Electronic Supplementary Information

A Unique Bi-Bi Bond Forming Reaction Using Organobismuth Oxides and Phosphorus Compounds Bearing a P(=O)H group

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General. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques or in a glovebox filled with nitrogen. Anhydrous toluene, 1,4-dioxane, hexane and dichloromethane were purchased from Kanto Chemicals and degassed before use. CDCl3 and [D8]toluene were distilled from CaH2 and Na/benzophenone ketyl, respectively. 1H, 13C and 31P spectra were recorded on Jeol LA500 or JNM-ECX400P spectrometers. Chemical Shifts are given in ppm using an external reference (tetramethylsilane (0 ppm) for 1H and 13C, and 85% H3PO4 (0 ppm) for 31P), and coupling constants were reported in hertz. Organobismuth oxide 2a and 12-chloro-6-methyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine 8c were prepared using the literature procedure.

1. Preparation of 2b and 2c.

Bis(2-bromophenylmethyl)(1,1,3,3-tetramethylbutyl)amine, 7b. To a DMF (60 mL) suspension of 2-bromobenzyl bromide (50.0 g, 200 mmol) and NaI (164 mg, 1.09 mmol) were added dicyclohexylmethylamine (42.5 mL, 200 mmol) and...
1,1,3,3-tetramethylbutylamine (15.1 mL, 91 mmol). The mixture was gradually heated to 120 °C and stirred for 16 hours at the same temperature. After cooling to room temperature, the mixture was filtered to remove solid, and the water (50 mL) and ether (100 mL) were added to the filtrate. The organic layer was separated, washed with water (3 x 50 mL), and dried over Na2SO4. After filtration, volatiles were removed under vacuum to leave crude product, which was treated with a mixture of ethanol (40 mL) and hexane (20 mL) to remove impurities, filtered, washed with ethanol, and dried under vacuum to give 36.0 g of the title compound as a colorless crystalline solid. Concentration of the filtrate to the half of the original volume further afforded 1.1 g of the title compound. Total 37.1 g, 87% yield. 

\[ ^1H \text{NMR (CDCl}_3, 399.8 \text{MHz): } \delta 1.05 (9H, s), 1.29 (6H, s), 1.69 (2H, s), 3.87 (4H, s), 6.87 (2H, td, } J = 7.8, 1.4 \text{ Hz), 7.07 (2H, t, } J = 7.8 \text{ Hz), 7.30 (2H, dd, } J = 7.8, 0.9 \text{ Hz), 7.53 (2H, dd, } J = 7.8, 1.4 \text{ Hz).} \]

\[ ^13C \text{NMR (CDCl}_3, 100.53 \text{MHz): } \delta 27.74, 31.25, 32.03, 49.08, 53.85, 60.18, 123.48, 126.59, 127.55, 131.16, 132.04, 140.50. \]

Anal. Calcd for C22H29Br2N: C, 56.55; H, 6.26; N, 3.00%. Found: C, 56.69; H, 6.07; N, 2.94%.

12-chloro-6-(1,1,3,3-tetramethylbutyl)-5,6,7,12-tetrahydrodibenzo[c,f][1,5]azabische
mecine, 8b. To an ether (70 mL) solution of bis(2-bromophenylmethyl)(1,1,3,3-tetramethylbutyl)amine (11.7 g, 25.0 mmol) was added a hexane solution of n-BuLi (1.59 M, 31.5 mL, 50.1 mmol) at –30 °C. The mixture was slowly warmed to room temperature with stirring during the period of 3 hours, and then added drop by drop to an ethereal (200 mL) suspension of BiCl3 (7.89 g, 25.0 mmol) cooled at –78 °C. The mixture was slowly warmed to room temperature during the period of 13 hours, and then stirred at the same temperature for 7 hours. The volatiles were removed under vacuum, and the residue was dissolved in a mixture of CHCl3 (200 mL) and 1N aqueous NH4Cl solution (100 mL). After filtration through Celite, the organic layer was separated, washed with water, dried over Na2SO4, filtered, and evacuated to remove volatiles to leave a crude product, which was treated with a 1:1 mixture of hexane and CH2Cl2 (150 mL). White solid deposited was filtered and dried under vacuum to give 8b (10.1 g). The filtrate was concentrated to ca. 10 mL, to which was added hexane (70 mL) to give additional 8b (1.8 g). Total 11.9 g (86% yield). M.p. 254-256 °C. 

\[ ^1H \text{NMR (CDCl}_3, 399.8 \text{MHz): } \delta 1.04 (9H, s), 1.37 (6H, s), 1.77 (2H, s), 4.11 (2H, d, } J = 15.6 \text{ Hz), 4.54 (2H, d, } J = 15.6 \text{ Hz), 7.32 (2H, td, } J = 7.3, 1.1 \text{ Hz), 7.41 (2H, d, } J = 7.3 \text{ Hz), 7.48 (2H, t, } J = 7.6 \text{ Hz), 8.65 (2H, d, } J = 7.3 \text{ Hz).} \]

\[ ^13C \text{NMR (CDCl}_3, 100.53 \text{MHz, 50 °C): } \delta 27.40, 31.73, 31.77, 50.68, 59.82, 64.33, 127.36, 128.12, 130.70, 138.30, 151.29, 170.78. \]

Anal. Calcd for C22H29BiClN: C, 47.88; H, 5.30; N, 2.54%. Found: C, 47.64; H, 5.09; N, 2.40%.

Bismuth oxide, 2b. A mixture of 8b (5.0 g, 9.1 mmol) in CH2Cl2 (100 mL) and aqueous NaOH solution (1.0 M, 91 mL, 91 mmol) was vigorously stirred at room temperature for 3 hours under N2. The organic layer was separated, washed with water, dried over Na2SO4, filtered, and evacuated to remove volatiles to give 2b as a colorless solid (4.6 g, 96%). M.p. 124-126 °C. 

\[ ^1H \text{NMR (CD}_6\text{D}_6, 499.1 \text{ MHz): } \delta \]
0.87 (18H, s), 1.11 (12H, s), 1.54 (4H, s), 3.68 (4H, d, J = 15.8 Hz), 4.02 (4H, d, J = 15.8 Hz), 7.09 - 7.14 (8H, m), 7.37 (4H, t, J = 7.3 Hz), 9.05 (4H, d, J = 7.3 Hz).

**Anal. Calcd for C$_{44}$H$_{58}$Bi$_2$N$_2$: C, 50.38; H, 5.57; N, 2.67%.

**Found: C, 50.48; H, 5.48; N, 2.56%.

**Bismuth oxide 2c.** A mixture of 8c (585 mg, 1.29 mmol) in CH$_2$Cl$_2$ (5 mL) and aqueous NaOH solution (0.5 M, 5 mL, 2.5 mmol) was vigorously stirred at room temperature for 1 hour under N$_2$. Organic layer was separated, washed with water, dried over Na$_2$SO$_4$, filtered, and evacuated to remove volatiles to give 2c as a colorless solid (486 mg, 88%). $^1$H NMR (C$_6$D$_6$, 499.1 MHz): δ 2.02 (6H, s), 3.28 (4H, d, J = 14.6 Hz), 3.60 (4H, d, J = 14.6 Hz), 7.07 (4H, d, J = 7.3 Hz), 7.13 (4H, t, J = 7.3 Hz), 7.39 (4H, t, J = 7.3 Hz), 8.99 (4H, d, J = 7.3 Hz).

**Dibismuthane 1b.** A 1,4-dioxane (40 mL) solution of 2b (3.00 g, 2.86 mmol) and 5 (412 mg, 1.91 mmol) was stirred at 90 °C for 1 hour. The precipitated red-orange solid was separated by filtration, washed with 1,4-dioxane, and dried under vacuum to give 1b (1.33 g). The filtrate was concentrated and mixed with 1,4-dioxane (15 mL) to leave a red-orange solid, which was separated by filtration, washed with 1,4-dioxane, and dried under vacuum to give additional 1b (0.22 g). Total 1.55 g (79% based on 5). M.p. 181-182 °C. $^1$H-NMR (C$_6$D$_6$, 499.1 MHz): δ 0.93 (18H, s), 1.27 (12H, s), 1.66 (4H, s) 3.83 (4H, d, J = 15.8 Hz), 4.05 (4H, d, J = 15.8 Hz), 6.85 (4H, t, J = 7.3 Hz), 7.06-7.12 (8H, m), 8.89 (4H, d, J = 7.3 Hz). Anal. Calcd for C$_{44}$H$_{58}$Bi$_2$N$_2$: C, 51.23; H, 5.73; N, 2.66%. Found: C, 51.52; H, 5.60; N, 2.57%.

**Dibismuthane 1c.** A 1,4-dioxane (10 mL) solution of 2c (400 mg, 0.46 mmol) and 5 (68 mg, 0.31 mmol) was stirred at 90 °C for 1 hour. The precipitated solid consisting of red-orange 2c and uncharacterized gray fine powder was separated by filtration, washed with 1,4-dioxane, and dried under vacuum to a crude mixture (338 mg). $^1$H NMR analysis of the mixture showed that the soluble part was almost pure 2b. The crude product was mixed with THF (100 mL) and filtered, and the filtrate was evacuated to give 2b (59 mg, 23%). $^1$H NMR (C$_6$D$_6$, 499.1 MHz): δ 2.19 (6H, s), 3.32 (4H, d, J = 14.2 Hz), 3.73 (4H, d, J = 14.2 Hz), 6.84 (4H, td, J = 7.3, 1.8 Hz), 7.01-7.09 (8H, m), 8.63 (4H, d, J = 7.3 Hz). Anal. Calcd for C$_{30}$H$_{30}$Bi$_2$N$_2$: C, 43.07; H, 3.61; N 3.35%. Found: C, 43.51; H, 3.42; N, 3.21%.

2. Reaction of dibismuthane 2b with disulfide 9.
2b (10 mg, 9.7 mmol) and 9 (3.2 mg, 9.6 mmol) in C_6D_6 (0.6 mL) in NMR tube was shaken under nitrogen at room temperature. After 10 min, all the solid dissolved, and the color of the mixture became pale yellow. ^1H NMR spectrum of the mixture showed almost complete consumption of 2b and 9, and nearly quantitative formation of 10. ^1H NMR (C_6D_6, 499.1 MHz): δ 0.79 (9H, s), 0.90 (6H, s), 1.35 (2H, s), 3.59 (2H, d, J = 15.5 Hz), 3.83 (2H, d, J = 15.5 Hz), 6.89 (1H, t, J = 7.3 Hz), 7.00-7.04 (3H, m), 7.12 (2H, td, J = 7.3, 1.4 Hz), 7.20 (2H, t, J = 7.3 Hz), 7.31 (1H, d, J = 7.8 Hz), 7.81 (1H, d, J = 7.8 Hz), 9.07 (2H, dd, J = 7.3, 1.4 Hz).

X-ray Crystallography. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα radiation, graphite monochromator). Data were corrected for absorption. The structures were solved by the Patterson method and expanded using Fourier techniques. Structure refinement was carried out by full-matrix least squares on F^2. The hydrogen atoms were placed in calculated positions and refined using a riding model. For compound 1c, the hydrogen atoms bound to the toluene molecule could not be located because of disorder. Structure solution and refinement were performed using CrystalStructure software package with Crystals program. Molecular structure drawings were generated using CrystalMaker program.

References:
S3 SADABS; G. M. Sheldrick, 1996.
S6 CrystalStructure version 3.8; Rigaku and Rigaku/MSC, 2006.
S8 CrystalMaker for Mac OSX, version 8.2.0; CrystalMaker Software Limited, 2009.