H <sub>27</sub> NP <sub>2</sub>
<i>M</i> <sub>r</sub>	427.44
Crystal size, mm <sup>3</sup>	0.34 × 0.29 × 0.26
Temperature, K	173(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	13.8136(11)
<i>b</i> , Å	8.3944(4)
<i>c</i> , Å	20.3473(16)
β, deg	90.145(6)
<i>V</i> , Å <sup>3</sup>	2359.4(3)
<i>Z</i>	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.20
μ (Mo <i>K</i> <sub>α</sub> ), mm <sup>-1</sup>	0.2
<i>F</i> (000), e	904
θ range for data collection, deg	4.26–26.29
<i>hkl</i> range	–17 ≤ <i>h</i> ≤ 16, –7 ≤ <i>k</i> ≤ 10, –25 ≤ <i>l</i> ≤ 23
Reflections collected/ independent/ <i>R</i> <sub>int</sub>	10 695/4779/0.0223
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0342/0.0861
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0513/0.0903
<i>S</i>	1.034
Δρ <sub>fin</sub> (max/min), e Å <sup>-3</sup>	0.32/–0.24

using Jeol Eclipse 270 and 400 instruments operating at 270/400 MHz (<sup>1</sup>H), 69/100 MHz (<sup>13</sup>C) and 109/162 MHz (<sup>31</sup>P), respectively. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

## Synthesis of bis(diphenylphosphanyl)propylamine (**1**)

To a solution of *n*-propylamine (0.90 mL, 11 mmol) in dichloromethane (30 mL), chlorodiphenylphosphane (2.07 mL, 11.2 mmol) and triethylamine (15 mL) were added at r. t. with stirring. After 30 min chlorodiphenylphosphane (2.07 mL, 11.2 mmol) was added again, and the mixture was stirred overnight. The solvent was evaporated to dryness under reduced pressure, and the remaining residue was dissolved in dichloromethane (30 mL). The organic layer was washed three times with a concentrated solution of sodium hydroxide and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue recrystallized from dichloromethane/acetonitrile (1 : 2) at 4 °C. The colorless crystals were filtered off, washed three times with 10-mL portions of cold pentane and dried *in vacuo*. Yield 3.03 g (63%). – <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 63.1 (s, PPh<sub>2</sub>). – <sup>1</sup>H NMR (270 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.63 – 6.96 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 3.17 (m, 2H, NCH<sub>2</sub>), 1.04 (m, 2H, –CH<sub>2</sub>CH<sub>3</sub>), 0.47 (t, 3H,

$^3J_{\text{HH}} = 7.48$  Hz,  $-\text{CH}_2\text{CH}_3$ ).  $^{-13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 139.9$  (t,  $J_{\text{PC}} = 6.15$  Hz, *ipso*- $\text{C}_6\text{H}_5$ ), 132.7 (t,  $^2J_{\text{PC}} = 10.8$  Hz, *m*- $\text{C}_6\text{H}_5$ ), 128.7 (*p*- $\text{C}_6\text{H}_5$ ), 128.0 (t,  $^3J_{\text{PC}} = 3.1$  Hz, *o*- $\text{C}_6\text{H}_5$ ), 54.8 (t,  $^2J_{\text{PC}} = 10.0$  Hz,  $\text{NCH}_2$ ), 24.7 ( $\text{CH}_2$ ), 10.7 ( $\text{CH}_3$ ).  $-\text{C}_{27}\text{H}_{27}\text{NP}_2$  (427.47): calcd. C 75.87, H 6.37, N 3.28; found C 75.71, H 6.25, N 3.45.

#### X-Ray crystal structure determination

Crystals of **1** for the X-ray structural analysis were obtained from dichloromethane/acetonitrile at 4 °C overnight. A suitable crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on an Oxford XCalibur diffractometer using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by Direct Methods (SHELXS-97) [10] and refined by full-matrix least-squares calculations on  $F^2$  (SHELXL-97) [11]. Anisotropic

displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **1** are summarized in Table 1.

CCDC 872228 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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