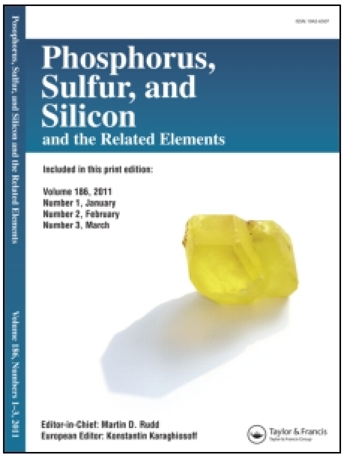

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Heike Hund[a]; Gerd-Volker Röschenthaler[a]
[a] Institut für Anorganische und Physikalische Chemie, Bremen, Federal Republic of Germany

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1,3,2-$\lambda^5\sigma^5$-DIAZAPHOSPHOLENES: VERSATILE REACTANTS

HEIKE HUND and GERD-VOLKER RÖSCHENTHALER†
Institut für Anorganische und Physikalische Chemie, Fachbereich 2 der Universität, Leobener Straße, D-2800 Bremen, Federal Republic of Germany

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In an oxidative addition reaction O,O′-*bis*(trimethylsilyl)diacetyldioxime **2** and triethylphosphite give 1,3,2-$\lambda^5\sigma^5$-diazaphospholene **3a** which hydrolyzes to form (Z)-2,3-*bis*(hydroxylamino)-2-butene **4**. Benzaldehyde and **4** condensate to furnish 1,3-dihydroxy-4,5-dimethyl-2-dimethyl-4-imidazoline **5**. *Tris*(trimethylsilyl)phosphite and **2** react to give the first *tris*(trimethylsiloxy)phosphorane **3b**.

Key words: O,O′-*Bis*(trimethylsilyl)diacetyldioxime; 1,3,2-$\lambda^5\sigma^5$-diazaphospholenes; (Z)-2,3-*bis*(hydroxylamino)-2-butene, 1,3-dihydroxy-4,5-dimethyl-2-phenyl-4-imidazoline.

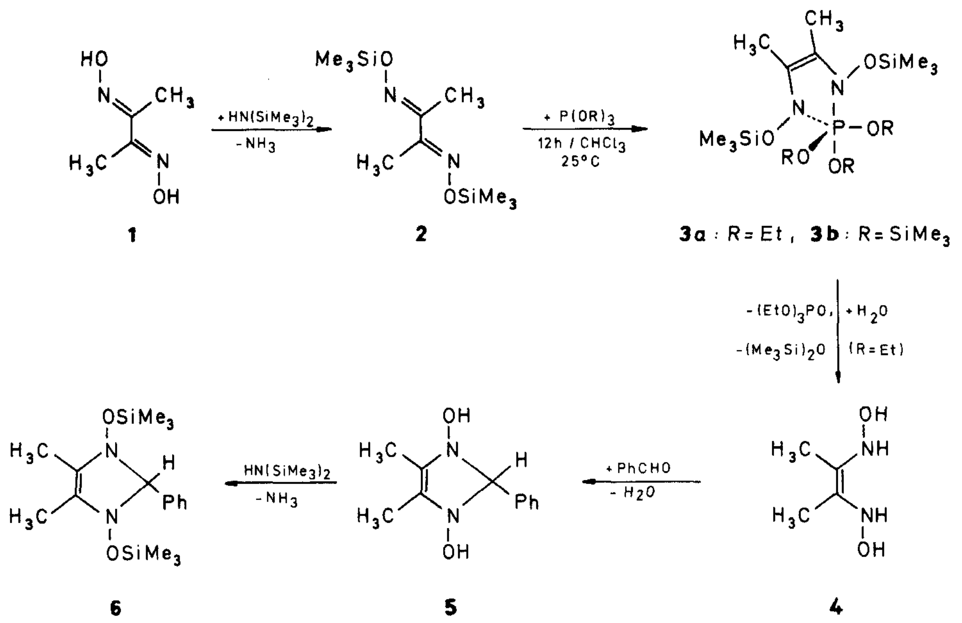
INTRODUCTION

Diacetyldioxime **1** is used frequently as a bidendate ligand in the analytical chemistry of nickel, cobalt and bismuth.[1] There is no report yet about chelating phosphorus resulting in the formation of a new 1,3,2-diazaphospholene ring system which may be a versatile precursor for (Z)-2,3-*bis*(hydroxylamino)-2-butene. Since the parent compound of **1**, butene-2,3-dione and appropriate phosphites furnished 1,3,2-dioxaphospholenes[2] we studied the behavior of compound **1** in order the obtain cyclic phosphoranes, too.

RESULTS AND DISCUSSION

We had no success in synthesizing the expected heterocycle using diacetyldioxime[3] but most striking after O,O′-silylation of **1**, triethylphosphite and *tris*(trimethylsilyl)phosphite were added to yield the liquid 1,3-*bis*(trimethylsiloxy)-4,5-dimethyl-1,3,2-$\lambda^5\sigma^5$-diazaphospholenes **3a** and **3b**. Phosphorane **3b**, to our knowledge represents the first *tris*(trimethylsiloxy) phosphorane stable at ambient temperature.

Both phospholenes showed no parent ion peak in their 70 eV mass spectra but the fragment $[M—CH_3]^+$. In the ^{13}C NMR spectra the expected upfield shift[4] for the sp^2 carbon was observed [**2**: δ = 177.0 ($\underline{C}$=NOSi), **3a**: δ = 158.0 ($\underline{C}$=$\underline{C}$—NO, $^2J_{PC}$ = 32.0 Hz), **3b**: δ = 152.0 ($\underline{C}$=$\underline{C}$—NO, $^2J_{PC}$ = 37.7 Hz)]. The ^{31}P resonances are found in the region typical for penta-coordinate phosphorus (**3a**: δ = −18.0, **3b**: δ = −36.0).[5] Hydrolysis of **3a** gave rise to the solid new (Z)-2,3-*bis*(hydroxylamino)-2-butene **4**, a potential chelating ligand in coordination chemistry, and precursor for imidazolines: *e.g.* benzaldehyde and **4** yielded the colorless,



Scheme 1.

N,N′ functionalized 4,5-dimethyl-2-phenyl-4-imidazoline **5** (Scheme I) which could be O,O′-silylated to form **6** using hexamethyldisilazane.

In the ^1H NMR spectrum of **4** N$\underline{H}$ and NO$\underline{H}$ resonances are well separated (δ = 4.25 and 9.20).[6] The resonances for the carbon nuclei of **5** and **6** in 2-position were found at δ = 147.8 and 148.2 respectively.[7]

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work. Elemental analysis: Mikroanalytisches Laboratorium Beller, Göttingen. MS: MAT 8222 spectrometer (El-ionization, electron energy 70 eV. IR: Nicolet 5 DX FT spectrometer, spectra were recorded either as KBr pellets or as films between NaCl plates. NMR: AC80 and WH 360 Bruker spectrometer, operating at 80.13 MHz (^{19}F, internal standard CCl_3F), 32.44 MHz (^{31}P, external standard 85% H_3PO_4) and 90.54 MHz (^{13}C, internal standard TMS). The phosphite $(Me_3SiO)_3P$ was synthesized by literature procedure.[8]

Butane-2,3-dione-bis(O,O′-trimethylsilyloxime) (**2**): Compound **1**, and 6.3 g (50 mmol) of hexamethyldisilazane were heated at 115°C until the evolution of ammonia ceased. Upon cooling the yellow liquid turned solid and was sublimed (25°C/0.01 Torr). Yield of compound **2**: 83%, m.p. 152°C. MS: *m/z* (%): 260 (20) [M$^+$], 245 (10) [M$^+$ − CH_3], 147 (100) [$(CH_3)_5Si_2O^+$), 73 (70) [$(CH_3)_3Si^+$], 59 (35) [CH_3NOH^+], 41 (6) [CH_3CN^+]. IR: $\tilde{\nu}$ = 1685 cm^{-1} *m* (C=N). NMR: ^1H ($CDCl_3$): δ = 0.15 (*s*, 18H, $Si(CH_3)_3$), 1.90 (*s*, 6H, CH_3); ^{13}C ($CDCl_3$): δ = −0.2 (9, $Si(CH_3)_3$, $^1J_{CH}$ = 121.3 Hz), 30.0 (*q*, CH_3, $^1J_{CH}$ = 117.3 Hz), 177.0 (*q*, C=NOSiMe$_3$, *J* = 5.4 Hz).

$C_{10}H_{24}N_2O_2Si_2$ (260.48)	Calcd:	C 46.20	H 9.22
	Found:	C 46.15	H 9.23

2,2,2-Triethoxy-1,3-bis(trimethylsiloxy)-4,5-dimethyl-1,3,2λ^{5}σ^5-diazaphospholene (**3a**): Compound **2** (13.0 g, 50 mmol) and 8.3 g (50 mmol) of triethylphosphite were reacted in 20 ml $CHCl_3$ at 25°C for 12 h. After pumping off the solvent the liquid phosphorane **3a** was obtained analytically pure in 100% yield.[9]

MS: *m*/*z* (%): 411 (5) $[M^+ - CH_3]$, 264 (15) $[M^+ - (CH_3)_6Si_2O]$, 147 (100) $[(CH_3)_5Si_2O^+]$, 137 (15) $[(C_2H_5O)_2PO^+]$, 130 (25) $[CH_3CNOSi(CH_3)_3^{+}]$, 73 (15) $[(CH_3)_3Si^+]$. IR: $\tilde{\nu}$ = 1660 cm^{-1} *m* (C═C). NMR: ^{1}H ($CDCl_3$): δ = 0.23 (*s*, 18H, $Si(CH_3)_3$), 1.20 (*t*, 9H, $CH_2C\underline{H}_3$, $^3J_{HH}$ = 7.4 Hz), 1.90 (*s*, 6H, CH_3), 3.50 (*dq*, 6H, $^3J_{PH}$ = 8.0, $^3J_{HH}$ = 4.0 Hz, CH_2); ^{13}C ($CDCl_3$): δ = −0.2 (*q*, $Si(CH_3)_3$, $^1J_{CH}$ = 124.2 Hz), 17.0 (*q*, $CH_2\underline{C}H_3$, $^1J_{CH}$ = 119.2 Hz), 32.0 (*q*, CH_3, $^1J_{CH}$ = 117.3 Hz), 57.0 (*t*, CH_2, $^1J_{CH}$ = 127.3 Hz), 158.0 (*dq*, $=\underline{C}(CH_3)$, $^2J_{PC}$ = 32.0, $^2J_{CH}$ = 7.0 Hz; ^{31}P ($CDCl_3$): δ = −18.0.

$C_{16}H_{39}N_2O_5PSi_2$ (426.64)	Calcd:	C 45.07	H 9.15	P 7.28
	Found:	C 44.48	H 8.89	P 6.98

1,2,2,2,3-Pentakis(trimethylsiloxy)-4,5-dimethyl-1,3,2λ⁵σ⁵-diazaphospholene (**3b**): Compound **2** (13.0 g, 50 mmol) and (14.9 g, 50 mmol) *tris*(trimethylsilyl)phosphite were reacted in 20 ml $CHCl_3$ at 25°C for 12 h. After pumping off all volatiles the liquid phosphorane **3b** was obtained analytically pure in 100% yield.[9] MS: *m*/*z* (%): 543 (15) $[M^+ - CH_3]$, 502 (20) $[M^+ - (CH_3)_2C{=}CH_2]$, 469 (25) $[M^+ - OSi(CH_3)_3]$, 369 (15) $[M^+ - (CH_3)_6Si_2O]$, 299 (32) $[[(CH_3)_3Si,O]_3PH^+]$, 147 (100) $[(CH_3)_5Si_2O^+]$, 130 (35) $[CH_3CNOSi(CH_3)_3^{+}]$, 89 (65) $[OSi(CH_3)_3^{+}]$, 73 (50) $[Si(CH_3)_3^{+}]$, 56 (15) $[(CH_3)_2\ C{=}CH_2^{+}]$. IR: $\tilde{\nu}$ = 1635 cm^{-1} *m* C═C. NMR: ^{1}H ($CDCl_3$): δ = 0.25 (*s*, 18H, $Si(CH_3)_3$) and 0.27 (*s*, 27H, $Si(CH_3)_3$), 2.30 (*s*, 6H, CH_3); ^{13}C ($CDCl_3$): δ = −0.2 (*q*, $NOSi(CH_3)_3$, $^1J_{CH}$ = 124.3 Hz], 0.2 (*q*, $POSi(CH_3)_3$, $^1J_{CH}$ = 125.0 Hz), 25.0 (*q*, CH_3, $^1J_{CH}$ = 116.2 Hz), 152.0 (*dq*, $=\underline{C}(CH_3)$, $^2J_{PC}$ = 31.7 Hz, $^2J_{CH}$ = 7.2 Hz); ^{31}P ($CDCl_3$): δ = −36.0.

$C_{19}H_{51}N_2O_5PSi_5$ (558.02)	Calcd:	C 40.80	H 9.17	P 5.50
	Found:	C 39.84	H 8.89	P. 5.78

(Z)-2,3-Bis(hydroxylamino)-2-butene (**4**): Phosphorane **3a** (4.3 g, 10 mmol) and 0.5 g water were stirred at 25°C for 12 h. The white solid formed was separated from the solution by filtration, washed three times using 2 ml $CHCl_3$ and sublimed (40°C/0.01 Torr). Yield of compound **4**: 0.7 g, 61%, m.p. 238°C. MS: *m*/*z* (%): 103 (10) $[M^+ - CH_3]$, 87 (25) $[M^+ - NOH]$, 59 (15) $[C_2H_5NO^+]$, 57 (100) $[C_2H_3NO^+]$, 41 (65) $[C_2H_3N^+]$. IR: $\tilde{\nu}$ = 3129 cm^{-1} broad (O—H and N—H), 3029 *m* (C—H), 1750 *m* (C═C). NMR: ^{1}H ($CDCl_3$): δ = 2.90 (*s*, 6H, CH_3), 4.25 (*s*, 2H, NH), 9.20 (*s*, 2H, NOH); ^{13}C ($CDCl_3$): δ = 48.5 (*q*, CH_3, $^1J_{CH}$ = 119.2), 153.8 (*qd*, C═C, $^2J_{CH}$ = 6.02 Hz, $^2J_{CH}$ = 1.7 Hz).

$C_4H_{10}N_2O_2$ (118.14)	Calcd:	C 40.76	H 8.53
	Found:	C 41.05	H 8.53

1,3-Dihydroxy-4,5-dimethyl-2-phenyl-4-imidazoline (**5**): Compound **4** (9.5 g, 80 mmol) and 8.6 g (80 mmol) of benzaldehyde were held for 8d at 45°C. After fractionational distillation at 62°C/15 Torr, 14.1 g (78%) of **5** was obtained. MS: *m*/*z* (%): 207 (15) $[M^+ + H]$, 206 (15) $[M^+]$, 145 (20) $[(CH_3C)_2NOH^+]$, 127 (10) $[M^+ - C_6H_7^{+}]$, 91 (100) $[C_7H_7^{+}]$, 78 (40) $[C_6H_6^{+}]$. IR: $\tilde{\nu}$= 3279 cm^{-1} *m* (O—H), 1642 *m* (C═C). NMR: ^{1}H ($CDCl_3$): δ = 2.40 (*s*, 6H, CH_3), 3.20 (*s*, 1H, CH), 6.90–7.60 (*m*, 5H, C_6H_5), 7.85 (*s*, 2H, NOH); ^{13}C ($CDCl_3$): δ = 31.0 (*q*, CH_3, $^1J_{CH}$ = 119.2 Hz), 124.9 (*d*, C_6H_5, C-4), 125.2 (*d*, C_6H_5, C-2), 127.9 (*d*, C_6H_5, C-3), 143.5 (*s*, C_6H_5, C-1), 147.8 (*d*, CH, $^1J_{CH}$ = 109.0 Hz), 158.5 (*q*, C═C, $^2J_{CH}$ = 6.2 Hz).

$C_{11}H_{14}N_2O_2$ (206.24)	Calcd:	C 64.07	H 6.80
	Found:	C 63.67	H 6.65

1,3-Bis(trimethylsiloxy)-4,5-dimethyl-2-phenyl-4-imidazoline (**6**): Imidazoline **5** (1.0 g, 5 mmol) and 0.8 g (5 mmol) of hexamethyldisilazane were held at 25°C for 16 h. After pumping of all volatiles the resulting solid **6** was sublimed at 25°C/0.001 Torr. The yield was 0.7 g (68%), m.p. 152°C. MS: *m*/*z* (%): 350 (15) $[M^+]$, 271 (10) $[M^+ - C_6H_7^{+}]$, 217 (20) $[(CH_3C)_2NOSi(CH_3)_3^{+}]$, 147 (100) $[(CH_3)_5Si_2O^+]$, 91 (75) $[C_7H_7^{+}]$, 89 (60) $[OSi(CH_3)_3^{+}]$, 82 (25) $[C_4H_6N_2^{+}]$, 79 (30) $[Si(CH_3)_3^{+}]$, 78 (40) $[C_6H_6^{+}]$, 56 (15) $[C_4H_8^{+}]$, 41 (25) $[CH_3CN^+]$. IR: $\tilde{\nu}$= 1635 cm^{-1} (C═C). NMR: ^{1}H ($CDCl_3$): δ = 0.35 (*s*, 9H, $Si(CH_3)_3$), 2.40 (*s*, 6H, CH_3), 2.97 (*s*, 1H, CH), 6.50–7.60 (*m*, 5H, C_6H_5); ^{13}C ($CDCl_3$): δ = 0.15 (*q*, $Si(CH_3)_3$, $^1J_{CH}$ = 124.2 Hz), 32.0 (*q*, CH_3, $^1J_{CH}$ = 119.2 Hz), 125.1 (*d*, C_6H_5, C-4), 126.3 (*d*, C_6H_5, C-2), 128.2 (*d*, C_6H_5, C-3), 144.2 (*s*, C_6H_5, C-1), 148.2 (*d*, CH, $^2J_{CH}$ = 112.1 Hz), 162.1 (*s*, C═C).

$C_{17}H_{30}N_2O_2Si_2$ (350.61)	Calcd:	C 58.28	H 8.87
	Found:	C 58.86	H 8.88

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