

SUPPORTING INFORMATION

Title: Dual Supermesityl Stabilization: A Room-Temperature-Stable 1,2,4-Triphosphole Radical, Sigmatropic Hydrogen Rearrangements, and Tetraphospholide Anion

Author(s): Alex S. Ionkin,* William J. Marshall, Brian M. Fish, Alexander A. Marchione, Laurie A. Howe, Fredric Davidson, Charles N. McEwen

Ref. No.: I200800265

General: All air-sensitive compounds were prepared and handled under a N₂/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Tris(trimethylsilyl)phosphine, dioxane, metallic cesium, cesium fluoride, 4-oxo-2,2,6,6-tetramethylpiperidinoxyl free radical (TEMPO) and THF were purchased from Aldrich. Melting points are uncorrected. The mass spectra were collected on an Orbitrap mass spectrometer (ThermoFisher Scientific Bremen, Germany).

Cesium bis(trimethylsilyl)phosphide as a complex with 2.5 molecules of 1,4-dioxane (4). A 5.00 g (19.9 mmol) sample of tris(trimethylsilyl)phosphine (2) and 3.03 g (19.9 mmol) of cesium fluoride (1) in 60 mL of dioxane were stirred at 90°C for 3 hours. The reaction mixture was allowed to cool to ambient temperature. The resultant white crystals were filtered off. The yield of cesium bis(trimethylsilyl)phosphide as a complex with 2.5 molecules of 1,4-dioxane (4) was 7.83 g (74%) with mp at 119-120°C (decomposition). ¹H NMR (500 MHz, THF-*d*₈, TMS): δ 0.07 (d, ³J_{PH} = 3.1 Hz, 18H, Me-Si), 3.40 (s, 20H, dioxane). ³¹P NMR (500 MHz, THF-*d*₈): δ -276.10 (s, 1P). The structure was determined by X-ray analysis.

Three-component reaction between tris(trimethylsilyl)phosphine (2), cesium fluoride (1) and 2,4,6-tri-*tert*-butyl-benzoyl chloride (3). A 5.00 g (19.9 mmol) sample of tris(trimethylsilyl)phosphine (2), 9.10 g (59.9 mmol) of cesium fluoride (1) and 6.16 g (19.9 mmol) of 2,4,6-tri-*tert*-butyl-benzoyl chloride (3) in 60 mL of dioxane were stirred at 90°C for 10 days. The reaction mixture was filtered while it was hot and allowed to cool to ambient temperature. The first crop of crystals (0.74 g, 7% yield on 2) was filtered off to give cesium bis(trimethylsilyl)phosphide as a complex with 2.5 molecules of 1,4-dioxane (4) according to ³¹P NMR and ¹H NMR spectra. The second crop of the crystals contained the cesium salt of (2,4,6-tri-*tert*-butyl-benzoylphosphanylidene)-(2,4,6-tri-*tert*-butyl-phenyl)-methoxide as a complex with one molecule of dioxane (11) as light gold crystals with mp at 188-189°C (decomposition), (1.27 g, 16% yield on 3). ¹H NMR (500 MHz, THF-*d*₈, TMS): δ 1.15 (s, 18H, Me), 1.45 (s, 36H, Me), 3.45 (s, 12H, dioxane), 7.60 (s, 4H, Ar-H). ¹³C NMR (500 MHz, THF-*d*₈): 29.90 (s, Me), 32.60 (s, Me), 33.10 (s, C-Me), 36.20 (s, C-Me), 65.33 (s, dioxane), 120.72 (s, Ar-C), 143.00 (d, ²J_{PC} = 44.1 Hz, Ar-C), 144.08 (d, ³J_{PC} = 2.1 Hz, Ar-C), 145.11 (s, Ar-C), 229.78 (d, ¹J_{PC} = 89.9 Hz, C=P). ³¹P NMR (500 MHz, THF-*d*₈): δ 117.24 (s, 1P). The structure was determined by X-ray analysis. The third crop of crystals was a cesium salt of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-4H-[1,2,4]triphosphole (12) as white crystals with mp at 230-235°C (decomposition), (1.80 g, 18% yield on 3). ¹H NMR (500 MHz, THF-*d*₈, TMS): δ 1.12 (s, 18H, Me), 1.39 (s, 36H, Me), 3.45 (s, 16H, dioxane), 7.60 (s, 4H, Ar-H). ³¹P NMR (500 MHz, THF-*d*₈): δ 287.55 (t, ²J_{PP} = 36.7 Hz, 1P), 267.87 (d, ²J_{PP} = 36.7 Hz, 2P). The structure was determined by X-ray analysis. The fourth crop of crystals obtained after the partial evaporation of dioxane was the cesium salt of 5-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,3,4]tetraphosphole (13) as light yellow crystals with mp at 243-244°C (decomposition), (3.73 g, 24% yield on 3). ¹H NMR (500 MHz, THF-*d*₈, TMS): δ 1.44 (s, 18H, Me), 1.50 (s, 9H, Me), 3.52 (s, 48H, 6 molecules of dioxane), 7.65 (br, 2H, Ar-H). ¹³C NMR (500 MHz, THF-*d*₈, selected signals): 210.50 (tt, ¹J_{PC} = 81.9 Hz, ²J_{PC} = 9.1 Hz, C-P₄). ³¹P NMR (500 MHz, THF-*d*₈, AA'MM' spin system): δ 341.60 ppm for P_A and P_{A'} atoms and at 386.50 ppm for P_M and P_{M'} atoms, ¹J_{AA'} = -485.60 Hz, ³J_{MM'} = 52.20 Hz, ¹J_{AM} = -486.80 Hz, ²J_{AM'} = 2.00 Hz (simulated values). The structure of 13 was determined by X-ray analysis. The mother liquor from the above recrystallization was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The following fractions were collected in order of elution. The yield of [4,6-di-*tert*-butyl-2-(2,4,6-tri-*tert*-butyl-phenyl)-benzofuran-3-yloxy]-trimethyl-silane (9) was 3.03 g (13%) as colorless crystals with a mp of 198°C. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ 0.01 (s, 9H, Me-Si), 1.20 (s, 9H, Me), 1.25 (s, 9H, Me), 1.26 (s, 9H, Me), 1.35 (s, 9H, Me), 1.36 (s, 9H, Me), 7.30 (br, 2H, Ar-H), 7.75 (br, 2H, Ar-H). The structure was determined by X-ray analysis. The yield of [[hydroxy-(2,4,6-tri-*tert*-butyl-phenyl)-methylene]-phosphanyl]-(2,4,6-tri-*tert*-butyl-phenyl)-methanone was 1.85 g (8%) as yellow crystals with a mp of 230°C (decomposition). ¹H NMR (500 MHz, THF-*d*₈, TMS): δ 1.25 (s, 9H, Me), 1.40 (s, 18H, Me), 7.50 (s, 2H, Ar-H). ¹³C NMR (500 MHz, THF-*d*₈): 31.76 (s, Me), 32.83 (s, Me), 34.40 (s, C-Me), 35.60 (d, ⁴J_{PC} = 2.57 Hz, C-Me), 123.81 (s, Ar-C), 136.72 (d, ²J_{PC} = 26.0 Hz, Ar-C), 147.65 (d, ³J_{PC} = 4.2 Hz, Ar-C), 151.30 (s, Ar-C), 238.28 (d, ¹J_{PC} = 91.0 Hz, C=P). ³¹P NMR (500 MHz, THF-*d*₈): δ 122.63 (s, 1P). The structure was determined by X-ray analysis.

3,5-Bis-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,4]triphosphole (14). A 0.50 g (0.457 mmol) sample of the cesium salt of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-4H-[1,2,4]triphosphole (12) and 0.01 mL of water in 20 mL of dioxane were stirred for 5 min at ambient temperature. The reaction mixture was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The yield of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,4]triphosphole (14) was 0.23 g (81%) as orange crystals with a mp of 240°C (decomposition). ¹H NMR (500 MHz, toluene-*d*₈, TMS): δ 1.30 (s, 18H, Me), 1.42 (s, 36H, Me), 6.90 (d, ⁵J_{PH} = 1.0 Hz, 2H, Ar-H), 7.10 (d, ⁵J_{PH} = 1.0 Hz, 2H, Ar-H). ³¹P NMR (500 MHz, toluene-*d*₈, 30°C): δ 314.21 (br). ³¹P NMR (500 MHz, toluene-*d*₈, -81°C): δ 310.22 (s, 1P), 299.20 (d, ¹J_{PP} = 405.9 Hz, 1P), 76.40 (dd, ¹J_{PP} = 405.9 Hz, ¹J_{PH} = 128.2 Hz, 1P). 3,5-Bis-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,4]triphosphole (14) was identified by mass-spectrometry (ASAP method), which gave MH⁺ ion at 608.38, corresponding to C₃₈H₅₉P₃. The structure was determined by X-ray analysis.

Cesium salt of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-4H-[1,2,4]triphosphole (12). A 0.05 g (0.0821 mmol) sample of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,4]triphosphole (14) and 0.109 g (0.082 mmol) of metallic cesium in 10 mL of dioxane were stirred for 36 hours at ambient temperature. The reaction mixture was concentrated in vacuum to 5 mL. The resultant white crystals were filtered off. The yield of the cesium salt of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-4H-[1,2,4]triphosphole (12) was 0.070 g (78%). The NMR data and mp were identical to those reported above.

3,5,3',5'-Tetrakis-(2,4,6-tri-*tert*-butyl-phenyl)-[1,1']bi[[1,2,4]triphospholyl] (15). A 1.5 g (2.45 mmol) sample of 3,5-bis-(2,4,6-tri-*tert*-butyl-phenyl)-1H-[1,2,4]triphosphole (14) was dissolved in 15 mL of methanol and left standing in air for 12 hours. The progress of the oxidation was monitored by mass-spectrometry. The resultant red-pink crystals were filtered. The yield of 3,5,3',5'-tetrakis-(2,4,6-tri-*tert*-butyl-phenyl)-[1,1']bi[[1,2,4]triphospholyl] (15) was 0.87 g (58%) as a red-pink crystals with a mp of 205°C (decomposition). 15 is paramagnetic when dissolved in commonly used solvents. 3,5,3',5'-Tetrakis-(2,4,6-tri-*tert*-butyl-phenyl)-[1,1']bi[[1,2,4]triphospholyl] (15) was identified by mass-spectrometry (ASAP method), which gave an M⁺ ion at 1214.75, corresponding to C₇₆H₁₁₆P₆. The structure was determined by X-ray analysis. The mother liquor gave additionally 0.15 g (21%) of 2,4,6-tri-*tert*-butyl-benzoic acid (16) as colorless crystals, with a mp of 275°C. ¹H NMR (500 MHz, CDCl₃, TMS): δ 1.20 (s, 9H, Me), 1.50 (s, 18H, Me), 7.40 (s, 2H, Ar-H). ¹³C NMR (500 MHz, CDCl₃): 29.74 (s, Me), 32.27 (s, Me), 35.8 (s, C-Me), 37.05 (s, C-Me), 122.20 (s, Ar-C), 127.53 (s, Ar-C), 146.40 (s, Ar-C), 150.72 (s, Ar-C), 179.85 (s, C=O).

ESR Experimental: ESR spectra were obtained on a Bruker EleXsys E-500 spectrometer operating at X-band frequency (~9.4 GHz). For the experiments in toluene-*d*₈, 1024 points were acquired over a sweep width of 250 G in 167 s. Microwave power 20 mW, modulation amplitude 1.0 G, and receiver time constant of 82 ms were employed. For the experiment in tetrahydrofuran-*d*₈ (acquired at room temperature), 512 points were acquired over a sweep width of 150 G in 84 s. Microwave power 10 mW, modulation amplitude 1.0 G, and receiver time constant of 41 ms were employed. g factors were calibrated against a solution of DPPH in benzene.