Supplementary Material (ESI) for Chemical Communications

A Stable Enol In Small Ring Systems: Clear Differentiation Between Penta- and Tri-valency Of Phosphorus Atoms.

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Supporting Information

Syntheses of compounds: 2,3-Di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**). Lithium bis(trimethyl-silyl)phosphide as a bis(tetrahydrafuran) complex (**1**) (7.55 g (0.0226 mol) and 4.59 g (0.0226 mol) of *trans*-2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl chloride (**2**)[1] were mixed in 40 ml of pentane at the room temperature. After 3 days, the mixture was filtered and purified by the kugelrohr distillation collecting the fraction between 32 and 38ºC at 0.1 mm of Hg. Yield of 2,3-di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**) was 4.53 g (58%) as a viscous oil. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.10 (s, 9H, Me-Si), 0.20 (s, 9H, Me-Si), 1.00 (s, 9H, Me), 1.10 (s, 9H, Me), 2.20 (s, 1H, CH-P). ^{13}C NMR (500 MHz, CD_2Cl_2, TMS): δ - 1.76 (s, Me-Si), 0.00 (s, Me-Si), 29.92 (s, Me), 30.02 (s, Me), 32.88 (s, C-Me), 35.00 (s, C-Me), 43.52 (d, $^{2}J_{PC}$ = 10.1 Hz, HC-P), 134.34 (d, $^{2}J_{PC}$ = 13.9 Hz, C=C), 144.54 (d, $^{2}J_{PC}$ = 5.1 Hz, C=C). ^{31}P NMR (500 MHz, CD_2Cl_2): δ - 40.16 (s, 1P). 2,3-Di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**) was identified by the mass-spectrometry (ASAP method), which gave MH^+ ion at 345.21 corresponding to $C_{17}H_{38}OPSi_2$.

3,4-Di-*tert*-butyl-1-oxo-1,4-dihydro-1λ^5-phosphet-2-ol (**6**). 0.3 g of (0.00087 mol) of 2,3-di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**) was dissolved in 5 ml of methylene chloride and left on air for 3 weeks. The resultant crystals of 3,4-di-*tert*-butyl-1-oxo-1,4-dihydro-1λ^5-phosphet-2-ol (**6**) were formed quantitatively with m.p. 100 ºC. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 1.15 (s, 9H, Me), 1.19 (s, 9H, Me), 2.95 (dd, $^{2}J_{PH}$ = 14.7 Hz, $^{3}J_{HH}$ = 0.8 Hz, 1H, CH-P), 7.15 (dd, $^{1}J_{PH}$ = 495.6 Hz, $^{3}J_{HH}$ = 0.8 Hz, 1H, PH), O-H proton was not observed. ^{13}C NMR (500 MHz, CD_2Cl_2, TMS): δ 29.00 (d, $^{4}J_{PC}$ = 1.9 Hz, Me), 30.00 (d, $^{3}J_{PC}$ = 8.5 Hz, Me), 33.90 (d, $^{2}J_{PC}$ = 20.3 Hz, C-Me), 34.20 (d, $^{3}J_{PC}$ = 16.8 Hz, C-Me), 57.20 (d, $^{1}J_{PC}$ = 56.1 Hz, C-P), 134.30 (d, $^{2}J_{PC}$ = 14.1 Hz, C=C), 154.60 (d, $^{1}J_{PC}$ = 80.9 Hz, C=C). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 4.17 (d, $^{1}J_{PH}$ = 495.6 Hz, 1P). The structure was proven by X-ray analysis.

Pyrolysis of 2,3-di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**): Tris(trimethylsilyl)phosphine (**8**), 1,2,5,6-Tetra-*tert*-butyl-3,7-bis-trimethylsilanyloxy-1*H*,5*H*-[1,2]diphospholo[1,2-*a*][1,2]diphosphole (**7**) and 3,4-Di-*tert*-butyl-1-(2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (**9**). A 2.0 g (0.0058 mol) sample of 2,3-di-*tert*-butyl-1-trimethylsilanyl-4-trimethylsilanyloxy-1,2-dihydro-phosphete (**3**) was placed in the kugelrohr distillation apparatus. The two receiving bulbs were cooled by dry ice/acetone bath. Oven flask was heated to 180 °C at 1 mm of Hg and following fractions were collected.

Tris(trimethylsilyl)phosphine (**8**) was collected first at temperature interval 180 °C to 220 °C in oven. Yield of **8** was 0.34 g (23%) as colorless liquid, which solidified upon standing. ^{31}P NMR (500 MHz, CD_2Cl_2): δ - 250.00 (s, 1P). The second fraction of the pyrolysis (at temperature interval 220 °C to 260 °C in oven) crystallized upon standing yielding 1,2,5,6-tetra-*tert*-butyl-3,7-bis-trimethylsilanyloxy-1*H*,5*H*-[1,2]diphospholo[1,2-*a*][1,2]diphosphole (**7**). The yield of **7** was 0.49 g (31%) with m.p. 169-172ºC. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.30 (s, 18H, Me-Si), 1.10 (s, 9H, Me), 1.20 (s, 9H, Me), 2.60 (br, 2H, CH-P). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 1.54 (s, Me-Si), 31.10 (s, Me), 32.00 (t, $^{4}J_{PC}$+$^{5}J_{PC}$ = 8.3 Hz, Me), 34.40 (s, C-Me), 38.06 (t, $^{1}J_{PC}$+$^{2}J_{PC}$ = 8.9 Hz, C-Me), 53.25 (t, $^{1}J_{PC}$+$^{2}J_{PC}$ = 15.3 Hz, C-P), 137.69 (t, $^{2}J_{PC}$+$^{3}J_{PC}$ = 3.4 Hz, C=C), 158.70 (t, $^{1}J_{PC}$+$^{2}J_{PC}$ = 16.5 Hz, C=C). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 10.60 (s, 1P). The structure was proven by X-ray analysis. 3,4-Di-*tert*-butyl-1-(2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (**9**) was isolated after the chromatography of the residue from the above pyrolysis. The chromatography was done on silica gel with eluent with eluent 20% of ethyl ether and 80% of hexane. Compound **9** was additionally purified by the sublimation of the combined chromatographic fractions at 50 ºC and 5 mm for 1 week. The yield of 3,4-di-*tert*-butyl-1-(2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (**9**) was 0.49 g (60%). The sample starts to sublime at 41-43ºC and completely melts at 104-106ºC. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 0.98 (s, 9H, Me), 1.05 (s, 9H, Me), 1.10 (s, 9H, Me), 1.13 (s, 9H, Me), 2.85 (dd, $^{2}J_{PH}$ = 6.8 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH-P), 3.44 (dd, $^{3}J_{PH}$ = 2.4 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH), 5.50 (d, $^{4}J_{PH}$ = 1.2 Hz, 1H, C=C-H). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 29.00 (s, Me), 29.90 (d, $^{3}J_{PC}$ = 8.9 Hz, Me), 31.20 (d, $^{4}J_{PC}$ = 1.7 Hz, Me), 31.40 (d, $^{4}J_{PC}$ = 4.8 Hz, Me), 32.30 (d, $^{1}J_{PC}$ = 17.4 Hz, C-H), 33.90 (s, C-Me), 35.05 (d, $^{2}J_{PC}$ = 6.9 Hz, C-Me), 36.30 (d, $^{3}J_{PC}$ = 1.5 Hz, C-Me), 38.90 (d, $^{3}J_{PC}$ = 5.0 Hz, C-Me), 77.90 (d, $^{2}J_{PC}$ = 21.2 Hz, C-H), 139.10 (d, $^{3}J_{PC}$ = 1.7 Hz, C=C), 149.50 (d, $^{2}J_{PC}$ = 32.5 Hz, C=C), 211.10 (d, $^{1}J_{PC}$ = 29.5 Hz, C=O), 211.50 (d, $^{1}J_{PC}$ = 76.3 Hz, C=O). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 104.00 (s, 1P). The structure was proven by X-ray analysis.

2-*tert*-Butyl-1-(2,3-di-*tert*-butyl-4-hydroxy-1-oxo-1,2-dihydro-1λ^5-phosphet-1-yl)-4,4-dimethyl-pent-2-en-1-one (**10**). 1.63 g (0.0045 mol) sample of 3,4-di-*tert*-butyl-1-(2-*tert*-butyl-4,4-dimethyl-pent-2-enoyl)-phosphetan-2-one (**9**) and 0.85 g (0.0089 mol) of pyridine-*N*-oxide were stirred in 20 ml of toluene at 90 ºC for 2 weeks. Then solvent was removed in vacuo at 1 mmHg, and the residue was purified by the chromatography on silica gel with the eluent petroleum ether/ethyl ether, 10:2. Yield of 2-*tert*-butyl-1-(2,3-di-*tert*-butyl-4-hydroxy-1-oxo-1,2-dihydro-1λ^5-phosphet-1-yl)-4,4-dimethyl-pent-2-en-1-one (**10**) was 0.27 g (16%) as colorless crystals with m.p. 70 ºC (decomposition). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 1.05 (s, 9H, Me), 1.10 (s, 9H, Me), 1.15 (s, 9H, Me), 1.25 (s, 9H, Me), 3.10 (br, 1H, CH-P), 5.56 (s, 1H, C=C-H), O-H proton was not observed. ^{13}C NMR (500 MHz, CD_2Cl_2, selected signals): δ 218.00 (d, $^{1}J_{PC}$ = 53.9 Hz, P-C=O). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 17.9 (s, 1P). The structure was proven by X-ray analysis.

1 A. S. Ionkin, W. J. Marshall, B. M. Fish, *Org. Lett.* 2008, **10**, 2303.