

Short Note

N-(diisopropylphosphanyl)benzamide

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Abstract: *N*-(diisopropylphosphanyl)benzamide, PhC(O)NHPiPr₂, has been synthesized in good yield following two alternative procedures that employ benzamide as the starting material. The first one is a two-step preparation, in which *N*-(trimethylsilyl)benzamide is reacted with PiPr₂Cl, to give the title compound in good yield, whereas the second one is a straightforward synthesis which converts benzamide into *N*-(diisopropylphosphanyl)benzamide by reaction with PiPr₂Cl in the presence of *N,N*-dimethylpyridin-4-amine (DMAP) and triethylamine. NMR spectroscopy and X-ray diffraction analyses have been performed to characterize the new compound and elucidate its molecular structure in the solid state. *N*-(diisopropylphosphanyl)benzamide adds to the limited family of amido-substituted phosphines, RC(O)NHPR'₂, which can be classified as bidentate hybrid P,O-ligands, both in their neutral and anionic forms, the latter achievable by deprotonation of the NH group.

Keywords: P ligands; P(III) compounds; sterically demanding ligands; hemilabile ligands.

1. Introduction

Bidentate hybrid ligands usually combine donor atoms with intrinsically different properties, which can be rationalized, in most cases, in terms of the well-known hard/soft classification proposed by Pearson in the early 1960s [1]. In particular, P,O donor ligands based on P(III) functionalities and O-containing organic groups, such as ketones, ethers, carboxylates, or amides, are representative examples of hemilabile ligands [2], which is easily recognizable when considering, for instance, the type of bonding, and consequent fluxional behavior and reactivity that they are expected to establish with soft metal centers. The interest of these of systems in transition metal catalyzed processes is evident [3,4].

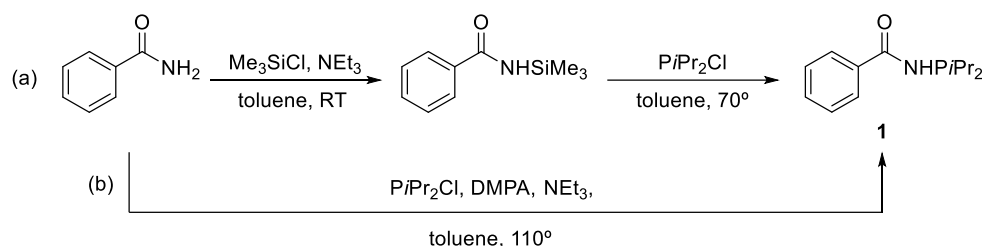
Besides perfectly fitting into the definition of hemilabile hybrid ligand [5], amido-substituted phosphines, RC(O)NHPR'₂, can straightforwardly be converted into the corresponding monoanions by selective deprotonation of the C(O)NH group, thus enhancing their versatility in coordination chemistry along with the tendency to act as chelating ligands. Over the last decades, only a few examples of amido-substituted P(III) ligands, generated from acetamide [6], picolinamide [7], benzamide and nicotinamide [8], have been described and used to prepare several transition metal complexes [6-16].

Herein, we report on the synthesis and spectroscopic and structural characterization of the sterically demanding *N*-(diisopropylphosphanyl)benzamide, PhC(O)NHPiPr₂, which incorporates to the class of hemilabile P,O-ligands derived from organic amides.

2. Results and Discussion

Inspired by the reaction strategy reported by Braunstein for the preparation of acetamide-substituted P,O ligands [6], benzamide was firstly converted into *N*-trimethylsilylbenzamide, which was subsequently reacted with PiPr₂Cl in toluene at 70

°C to obtain the title compound, **1**, as an air-sensitive colorless material in a *ca.* 80% yield (Scheme 1, a). In order to optimize the synthesis of PhC(O)NHP*i*Pr₂ circumventing the first step of the aforementioned procedure, benzamide was directly treated with an equimolar amount of P*i*Pr₂Cl in refluxing toluene in the presence of DMPA and NEt₃ (Scheme 1, b) [8]. Although the target compound was actually obtained, the low reaction yield (less than 40%) clearly makes this alternative procedure (b) less convenient than the two-step synthesis that involves the formation of *N*-trimethylsilylbenzamide (a).



Scheme 1. Two alternative syntheses of *N*-(diisopropylphosphanyl)benzamide (**1**).

PhC(O)NHP*i*Pr₂ was characterized by NMR spectroscopy in solution (CDCl₃), with corresponding informative data resumed as follows: *i*) the ³¹P{¹H} NMR spectrum consists of a singlet at 48.2 ppm; *ii*) in the ¹H NMR spectrum the isopropyl groups give rise to a broad signal at *ca.* 2.0 ppm assigned to the methyne protons and a multiplet in the range 1.2–1.0 ppm due to the diastereotopic methyl groups; *iii*) the NH proton resonates as a broad singlet at *ca.* 6.0 ppm; *iv*) in the ¹³C{¹H} NMR spectrum the CH₃ protons generate two well-defined doublets at 18.8 and 17.9 ppm with ²J_{CP} of 13 and 21 Hz, respectively. In order to provide additional spectroscopic information, the IR spectrum of **1** was recorded and two diagnostic absorptions due to the stretching vibrations of the N–H and C=O bonds were found at 3288 and 1651 cm^{−1}, respectively.

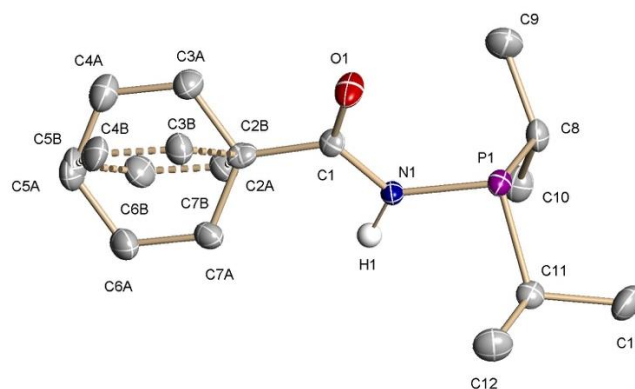


Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at the 30% probability level and showing the positional disorder of the phenyl group at two refined extreme positions, both of them with coefficients of 0.5. Hydrogen atoms, except H1, were omitted for clarity. Selected bond distances (Å) and angles (°): C1–O1 1.231(6), C1–N1 1.363(6), P1–N1 1.735(3), P1–C8 1.851(5), P1–C11 1.829(5); O1–C1–N1 122.3(5), C1–N1–P1 122.4(3), N1–P1–C8 100.1(2), N1–P1–C11 98.6(2), C8–P1–P1 102.8(2).

The molecular structure of **1** in the solid state was ascertained by X-ray diffraction analyses on suitable single crystals, which were grown from toluene solutions by slow evaporation of the solvent at room temperature. Figure 1 shows a representation of a single molecule of compound **1** together with selected bond distances and angles, whereas views of the corresponding packing diagrams are provided in Figure 2. Similarly to what observed for the related phosphanylamide CH₃C(O)NHPPH₂ [6], the P1, N1,

C1, O1, C2 atoms are essentially coplanar, with the P lone pair pointing towards the oxygen atom with a deviation of approximately 15° from the plane. This conformation is expected to enthalpically favor the P,O chelating binding mode in metal complexes. As shown in Figure 2, intermolecular hydrogen bonds involving the amide groups [$\text{N}\cdots\text{O}$ 3.025(5) Å, $\text{NH}\cdots\text{O}$ 2.10(3)] are responsible for the chain disposition of the molecules of PhC(O)NHPiPr_2 in the lattice.

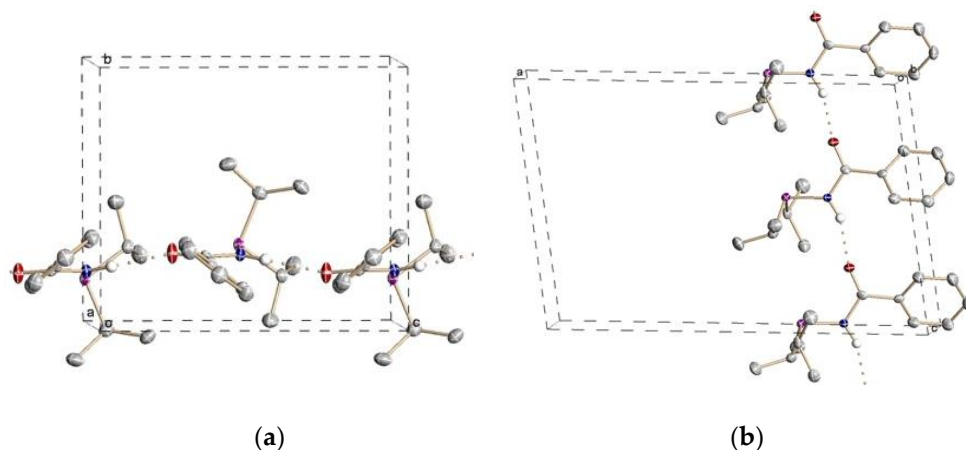


Figure 2. Partial packing diagrams for 1: (a) view along the crystallographic *a*-axis; (b) view along the crystallographic *b*-axis. Hydrogen bonds are represented as dotted lines connecting N—H and C=O fragments.

4. Materials and Methods

All manipulations were carried out using standard Schlenk and glove-box techniques, under an atmosphere of high-purity nitrogen. Solvents were rigorously dried and degassed before use. *N*-(trimethylsilyl)benzamide was prepared by a modified version of a previously reported procedure [18]. Other chemicals were purchased from Sigma-Aldrich and used as received. NMR spectra were recorded on a Bruker DRX-400 spectrometer. Solvent peaks were used as the internal reference for ^1H and ^{13}C spectra, whereas ^{31}P NMR chemical shifts were referenced to H_3PO_4 . For elemental analyses, a LECO TruSpec CHN elementary analyzer was utilized.

Synthesis of *N*-(diisopropylphosphanyl)benzamide, 1. Methode (a): triethylamine (0.35 mL, 2.5 mmol) and chlorotrimethylsilyl (0.38 mL, 3.0 mmol) were added to a solution of benzamide (0.30 g, 2.5 mmol) in toluene (20 mL) and allowed to react at room temperature under stirring for 1 h. Solid materials were removed by filtration and the resulting solution was taken to dryness under reduced pressure to afford *N*-(trimethylsilyl)benzamide as a colorless solid, which can be stored, or entirely used, as the starting material for the following step of this synthesis. A solution of *N*-(trimethylsilyl)benzamide (0.10 g, 0.52 mmol) in toluene (10 mL) was added with PiPr_2Cl (0.083 mL, 0.52 mmol) and allowed to stir for *ca.* 12 h at 70 °C. The volatiles were removed by evaporation under reduced pressure and the resulting colorless solid substance was washed with pentane (2×3 mL) and dried under vacuum (95 mg, 77%). **Methode (b):** solid samples of benzamide (1.0 g, 8.3 mmol) and DMAP (0.22 g, 1.8 mmol) were dissolved in toluene (20 mL), after which triethylamine (1.2 mL, 8.3 mmol) and PiPr_2Cl (1.3 mL, 8.3 mmol) were added. The reaction mixture was heated overnight at 110 °C under stirring. The resulting suspension was filtered to obtain a colorless solution, which was taken to dryness under reduced pressure. The colorless solid residue was washed with pentane (2×5 mL) and dried under vacuum (0.70 g, 36%). ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.70 (m, 2H, *o*-Ph), 7.50-7.30 (m, 3H, *m*- and *p*-Ph), 6.06 (br s, 1H, NH), 1.93 (br s, 2H, $\text{CH}(\text{CH}_3)_2$) 1.20-1.00 (m, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 48.2 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.2 (s, C=O), 135.1 (s, C-C=O), 131.8 (br s, *o*-Ph), 128.8 (s, *m*-Ph), 127.3 (s, *p*-Ph), 25.9 (d, $^1J_{\text{CP}} = 13$ Hz, $\text{CH}(\text{CH}_3)_2$), 18.8 (d, $^2J_{\text{CP}} = 21$ Hz, CH_3), 17.9 (d, $^2J_{\text{CP}} = 8$ Hz, CH_3) ppm. IR (neat): 3288 ($\tilde{\nu}_{\text{N-H}}$), 1651 ($\tilde{\nu}_{\text{C=O}}$) cm^{-1} . Anal. Calc. for $\text{C}_{13}\text{H}_{20}\text{NOP}$: C, 65.8; H, 8.50; N, 5.90. Found: C, 65.9; H, 8.6; N, 5.9.

X-ray diffraction analyses. A summary of the crystallographic data and the structure refinement results for compound **1** are given in Table S1 (Supplementary Materials). A crystal of suitable size for X-ray diffraction analysis was coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream ($T = 213$ K) to the goniometer head. Data collection was carried out on a Bruker-Nonius X8kappa APEX II CCD area detector, using monochromatic radiation $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, by means of ω and φ scans with a width of 0.50 degrees. The data were reduced (SAINT) [19] and corrected for absorption effects by the multi-scan method (SADABS) [19,20]. The structures were solved by direct methods (SIR-2002) [21] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-2018/3) [22,23] minimizing $w[\text{Fo}^2 - \text{Fc}^2]^2$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. CCDC 2263762 (**1**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via: <https://www.ccdc.cam.ac.uk/structures/>.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: title; Table S1: title; Video S1: title.

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