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Synthesis and structural characterizations of *para*-bis(dialkyl/diarylphosphino)phenylenes built around tetrahalogenated benzene cores

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Abstract

Double deprotonation of 1,2-dibromo-4,5-difluorobenzene and 1-bromo-2-chloro-4,5-difluorobenzene by lithium diisopropylamide (LDA) in ethereal solutions is facile at very low temperatures ($T < -90$ °C). The organo-dilithium intermediates thus generated react readily with chlorophosphines $ClPR_2$ (R = Ph and/or ^{i}Pr), producing 1,2-dibromo-3,6-bis(diphenylphosphino)-4,5-difluorobenzene (**1a**), 1,2-dibromo-3,6-bis(diisopropylphosphino)-4,5-difluorobenzene (**1b**) and 1-bromo-2-chloro-3,6-bis(diphenylphosphino)-4,5-difluorobenzene (**1c**). Corresponding P-oxides **2a**–**c** are obtained by oxidation of **1a**–**c** with H_2O_2. Analogous reactions of 1,2-dibromo-4,5-difluorobenzene and 1-bromo-2-chloro-4,5-difluorobenzene with only 1 equiv. of LDA do not result in selective monodeprotonations, as **1a** and **1c** are formed preferentially after $ClPPh_2$ quench. All of the isolated new compounds were fully characterized by multinuclear NMR spectroscopy, elemental analysis and/or mass-spectrometry. In addition, **1a**, **1c**, **2a**, and **2b** were characterized by single crystal X-ray diffraction methods.

Keywords: Diphosphines; Dilithiation; P-oxides; X-ray crystal structures

1. Introduction

Various 1,4-bis-phosphinobenzenes have been successfully used as linker ligands for bimetallic and polymetallic transition metal compounds [1–8]. Analogous bis-phosphinobenzenes with perhalogenated central phenyl rings have attracted lesser attention [9,10]. Recently, we have demonstrated that the presence of heavier, more reactive halogens in 1,4-bis-phosphinobenzenes built on the C_6Hal_4 core (e.g., 1,4-dibromo-2,5-bis(diphenylphosphino)-3,6-difluorobenzene **3**, Fig. 1) can be utilized for the construction of more complex polydentate phosphine ligands [11].

Compound **3** was obtained in high yields (~70%) via double deprotonation of 1,4-dibromo-2,5-difluorobenzene at very low temperatures ($T < -90$ °C) followed by $ClPPh_2$ quench. The same structural motif (two protons *para* to each other, each flanked by a fluorine and a bromine) is characteristic also to 1,2-dibromo-4,5-difluorobenzene. We found that upon subjection of the later to the same reaction conditions (THF, $T < -90$ °C, 2 LDA/2 $ClPR_2$), dilithiation and $-PR_2$ incorporation are also facile, leading to the isolation of 1,2-dibromo-3,6-bis(dialkyl/arylphosphino)-4,5-difluorobenzenes **1a**–**b**. Dilithiation also dominates in reactions containing equimolar ratios of 1,2-dibromo-4,5-difluorobenzene and LDA, as well as in analogous reactions of 1-bromo-2-chloro-4,5-difluorobenzene, rendering isolation of 1-bromo-2-chloro-3,6-bis(diphenylphosphino)-4,5-difluorobenzene **1c**. Compounds **1a**–**c** and corresponding

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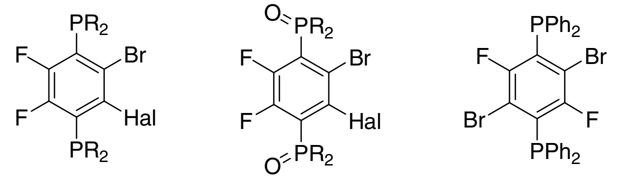

1a (R = Ph, Hal = Br) **2a** (R = Ph, Hal = Br) **3**
1b (R = ^{i}Pr, Hal = Br) **2b** (R = ^{i}Pr, Hal = Br)
1c (R = Ph, Hal = Cl) **2c** (R = Ph, Hal = Cl)

Fig. 1. *P*-bis(dialkyl/diarylphosphino)phenylenes and their P-oxides.

P-oxides **2a–c** (Fig. 1) (obtained by H_2O_2 oxidations of parent bis-phosphinobenzenes) can potentially be used as building blocks for construction of elaborate multidentate polyphosphine or polyphosphine-oxide ligand systems, or as ligands for bimetallic/polymetallic complexes. Herein we report pertinent synthetic details of **1a–c/2a–c**, and structural characterizations of **1a**, **1c**, **2a**, and **2b**.

2. Experimental

2.1. General procedures

Manipulations requiring inert atmospheres were carried out by using Schlenk techniques or in a dry box under a N_2 atmosphere. Low temperature reactions were performed in Schlenk flasks immersed in hexanes/liquid N_2 or ethanol/liquid N_2 slush, contained in a Dewar flask. Solvents were purified before use by distillation from Na-benzophenone ketyl (ether, THF, hexanes) or CaH_2 (toluene, acetonitrile) under a N_2 atmosphere. Methanol was deoxygenated by bubbling nitrogen through it for 1 h. Commercially available chlorophosphines $ClPR_2$ were purified prior to use: $ClPPh_2$ was vacuum distilled, and ClP^iPr_2 was frozen and degassed while thawing under vacuum (repeated three times). LDA (lithium diisopropylamide) was freshly prepared immediately prior to use according to a published procedure [12]. 1-bromo-2-chloro-4,5-difluorobenzene was obtained in 89% yield from commercially available 1-chloro-3,4-difluorobenzene utilizing the bromination conditions employed for the synthesis of 1,2-dibromo-4,5-difluorobenzene [13]. Other reagents were obtained from commercial suppliers. ^1H, ^{31}P, and ^{19}F NMR spectra were recorded on Varian INOVA spectrometer operating at 400, 161, and 376 MHz, respectively. Spectra are referenced to tetramethysilane (^1H), 85% H_3PO_4 (^{31}P) (external reference), and $CFCl_3$ (^{19}F) (internal reference in a sealed capillary tube). Low resolution mass spectrometric measurements were performed on a Shimadzu QP5050A instrument; high resolution measurements were performed at Mass Spectrometric Facility of Michigan State University. Elemental analyses were performed at Galbraith Laboratories, Inc.

2.2. Syntheses

2.2.1. 1-bromo-2-chloro-4 5-difluorobenzene

A round bottom flask (100 ml) was charged with 1-chloro-3,4-difluorobenzene (12.00 g, 80.8 mmol), iron powder (0.451 g, 80.8 mmol), and bromine (14.20 g, 88.8 mmol). The flask was wrapped in aluminum foil to afford protection from light, and the contents were heated at 70–75 °C overnight. The reaction mixture was quenched with saturated $K_2S_2O_3$ solution until the disappearance of brown color, and extracted with chloroform. Liquids were removed using a rotary evaporator, and the residual heavy liquid was recrystallized from pentane at −28 °C. Yield: 16.5 g (89%). NMR spectroscopic characterizations were in accordance with previously reported data [14].

2.2.2. General procedures for syntheses of *1a–b*

To a stirred solution of 1,2-dibromo-4,5-difluorobenzene (2.0 g, 7.36 mmol) in 250 ml THF at −95 °C was added 2.0 equiv. of freshly prepared LDA in the same solvent through a cannula. After 5 min, a solution of the corresponding $ClPR_2$ (2.3–2.5 equiv.) in THF was added slowly via a cannula. The reaction mixture was stirred at −95 °C for 1 h and then stirred overnight while slowly warming up to room temperature. The resulting clear yellowish brown solution was filtered and all volatiles removed under reduced pressure yielding an oily yellow solid.

2.2.3. 1,2-dibromo-3,6-bis(diphenylphosphino)-4,5-difluorobenzene (*1a*)

The solid obtained was subsequently washed with acetonitrile (25 mL) and methanol (70 mL), and dried in vaccuo, yielding **1a** as pale yellow powder (3.026 g, 64% yield). X-ray quality crystals were grown by slow pentane diffusion into toluene solution of **1a**. M.p. 164–166 °C. *Anal.* Calc. for $C_{30}H_{20}Br_2F_2P_2$: C, 56.28; H, 3.15. Found: C, 55.35; H, 3.33%. (Analyses consistently low on carbon have been obtained for **1a** on two different samples of recrystallized material, even though no impurities could be detected by multinuclear NMR and GC/MS). ^1H NMR ($CDCl_3$): δ 7.37 (m). ^{31}P NMR: δ 6.44 (dd), $^3J_{PF} = 14$ Hz, $^4J_{PF} = 9$ Hz; ^{19}F NMR (C_6D_6): δ −118.65 (dd), $^3J_{FP} = 14$ Hz, $^4J_{FP} = 9$ Hz. MS (EI): *m*/*z* = 640 (M^+).

2.2.4. 1,2-dibromo-3,6-bis(diisopropylphosphino)-4,5-difluorobenzene (*1b*)

The reaction was carried out by the same general procedure but with 1.00 g of 1,2-dibromo-4,5-difluorobenzene. The solid obtained was washed with methanol (60 mL) and dried in vaccuo yielding **1b** as a light yellow