

Supporting Information

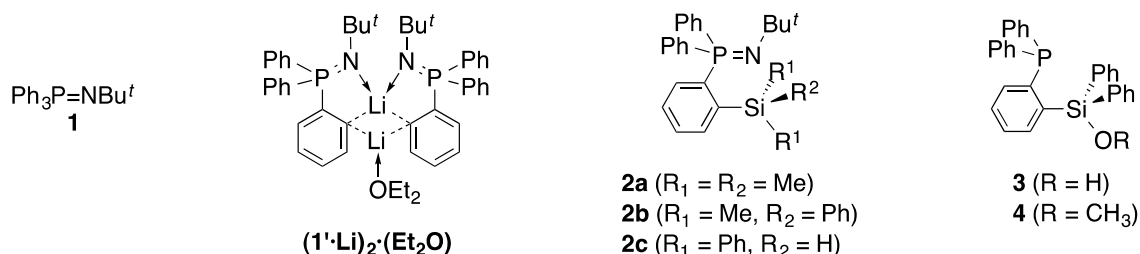
Synthesis of a Phosphine Imide Bearing a Triarylhydrosilane Moiety, and Its Water-Driven Reduction to a Phosphine

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Experimental details

All the experiments were carried out under nitrogen or argon atmosphere. All the solvents and reagents were purified and dried prior to use.



Lithiation of triphenylphosphine *N-tert*-butylimide (**1**).

An Et₂O solution of methyllithium (1.09 M, 20 mL) was added to iminophosphorane **1** (3.87 g, 11.6 mmol) at room temperature and stirred for 2 hours. After evaporation of the solvent in vacuo, the resulting yellow solid was washed with dry hexane in a glovebox and dried in vacuo to give the almost pure lithiated iminophosphorane [2-C₆H₄(PPh₂N(*tert*-butyl))Li]₂·Et₂O ((**1'**·Li)₂·(Et₂O)) (3.51 g, 93%). It was used for the synthesis of **2a-c** without further purification.

(1'·Li)₂·(Et₂O): pale yellow powder, ¹H NMR (400 MHz, C₆D₆) δ 1.08 (t, *J* = 6.8 Hz, 6H), 1.14 (s, 18H), 3.24 (q, *J* = 6.8 Hz, 4H), 7.07-7.14 (m, 16H), 7.24-7.31 (m, 4H), 7.87-7.99 (m, 8H). ³¹P NMR (162 MHz, C₆D₆) δ 14.4.

Synthesis of diphenyl(2-trimethylsilylphenyl)phosphine *N-tert*-butylimide (**2a**)

Chlorotrimethylsilane (0.250 μL, 1.05 mmol) was added to an Et₂O solution (10 mL) of lithiated iminophosphorane (**1'**·Li)₂·(Et₂O) (390 mg, 0.520 mmol) at −78 °C, and then warmed gradually up to room temperature for overnight. After evaporation of the solvent, water was added to the white solid, and it was extracted with CH₂Cl₂ and dried with MgSO₄. After filtration of MgSO₄ and evaporation of the solvent, recrystallization from ethanol gave **2a** (251 mg, 60%) as colorless crystals. The yield of **2a** was calculated that 1 mol of (**1'**·Li)₂·(Et₂O) gave 2 mol of **2a** in 100% yield. The yield of **2a** for two steps from **1** is 56%.

2a: colorless crystals, mp 150.0-152.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 0.36 (s, 9H), 1.16 (s, 9H), 7.17-7.22 (m, 2H), 7.33-7.40 (m, 7H), 7.55-7.60 (m, 4H), 7.76-7.80 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 3.23 (s), 35.41 (d, *J*_{PC} = 10.7 Hz), 52.36 (d, *J*_{PC} = 4.8 Hz), 127.45 (d, *J*_{PC} = 15.3 Hz), 128.08 (d, *J*_{PC} = 10.5 Hz), 129.21 (d, *J*_{PC} = 2.9 Hz),

130.30 (d, $J_{\text{PC}} = 2.9$ Hz), 133.12 (d, $J_{\text{PC}} = 9.5$ Hz), 133.80 (d, $J_{\text{PC}} = 18.1$ Hz), 136.84 (d, $J_{\text{PC}} = 14.3$ Hz), 138.29 (d, $J_{\text{PC}} = 75.3$ Hz), 140.90 (d, $J_{\text{PC}} = 134.4$ Hz), 145.45 (d, $J_{\text{PC}} = 12.4$ Hz). ^{29}Si NMR (79 MHz, CDCl_3) $\delta -2.8$. ^{31}P NMR (162 MHz, CDCl_3) $\delta -1.9$. Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{NPSi}$: C, 74.03; H, 7.95; N, 3.45. Found: C, 73.86; H, 8.06; N, 3.26%.

Synthesis of [(2-dimethylphenylsilyl)phenyl]diphenylphosphine *tert*-Butylimide (**2b**)

Similarly to the synthesis of **2a**, reaction of the lithiated iminophosphorane $(1' \cdot \text{Li})_2 \cdot (\text{Et}_2\text{O})$ (566 mg, 0.751 mmol) and chlorodimethylphenylsilane (0.280 μL , 1.67 mmol) gave **2b** (442 mg, 63%) as colorless crystals. The yield of **2b** for two steps from **1** is 59%.

2b: colorless crystals, mp 130.0-132.5 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 0.68 (s, 6H), 1.08 (s, 9H), 7.17-7.66 (m, 19H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 2.10 (s), 35.31 (d, $J_{\text{PC}} = 9.9$ Hz), 52.42 (d, $J_{\text{PC}} = 5.1$ Hz), 127.55 (s), 127.61 (d, $J_{\text{PC}} = 12.4$ Hz), 128.04 (d, $J_{\text{PC}} = 10.7$ Hz), 128.20 (s), 128.98 (d, $J_{\text{PC}} = 2.4$ Hz), 130.31 (d, $J_{\text{PC}} = 2.5$ Hz), 133.11 (d, $J_{\text{PC}} = 9.1$ Hz), 133.72 (d, $J_{\text{PC}} = 18.1$ Hz), 134.61 (s), 138.09 (d, $J_{\text{PC}} = 75.9$ Hz), 138.85 (d, $J_{\text{PC}} = 14.1$ Hz), 141.53 (d, $J_{\text{PC}} = 135$ Hz), 142.92 (s), 142.93 (d, $J_{\text{PC}} = 12.4$ Hz). ^{29}Si NMR (79 MHz, CDCl_3) $\delta -5.2$. ^{31}P NMR (162 MHz, CDCl_3) $\delta -1.3$. Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{NPSi}$: C, 77.05; H, 7.33; N, 3.00. Found: C, 76.95; H, 7.45; N, 2.95%.

Synthesis of [(2-methyldiphenylsilyl)phenyl]diphenylphosphine *tert*-Butylimide (**2c**)

Chlorodiphenylsilane (190 μL , 0.969 mmol) was added dropwise to $(1' \cdot \text{Li})_2 \cdot (\text{Et}_2\text{O})$ (332 mg, 0.441 mmol) in diethyl ether (8 mL) at room temperature. The reaction mixture was stirred for 1 hour. After evaporation of the solvent, diethyl ether (15 mL) was added to the crude solid to dissolve it. Solid was removed by filtration and washed with diethyl ether (5 mL \times 3). After concentration of the solution, recrystallization from diethyl ether gave **2c** (312 mg, 69%) as colorless crystals. The yield for two steps from **1** is 64%.

Spectral data of **2c**: mp 176-178 $^{\circ}\text{C}$. ^1H NMR (500 MHz, C_6D_6) δ 1.16 (s, 9H), 6.75 (s, 1H), 6.81-6.85 (m, 2H), 6.98-7.08 (m, 6H), 7.11-7.16 (m, 5H), 7.23-7.29 (m, 1H), 7.55-7.63 (m, 5H), 7.68-7.75 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 34.82 (d, $J_{\text{PC}} = 10.3$ Hz), 53.31 (d, $J_{\text{PC}} = 4.7$ Hz), 127.77 (s, CH), 128.23 (d, $J_{\text{PC}} = 10.8$ Hz, CH), 128.66 (d, $J_{\text{PC}} = 14.5$ Hz, CH), 128.84 (s, CH), 129.57 (s, CH), 130.55 (s, CH), 132.32 (d, $J_{\text{PC}} = 17.5$ Hz, CH), 133.42 (d, $J_{\text{PC}} = 9.6$ Hz, CH), 136.74 (s, CH), 137.02 (d, $J_{\text{PC}} = 71.3$ Hz), 139.42 (s), 139.53 (d, $J_{\text{PC}} = 10.2$ Hz), 139.69 (d, $J_{\text{PC}} = 13.0$ Hz, CH), 142.21 (d, $J_{\text{PC}} =$

137.3 Hz). ^{29}Si NMR (79 MHz, C_6D_6) δ -26.4 (d, $^1J_{\text{SiH}} = 231$ Hz). ^{31}P NMR (162 MHz, C_6D_6) δ -2.8 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{25}\text{NPSi}$: C, 79.19; H, 6.65; N, 2.72. Found: C, 79.04; H, 6.86; N, 2.64%.

Reaction of **2c** with water.

To a C_6D_6 (0.5 mL) solution of diphenylhydrosilane **2c** (31.3 mg, 0.0683 mmol) was added water (25 μL) at room temperature, and shaken for 10 minutes. After removal of the solvent under reduced pressure, recrystallization from diethyl ether/hexane gave **3** (28.0 mg, 87%) as colorless solid.

Spectral data of **3**: mp 180.0-181.0 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 3.94 (d, $J = 10.2$ Hz, 1H), 7.08 (td, $J = 7.9$, 1.6 Hz, 2H), 7.17-7.28 (m, 11H), 7.30-7.46 (m, 7H), 7.51 (t, $J = 1.8$ Hz, 2H), 7.53 (t, $J = 1.4$ Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 127.64 (s, CH), 128.31 (d, $J = 6.9$ Hz, CH), 128.48 (s, CH), 128.57 (d, $J = 1.1$ Hz, CH), 129.67 (s, CH), 130.04 (d, $J = 0.8$ Hz, CH), 133.23 (d, $J = 17.9$ Hz, CH), 135.10 (s, CH), 135.23 (d, $J = 1.4$ Hz, CH), 135.90 (d, $J = 0.9$ Hz, quaternary), 136.11 (d, $J = 5.5$ Hz, CH), 136.85 (d, $J = 5.9$ Hz, CH), 143.50 (d, $J = 89.8$ Hz, quaternary), 143.84 (d, $J = 50.9$ Hz, quaternary). ^{29}Si NMR (79 MHz, CDCl_3) δ -10.3. ^{31}P NMR (162 MHz, CDCl_3) δ -10.1. MS (FAB) m/z 461 ($\text{M}+\text{H}^+$, 30%). IR (CDCl_3) ν 3445 cm^{-1} (O-H).

Reaction of **2c** with methanol.

Three drops of dehydrated methanol were added to a THF (1 mL) solution of diphenylhydrosilane **2c** (10.8 mg, 20.9 μmol) at room temperature, and the reaction solution was stirred for 20 minutes. After removal of the solvent under reduced pressure, separation by preparative thin layer chromatography (silica gel, ethyl acetate:hexane = 1:4) gave **4** (6.4 mg, 64%) as colorless solid.

4: mp 123.0-123.8 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 3.52 (s, 3H), 6.93 (td, $J = 1.0$, 7.8 Hz, 4H), 7.14 (td, $J = 1.5$, 7.3 Hz, 4H), 7.17-7.24 (m, 7H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.36-7.44 (m, 2H), 7.65 (dd, $J = 1.5$, 9.0 Hz, 4H), 7.90-7.94 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 51.66 (d, $J = 1.7$ Hz, CH_3), 127.52 (s, CH), 127.87 (s, CH), 127.99 (d, $J = 6.3$ Hz, CH), 128.57 (d, $J = 0.7$ Hz, CH), 129.52 (s, CH), 130.23 (s, CH), 133.11 (d, $J = 18.4$ Hz, CH), 134.81 (d, $J = 3.2$ Hz, quaternary), 135.57 (d, $J = 1.5$ Hz, CH), 135.67 (d, $J = 2.9$ Hz, CH), 136.83 (d, $J = 16.7$ Hz, CH), 137.76 (d, $J = 11.7$ Hz, quaternary), 143.02 (d, $J = 103.0$ Hz, quaternary), 143.42 (d, $J = 68.2$ Hz, quaternary). ^{29}Si NMR (99 MHz,

CDCl_3) δ -12.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -10.3. ESI-MS m/z 475.16 (M+H).

Crystallographic analysis of **2a** and **2c**.

All data for **2a** and **2c** were recorded on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71070$ Å). Data were collected and processed using CrystalClear (Rigaku). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELX-97) and expanded using Fourier techniques (Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Crystallographic data are shown below

Crystallographic data of **2a**: $\text{C}_{25}\text{H}_{32}\text{NPSi}$, $M = 405.58$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.745(2)$, $b = 16.531(4)$, $c = 16.017(4)$ Å, $\beta = 97.8059(11)^\circ$, $U = 2294.0(10)$ Å³, $T = 120(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.183$ mm⁻¹, $D_{\text{calc}} = 1.076$ g cm⁻³, $R1 = 0.0335$ ($I > 2\sigma(I)$), $wR2 = 0.0928$ (all data), GOF = 1.076. CCDC-867751.

Crystallographic data of **2c**: $\text{C}_{34}\text{H}_{34}\text{NPSi}$, $M = 515.68$, monoclinic, space group Cc , $Z = 4$, $a = 17.002(9)$, $b = 8.839(5)$, $c = 20.361(12)$ Å, $\beta = 112.6137(19)^\circ$, $U = 2825(3)$ Å³, $T = 120(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.163$ mm⁻¹, $D_{\text{calc}} = 1.213$ g cm⁻³, $R1 = 0.0402$ ($I > 2\sigma(I)$), $wR2 = 0.0390$ (all data), GOF = 0.0790. CCDC-867750.