Supporting Information for:

Hydrophosphination-Type Reactivity Promoted by Bismuth Phosphanides: Scope and Limitations

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Table of Contents

Page

Synthetic Procedures

General. All manipulations were performed under dry nitrogen using standard Schlenk-line techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300.1(^{1}H), 75.4 (^{13}C) and 121.7 (^{31}P) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. InfraRed spectra were recorded on a PerkinElmer Spectrum One FTIR Spectrophotometer as a Nujol mull, using KBr plates. Mass spectra were recorded on an Agilent 6530 Accurate Mass Q-TOF LC/MS High Resolution Mass Spectrometer (HRMS). Elemental analyses were performed by S. Boyer at London Metropolitan University. Bi(NON^{Ar})(PCy$_2$) (**1**) was prepared according to literature procedures.

Preparation of Bi(NON^{Ar})(OC{PCy$_2$}NPh) (2): A solution of phenylisocyanate (25 μL, 0.229 mmol.) in Et$_2$O (5 mL) was added drop wise to a stirring solution of **1** (0.20 g, 0.225 mmol.) in Et$_2$O (5 mL). The resulting solution was allowed to stir for 24 h at room temperature, followed by concentration of the solution, during which time, pale yellow crystals of **2** formed. Yield 0.152 g, 67 %.

Anal. Calcd. for $C_{47}H_{68}BiN_3O_2PSi_2$ (*1008.24*): C, 55.99; H, 7.30; N, 4.17 %. Found: C, 55.81; H, 7.23; N, 4.21 %. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.26 (dd, J = 7.8, 1.5 Hz, 2H, *m*-C_6H_5), 7.01 (m, 4H, *m*-C_6H_3), 6.89 (m, 2H, *p*-C_6H_3), 6.81 (t, J = 7.8 Hz, 1H, *p*-C_6H_5), 6.71 (d, J = 7.8 Hz, 2H, *o*-C_6H_5), 4.18, 3.78 (sept, 2H, C*H*Me$_2$), 2.2 - 0.9 (br m, 20H, C_6H_{11}), 1.59, 1.37, 1.27, 1.14 (d, J = 6.6 Hz, 6H, CH*Me$_2$*), 0.58, 0.28 (s, 6H, SiMe$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 175.0 (d, J_{PC} = 51 Hz, N*C*(P)O), 149.7, 147.2, 140.8, 129.6, 129.3, 129.0, 128.3, 125.9, 125.6, 124. 8, 124.3, 124.1, 123.9, 123.7 (*C$_6$*H$_3$ and *C$_6$*H$_5$), 32.6 (d J_{PC} = 17 Hz), 30.6 (d, J_{PC} = 7.5 Hz), 28.4, 28.1, 28.0, 27.9, 27.8, 27.7, 27.5 (d, J_{PC} = 8.5 Hz), 26.6, 25.2 (d, J_{PC} = 11 Hz) (*C*HMe$_2$, CH*Me$_2$* and *C$_6$*H$_{11}$), 4.1, 3.1(Si*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 10.0. IR (Nujol, KBr): 2954(s), 2923(s), 2854(s), 1531(m, C=O), 1430(m) cm^{-1}.

Preparation of Cy$_2$PC(O)N(H)Ph (3): A solution of phenylisocyanate (0.11 mL, 0.98 mmol.) in THF (5 mL) was added drop wise to a stirring solution of LiPCy$_2$ (0.20 g, 0.98 mmol.) in THF (5 mL). The solution was stirred for 12 h at room temperature and then quenched by adding HNEt$_3$Cl (0.16 g, 1.18 mmol.) and stirring for 24 h. The suspension was filtered and the solvent removed *in vacuo* to give an air stable colourless powder.

Recrystallisation of the solid from acetonitrile yielded colourless crystals of **7**. Yield 0.25 g, 80 %.

^{1}H NMR (C_6D_6, 300 MHz): δ 7.42 (d, *J* = 7.9 Hz, 2H, *o*-C_6H_5), 7.34 (br, 1H, N*H*), 7.03 (t, *J* = 7.9 Hz, 2H, *m*-C_6H_5), 6.84 (t, *J* = 7.9 Hz, 1H, *p*-C_6H_5), 2.2 - 1.0 (m, 22H, C_6H_{11}). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 175.8 (d, J_{PC} = 24 Hz, N*C*(P)O), 138.6, 129.2, 124.4, 119.7 (C_6H_5), 33.4 (d, J_{PC} = 15 Hz α-C_6H_{11}), 29.9 (br), 29.8, 27.1 (d, J_{PC} = 12 Hz), 26.9 (d, J_{PC} = 9 Hz), 26.3 (C_6H_{11}). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz): δ 19.5. IR (Nujol, KBr): 3308(m, N-H), 2923(s), 2853(s), 1631(m, C=O), 1594(m), 1436 cm^{-1}. Mass Spec. (ESI, CH_3CN): *m*/*z* 318.1977 (calc'd 318.1981).

Crystallography

Crystals were covered in inert oil and suitable single crystals were selected under a microscope and mounted on an Agilent SuperNova diffractometer fitted with an Atlas (**2**) or EOS S2 (**3**) detector. Data were collected at the temperature indicated using focused microsource Mo Kα radiation at 0.71073 Å (**2**) or Cu Kα radiation at 1.5418 Å (**3**). Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods.[1] Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS[2] refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97[3] within OLEX-2.3 (**2**)[4] of WinGX (**3**).[5] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate unless otherwise stated. The functions minimized were $\Sigma w(F2\mathrm{o}\text{-}F2c)$, with $w = [\sigma 2(\mathrm{F2o}) + a\mathrm{P2} + bP]\text{-}1$, where $P = [\max(\mathrm{Fo})2 + 2\mathrm{F2c}]/3$. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Table S1 Crystal structure and refinement data for Bi(NON^{Ar})(Cy$_2$PC(O)NPh) (**2**) and Cy$_2$PC(O)N(H)Ph (**3**).

	2	**3**
CCDC number	1446891	1446892
Empirical formula	$C_{141}H_{219}Bi_3N_9O_6P_3Si_6$	$C_{19}H_{28}NOP$
M_r	3024.63	317.39
Radiation (wavelength [Å])	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
T [K]	120.02(10)	120.01(10)
Crystal size [mm]	0.45 × 0.38 × 0.26	0.37 × 0.10 × 0.08
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No.2)	$P2_1/n$ (alternative No.14)
a [Å]	17.6927(4)	12.87859(7)
b [Å]	18.2618(4)	18.69702(10)
c [Å]	25.0124(5)	37.4280(2)
α [°]	87.6009(17)	90
β□ [°]	78.6468(18)	99.5776(5)
γ [°]	66.154(2)	90
V [Å^3]	7240.6(3)	8886.72
Z	2	20
$D_{calc.}$ [mg m^{-3}]	1.387	1.186
Absorption coefficient [mm^{-1}]	3.774	1.368
θ range for data collection [°]	5.29 to 50.5	8.4168 to 143.3518
Reflections collected	62744	61225
Independent reflections (R_{int})	26168 (0.034)	17290 (0.035)
Data/restraints/parameters	26168 / 0 / 1546	17290 / 234 / 1103
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.031$ w$R_2 = 0.071$	$R1 = 0.050$ w$R_2 = 0.140$
Final R indices (all data)	$R1 = 0.041$ w$R_2 = 0.075$	$R1 = 0.054$ w$R_2 = 0.145$
GOOF on F^2	1.022	1.102
Largest diff. peak/hole [e.Å^{-3}]	3.36 and –2.15	0.86 and –0.41

Figure S1 ORTEP of Bi(NON^{Ar})(OC{PCy$_2$}NPh) (**2**, ellipsoids at 30%, H-atoms omitted).

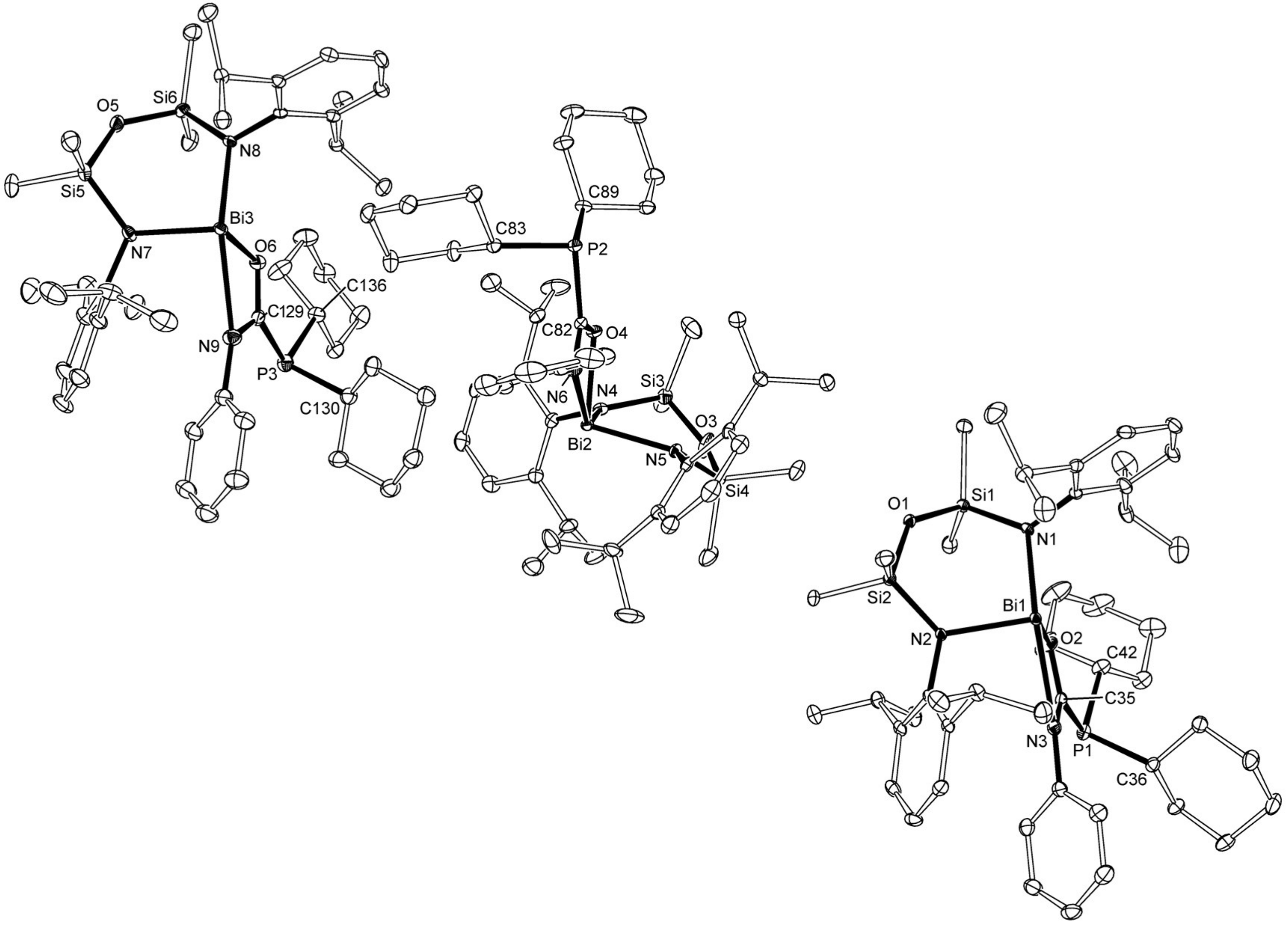
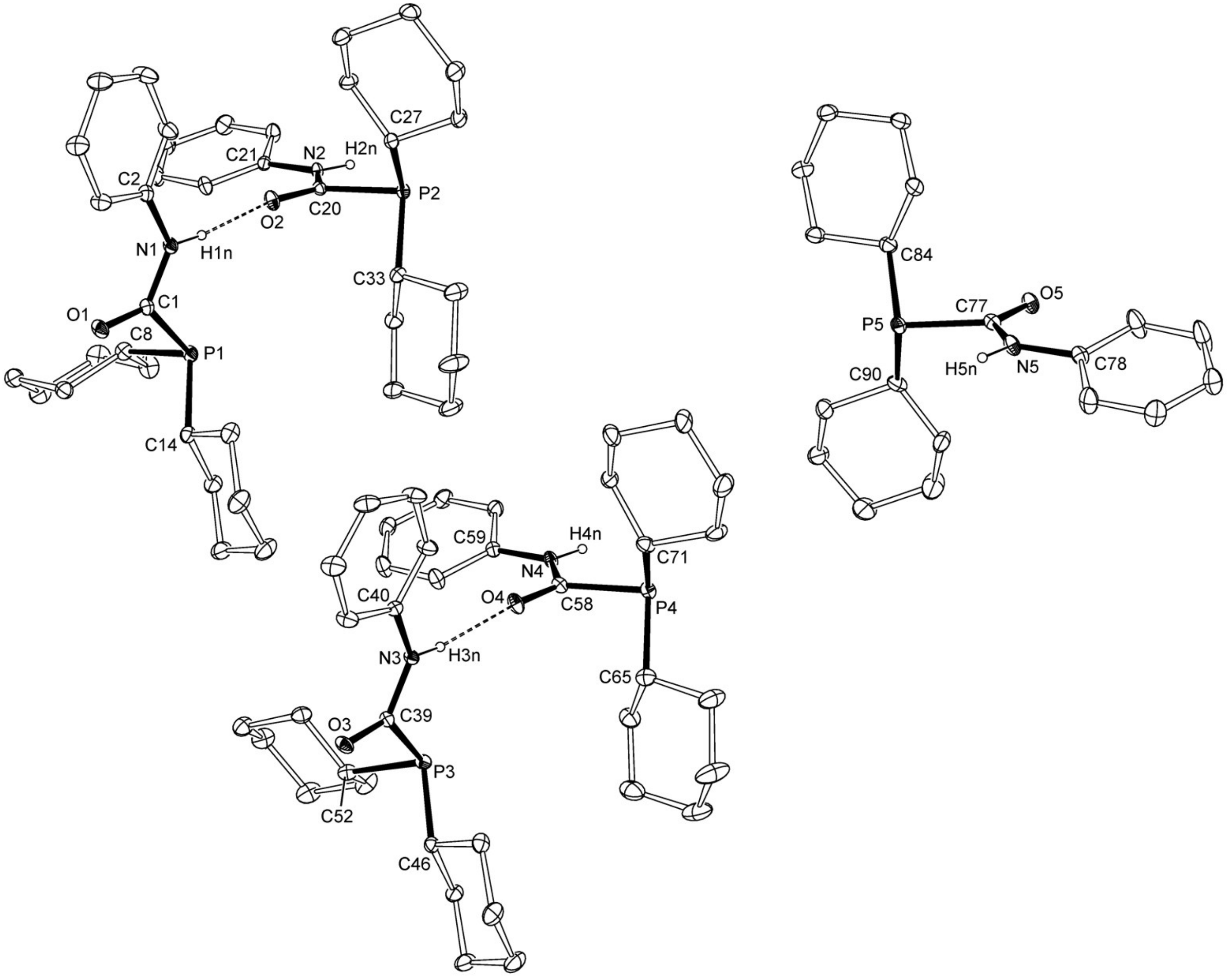


Figure S2 ORTEP of $Cy_2PC(O)N(H)Ph$ (**3**, ellipsoids at 30%, H-atoms except N*H* omitted).



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