SHORT PAPER

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Synthesis and single crystal X-ray structure of *N,N'*-bis(diphenylphosphino)piperazine†

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The reaction of piperazine with chlorodiphenylphosphine in toluene under refluxing conditions yields $Ph_2PN(C_4H_8)NPPh_2$ in quantitative yield. The structure is confirmed by single crystal X-ray diffraction studies.

Keywords: bis(phosphines), piperazine derivative, X-ray structure

The interest in synthesis and transition metal chemistry of bis(phosphine) ligands containing more than one type of spacer in the ligand framework is growing rapidly due to their steric and electronic versatility and interesting coordinating properties.[1,2] These ligands can also be used in a variety of metal-mediated organic syntheses.[3] The syntheses and reactivity of bis(phosphine) derived from piperazine has been reported.[4] Herein, we report the improved synthesis and X-ray crystal structure of *N*,*N'* bis(diphenylphosphino)piperazine, $Ph_2PN(C_4H_8)NPPh_2$ (**1**).

Although, Rao and co-workers reported[4c] the synthesis of the title compound **1** in 1993, its coordinating properties were not explored. Recently, we have explored the reactivity[4a] of **1** and Woollins and coworkers have reported[4b] the synthesis and some transition metal complexes of the title compound **1**. However, we have prepared the compound **1** using a modified high yield procedure. The reaction of piperazine with chlorodiphenylphosphine in refluxing toluene affords the compound **1** in almost quantitative yield. The ^{31}P NMR spectrum shows a single resonance at 62.4 ppm and is consistent with the literature-reported value. Further, the structure is established by single crystal X-ray diffraction.

The perspective view of the molecule is displayed in Fig.1 with important bond lengths and bond angles. Compound **1** crystallises in the extended conformation and possesses crystallographically imposed centrosymmetry. The P–N bond length of 1.7053(16) Å is longer than the same observed in the compounds containing either an ethylenediamine back bone[1b] or with nitrogen bridged bis(phosphines).[1a] The normally accepted value for a single P–N bond length is 1.77 Å [20]. The geometry around the nitrogen is distinctly pyramidal with sum of the angles about N being 348.7°. The phosphorus centres are in typical tetrahedral environments.

Experimental

A solution of PPh_2Cl (5.51 g, 25 mmol) in dry toluene (20 ml) was added with stirring to piperazine (2.15 g, 25 mmol) in toluene (80 ml) at 0 °C. The reaction mixture was refluxed under nitrogen with stirring for 18–20 h. The solution was cooled to 25 °C and then filtered through celite. The solvent from the clear filtrate was evaporated under reduced pressure to give a white residue of **1**. The white solid obtained was crystallised from CH_2Cl_2–hexane (4:1) (5.4 g, 95%), m.p. 132–134 °C. Found: C, 73.12; H, 6.20; N, 5.96. $C_{28}H_{28}N_2P_2$ requires C, 73.99; H, 6.21; N, 6.16%); $\delta_H(CDCl_3)$ 7.22–7.91 (20 H, m, Ph), 2.64 (8 H, t); $\delta p(CDCl_3)$ 62.4 (2 P, s).

X-ray crystal structure

A colourless crystal of **1** (0.26 × 0.52 × 0.53 Å) crystallised from CH_2Cl_2 at 0°C was mounted on Pyrex filaments with epoxy resin.

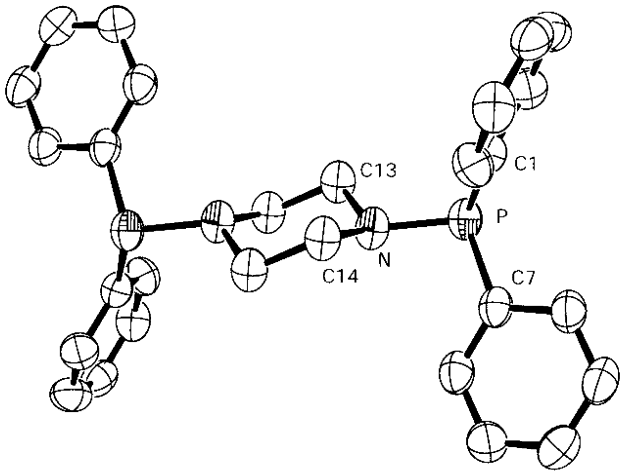

Fig. 1 Perspective view of $Ph_2PN(C_4H_8)NPPh_2$ (**1**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): P–N, 1.7053(16); P–C1, 1.842(2); P–C7, 1.8309(16); N–C13, 1.471(2); N–C14, 1.465(3). Selected bond angles (°): N–P–C1, 107.89(9); N–P–C7, 102.91(8); C1–P–C7, 99.31(8); P–N–C13, 114.93(12); P–N–C14, 123.71(13); C13–N–C14, 110.10(14).

The general procedure for crystal alignment, unit cell determination and refinement and collection of intensity data on the Enraf -Nonius CAD-4 diffractometer have been published.[6] The details of the crystal and data collection for **1** $C_{28}H_{28}N_2P_2$: M = 454.46, monoclinic, *a* (Å) = 8.6880 (7), *b* (Å) = 18.942 (3), *c* (Å) = 8.0739 (5); β (°) = 114.035 (6), *Z* = 2, V(Å^3) = 1213.5 (2), *T* (K) = 293(2). Space group $P2_1/c$ (No. 14), *D*(calc) (g/cm^3) = 1.244, μ (Mo–Kα) = 0.198 mm^{-1}, reflections observed, 1726. The final R_1 was 0.0331 (all data) and wR_2 = 0.0944 (all data), goodness-of-fit (*S*) 1.05. All calculations were performed with the SHELXTL PLUS[7] program package. Hydrogen atoms were included in calculated positions as riding atoms with isotropic displacement parameters 20% larger than those of the attached atoms. The data are deposited in Cambridge Crystallographic Data Centre and the CCDC reference number is 202409.

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References

1 (a) M.S. Balakrishna, R.M. Abhyankar and J.T. Mague, *J. Chem. Soc. Dalton Trans*., 1999, 1407; (b) M.S. Balakrishna and R. McDonald, Inorg. *Chem. Commun*., 2002, **5**, 782; (c) M.S. Balakrishna, R. Panda and J.T. Mague, *Inorg. Chem.*, 2001, **40**, 5620; (d) M.S. Balakrishna and M.G. Walawalkar, *J. Organomet. Chem*. 2001, **628**, 76; (e) M.S. Balakrishna, R.M. Abhyankar and M.G. Walawalkar, *Tetrahedron Lett*, 2001, 42, 2733; (f) M.S. Balakrishna, R. Panda and J.T. Mague, *J. Chem. Soc., Dalton Trans*., 2002, 4617; (g) M.S. Balakrishna, R. Panda and J.T. Mague, *Polyhedron*, 22, 2003, 587.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

2 (a) A.M.Z. Slawin, M.B. Smith and J.D. Woollins, *Chem. Commun*., 1996, 2095; (b) A.M.Z. Slawin, M.B. Smith and J.D. Woollins, *J. Chem. Soc. Dalton Trans.*, 1998, 1537; (c) K.V. Katti, V.S.R. Reddy and P.R. Singh, *Chem. Soc. Rev*., 1995, 97.

3 (a) H. Bricout, J.F. Carpentier and A. Mortreuz, *Tetrahedron Lett*., 1996, **37**, 6105; (b) I. Suisse, H. Bricout and A. Mortreux, *Tetrahedron Lett*., 1994, **35**, 413; (c) D. Gleich, R. Schmid and W.A. Herrmann, *Organometallics*, 1998, **17**, 2141; (d) S. Ganguly and R.M. Roundhill, *Organometallics*, 1993, **12**, 4825; (e) B. Cornils and E.G. Kuntz, *J. Organomet. Chem*., 1995, **502**, 177.

4 (a) S. Priya, M.S. Balakrishna, S.M. Mobin and J.T. Mague, *Inorg. Chem*., 2003, **42**, 0000; (b) M. Rodriguez i Zubiri, A.M.Z. Slawin, M. Wainwright and J.D. Woollins, *Polyhedron*, 2002, **21**, 1729; (c) C.J. Thomas, M.N.S. Rao, *Z. Anorg. Allg. Chem*., 1993, **619**, 433.

5 D.E.C. Corbridge, *Phosphorus: An outline of its Chemistry, Biochemistry and Uses*, Elsevier, Amsterdam, 1995.

6 K. Harms and S. Wocadlo, Program to Extract Intensity Data from Enraf-Nonius CAD-4 Files, University of Marburg, 1987.

7 SHELXTL PLUS version 5.0, Bruker AXS, Inc., WI, 1995.