

Electronic Supplementary Information

A novel route to C-unsubstituted 1,2-oxaphosphetane and 1,2-oxaphospholane complexes

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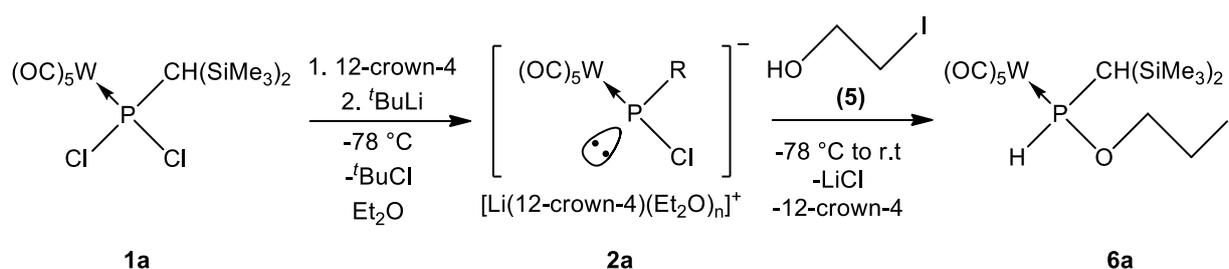
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Experimental section

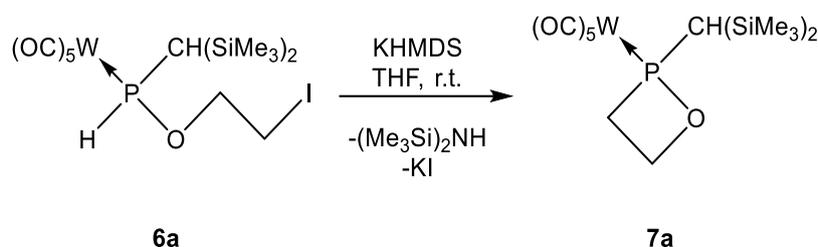
General procedures. All operations were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire/benzophenone and further purified by subsequent distillation. All NMR spectra were recorded on a Bruker AX-300 spectrometer (300.1 MHz for ^1H , 75.5 MHz for ^{13}C , 59.6 MHz for ^{29}Si and 121.5 MHz for ^{31}P). The ^1H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus, they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. IR spectra of all compounds were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment. The X-ray analyses were performed on a Bruker APEX-II CCD, Bruker D8-Venture or a Bruker X8-KappaApexII type diffractometer at 100(2) K. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97^[1] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1470388 (**6a**), CCDC-1470387 (**7a**), CCDC-1483069 (**12**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



Preparation of 6a. In a Schlenk tube, 1.0 mmol of the dichlorophosphane complex **1a** was dissolved in 20 mL of diethyl ether. To it 0.16 mL (1.0 mmol) of 12-crown-4 was added at ambient temperature and the mixture was cooled to $-78\text{ }^\circ\text{C}$. Then 0.64 mL (1.1 mmol, 1.7 M in *n*-hexane) of *t*-BuLi was added upon which a change to a light yellow color was observed. It was kept on stirring for 10 minutes. Subsequently 1.03 mmol of 2-iodoethanol (0.08 mL, 1.03 eq) was added and the mixture was stirred while slowly warming up to room temperature. After the reaction was completed (checked by ^{31}P NMR), all volatiles were removed *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar). The crude mixture was extracted with *n*-pentane and the solvent was removed *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar) to yield **6a** as yellow oil.

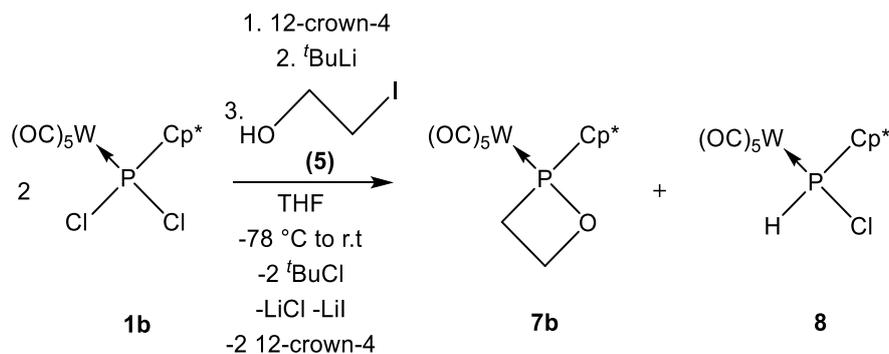
Complex 6a: Yield: (0.624 g, 0.91 mmol, 91%). ^1H NMR (300.1 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ = 0.22 (s, 9 H, SiMe_3), 0.30 (s, 9 H, SiMe_3), 0.95 (s, 1 H, P-CH), 3.30 (dd, 2 H, $^3J_{\text{H,H}} = 6.0$ Hz, $^3J_{\text{H,H}} = 6.0$ Hz, $\text{CH}_2\text{-I}$), 3.73 – 3.91 (m, 1 H, P- OCH_2), 4.00 – 4.18 (m, 1 H, P- OCH_2), 7.96 (dd, 1 H,

$^1J_{P,H} = 321.4$ Hz, $^3J_{H,H} = 1.20$ Hz, P-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 25 °C): $\delta = 0.4$ (d, $^3J_{P,C} = 2.3$ Hz, SiMe₃), 1.3 (d, $^3J_{P,C} = 9.1$ Hz, CH₂-I), 2.4 (d, $^3J_{P,C} = 3.2$ Hz, SiMe₃), 23.7 (d, $^1J_{P,C} = 13.6$ Hz, P-CH), 70.0 (d, $^2J_{P,C} = 2.6$ Hz, P-OCH₂), 196.6 (d_{sat}, $^1J_{W,C} = 125.1$ Hz, $^2J_{P,C} = 7.4$ Hz, *cis*-CO), 199.1 (d, $^2J_{P,C} = 25.2$ Hz, *trans*-CO). ^{29}Si (59.6 MHz, CDCl_3 , 25 °C) $\delta = 0.89$ (d, $^2J_{P,Si} = 5.8$ Hz), 2.61 (d, $^2J_{P,Si} = 9.2$ Hz). ^{31}P NMR (121.5 MHz, CDCl_3 , 25 °C): $\delta = 106.7$ (d_{sat}, $^1J_{W,P} = 270.3$ Hz, $^1J_{P,H} = 321.4$ Hz). IR (ATR, $\tilde{\nu}$ [cm^{-1}]): $\tilde{\nu} = 2263$ (w, $\nu(\text{PH})$), 2071 (s, $\nu(\text{CO})$), 1981 (w, $\nu(\text{CO})$), 1904 (vs, $\nu(\text{CO})$). MS (EI, 70 eV): m/z (%) = 686.0 (15) [M^{*+}], 657.9 (10) [M-CO^+], 602.0 (20) [M-3CO^+], 574.0 (30) [M-4CO^+], 546.0 (25) [M-5CO^+], 73.1 (100) [SiMe_3^+].



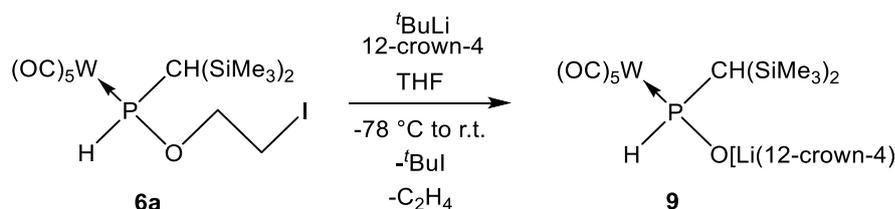
Preparation of 7a. In a Schlenk tube, 1.26 mmol of complex **6a** were dissolved in 30 mL of THF. To it 315 mg (1.58 mmol) of potassium hexamethyldisilazide in 3 mL THF were added drop wise at room temperature. The solution was kept on stirring for 1h. During addition a rapid formation of precipitate and a change of the colour to yellow-brown was observed. All volatiles were removed *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar). The product was purified by extraction with *n*-Pentane (4 times 20 mL) and subsequent precipitation from and washing with *n*-pentane at -100 °C (4 times 5 mL). Complex **7a** was obtained as white powder after drying *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar).

Complex 7a: Yield: (0.457 g, 0.819 mmol, 65 %), melting point: 77 °C. ^1H NMR (300.1 MHz, C_6D_6 , 25 °C): $\delta = 0.08$ (d, $^4J_{P,H} = 0.4$ Hz, 9H, SiMe₃), 0.16 (s, 9 H, SiMe₃), 2.00 (d, 1 H, $^2J_{P,H} = 8.8$ Hz, PCH), 2.64 (ddd, 1 H, $^2J_{H,H} = 13.3$ Hz, $^3J_{H,H} = 8.2$ Hz, $^3J_{H,H} = 5.0$ Hz, CH₂), 2.98 (dddd, 1 H, $^2J_{P,H} = 13.0$ Hz, $^2J_{H,H} = 13.3$ Hz, $^3J_{H,H} = 10.2$ Hz, $^3J_{H,H} = 8.2$ Hz, CH₂), 4.04 (dddd, 1 H, $^3J_{P,H} = 4.5$ Hz, $^3J_{H,H} = 10.2$ Hz, $^2J_{H,H} = 7.5$ Hz, $^3J_{H,H} = 5.0$ Hz, CH₂), 4.48 (dddd, 1 H, $^3J_{P,H} = 4.5$ Hz, $^3J_{H,H} = 8.2$ Hz, $^3J_{H,H} = 8.2$ Hz, $^2J_{H,H} = 7.5$ Hz, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , 25 °C): $\delta = 1.7$ (d, $^3J_{P,C} = 4.2$ Hz, SiMe₃), 2.1 (d, $^3J_{P,C} = 2.6$ Hz, SiMe₃), 35.4 (d_{broad}, CH₂), 38.5 (d, $^1J_{P,C} = 14.6$ Hz, PCH), 68.9 (d, $^2J_{P,C} = 15.2$ Hz, PCH₂), 197.5 (d_{sat}, $^1J_{W,C} = 125.8$ Hz, $^2J_{P,C} = 7.8$ Hz, *cis*-CO), 200.7 (d, $^2J_{P,C} = 25.2$ Hz, *trans*-CO). ^{29}Si (59.6 MHz, C_6D_6 , 25 °C) $\delta = 0.05$ (d, $^2J_{P,Si} = 6.0$ Hz), - 2.52 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , 25 °C): $\delta = 190.3$ ppm (s_{sat}, $^1J_{W,P} = 267.7$ Hz). IR (ATR, $\tilde{\nu}$ [cm^{-1}]): $\tilde{\nu} = 2071$ (s, $\nu(\text{CO})$), 1992 (w, $\nu(\text{CO})$), 1908 (vs, $\nu(\text{CO})$). MS (EI, 70 eV): m/z (%) = 558.1 (50) [M^{*+}], 502.1 (20) [M-2CO^+], 474.1 (30) [M-3CO^+], 446.0 (20) [M-4CO^+], 418.0 (40) [M-5CO^+], 390.0 (100) [$\text{M-5CO-C}_2\text{H}_4^+$], 73.1 (70) [SiMe_3^+]. EA: calc. for $\text{C}_{14}\text{H}_{23}\text{O}_6\text{P}_2\text{Si}_2\text{W}$: C 30.12, H 4.15 found: C 30.28, H 4.30.



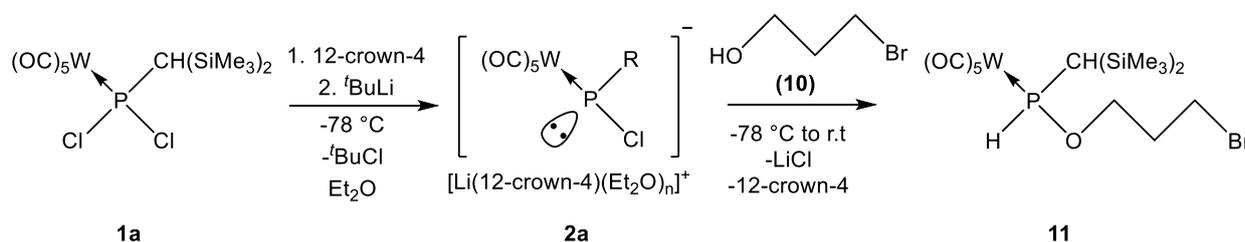
Preparation of 7b. In a Schlenk tube, 841.5 mg (1.5 mmol) of complex **1b** were dissolved in 60 mL of THF. To it 0.24 mL (1.5 mmol) of 12-crown-4 was added at ambient temperature and the mixture was cooled to -78 °C. Then 0.96 mL (1.63 mmol, 1.7 M in *n*-hexane) of *t*-BuLi was added upon which a change to a light yellow color was observed. It was kept on stirring for 10 minutes. Subsequently 2.58 mmol of 2-iodoethanol (0.2 ml, 1.7 eq) was added and the mixture was stirred while slowly warming up to room temperature. After the reaction was completed (checked by ^{31}P NMR), all volatiles were removed in vacuo ($\sim 2 \cdot 10^{-2}$ mbar). The crude mixture was purified by low temperature column chromatography ($\varnothing = 2\text{cm}$, $h = 5\text{ cm}$, PE, SiO_2 , -20 °C) and obtained, after a first yellow fraction was separated with pure petrolether, as orange fraction using petrolether and diethyl ether (ratio 50 : 0.5). After removing of all volatiles *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar), the product was sublimed (1 h, 110° C, $2.6 \cdot 10^{-2}$ mbar) and complex **7b** was obtained as slightly orange solid.

Complex 7b: Yield: (0.160 g, 0.29 mmol, 40 %), melting point: 59-60 °C. ^1H NMR (300.1 MHz, CDCl_3 , 25 °C): $\delta = 1.74$ (d, $J_{\text{P,H}} = 11.0$ Hz, 3 H, C_5Me_5), 1.75 (s, 3 H, C_5Me_5), 1.80 (dq, $J_{\text{P,H}} = 5.0$ Hz, $J_{\text{H,H}} = 1$ Hz, 3 H, C_5Me_5), 1.82 (dq, $J_{\text{P,H}} = 4.3$ Hz, $J_{\text{H,H}} = 1.0$ Hz, 3 H, C_5Me_5), 1.93 (s, 3 H, C_5Me_5), 3.34 (dddd, 1 H, $^2J_{\text{P,H}} = 0.4$ Hz, $^2J_{\text{H,H}} = 13.8$ Hz, $^3J_{\text{H,H}} = 9.2$ Hz, $^3J_{\text{H,H}} = 6.6$ Hz, CH_2), 3.63 (dddd, 1 H, $^2J_{\text{P,H}} = 5.3$ Hz, $^2J_{\text{H,H}} = 13.8$ Hz, $^3J_{\text{H,H}} = 9.7$ Hz, $^3J_{\text{H,H}} = 6.5$ Hz, CH_2), 5.05 (dddd, 1 H, $^3J_{\text{P,H}} = 2.2$ Hz, $^2J_{\text{H,H}} = 7.1$ Hz, $^3J_{\text{H,H}} = 9.7$ Hz, $^3J_{\text{H,H}} = 6.6$ Hz, CH_2), 5.16 (dddd, 1 H, $^3J_{\text{P,H}} = 3.3$ Hz, $^2J_{\text{H,H}} = 7.1$ Hz, $^3J_{\text{H,H}} = 9.2$ Hz, $^3J_{\text{H,H}} = 6.5$ Hz, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 25 °C): $\delta = 11.5$ (d, $J_{\text{P,C}} = 2.8$ Hz, C_5Me_5), 11.5 (d, $J_{\text{P,C}} = 1.5$ Hz, C_5Me_5), 11.7 (d, $J_{\text{P,C}} = 1.5$ Hz, C_5Me_5), 11.8 (d, $J_{\text{P,C}} = 2.0$ Hz, C_5Me_5), 13.2 (d, $^2J_{\text{P,C}} = 4.8$ Hz, C_5Me_5), 32.2 (d, $^1J_{\text{P,C}} = 23.5$ Hz, P- CH_2), 65.4 (d, $^1J_{\text{P,C}} = 2.9$ Hz, P- C_5Me_5), 73.1 (d, $^2J_{\text{P,C}} = 13.7$ Hz, P- CH_2), 132.7 (d, $J_{\text{P,C}} = 7.3$ Hz, C_5Me_5), 138.9 (d, $J_{\text{P,C}} = 1.7$ Hz, C_5Me_5), 141.4 (d, $J_{\text{P,C}} = 5.9$ Hz, C_5Me_5), 143.4 (d, $J_{\text{P,C}} = 7.0$ Hz, C_5Me_5), 196.1 (d_{sat} , $^1J_{\text{W,C}} = 125.6$ Hz, $^2J_{\text{P,C}} = 7.8$ Hz, *cis*-CO), 199.4 (d_{sat} , $^1J_{\text{W,C}} = 139.2$ Hz, $^2J_{\text{P,C}} = 28.0$ Hz, *trans*-CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , 25 °C): $\delta = 204.8$ ppm (s_{sat} , $^1J_{\text{W,P}} = 275.5$ Hz). IR (ATR, $\tilde{\nu}$ [cm^{-1}]): $\tilde{\nu} = 2069$ (s, $\nu(\text{CO})$), 1977 (w, $\nu(\text{CO})$), 1896 (vs, $\nu(\text{CO})$). MS (EI, 70 eV): m/z (%) = 534.0 (35) $[\text{M}]^{++}$, 450.0 (5) $[\text{M}-3\text{CO}]^+$, 398.8 (65) $[\text{M}-\text{C}_5\text{Me}_5]^+$, 370.8 (100) $[\text{M}-\text{C}_5\text{Me}_5-\text{CO}]^+$, 342.8 (30) $[\text{M}-\text{C}_5\text{Me}_5-2\text{CO}]^+$, 314.8 (15) $[\text{M}-\text{C}_5\text{Me}_5-3\text{CO}]^+$, 286.8 (15) $[\text{M}-\text{C}_5\text{Me}_5-4\text{CO}]^+$, 258.9 (10) $[\text{M}-\text{C}_5\text{Me}_5-5\text{CO}]^+$, 135.0 (70) $[\text{C}_5\text{Me}_5]^+$, 119.0 (55) $[\text{C}_5\text{Me}_5-\text{CH}_4]^+$, 105.0 (35) $[\text{C}_5\text{Me}_5-\text{C}_2\text{H}_6]^+$, 91.0 (25) $[\text{C}_5\text{Me}_5-\text{C}_3\text{H}_8]^+$. HR-MS: found 532.0404, calculated value for $\text{C}_{17}\text{H}_{19}\text{O}_6\text{PW}$: 532.0402. EA: calc. for $\text{C}_{17}\text{H}_{19}\text{O}_6\text{PW}$: C 38.23, H 3.59 found: C 38.60, H 3.74.



Preparation of 9. In a Schlenk tube, 643.2 mg (0.924 mmol) of complex **6a** were dissolved in 30 mL of Et₂O. To it 0.148 mL (0.925 mmol) of 12-crown-4 was added at ambient temperature and the mixture was cooled to -78 °C. Then 0.55 mL (0.93 mmol, 1.7 M in *n*-hexane) of *t*-BuLi was added upon which a change to a light yellow color and the formation of a yellow precipitate was observed. It was kept on stirring while slowly warming up to room temperature. After the reaction was completed (checked by ³¹P NMR), all volatiles were removed in vacuo (~ 2 · 10⁻² mbar). The crude mixture was purified by washing it three times with 5 mL of *n*-pentane and drying it in vacuo (~ 2 · 10⁻² mbar).

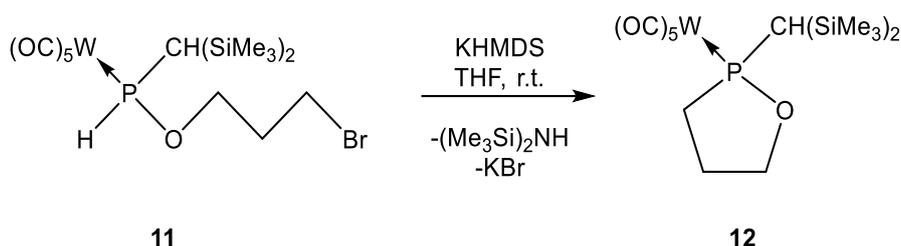
Complex 9: Yield: (0.547 g, 0.77 mmol, 83 %), slightly yellow solid, the data are in good accordance to the previously reported ones. ³¹P{¹H} NMR (121.5 MHz, [D8]THF, 25 °C): δ = 46.0, (*s*_{sat}, ¹J_{W,P} = 244.1 Hz, ¹J_{P,H} = 302.6 Hz).^[2]



Preparation of 11. In a Schlenk tube, 1.5 mmol of the dichlorophosphane complex **1a** was dissolved in 45 mL of diethyl ether, and 0.24 mL (1.5 mmol) of 12-crown-4 was added at ambient temperature and the mixture was cooled to -78 °C. Then 0.90 mL (1.53 mmol, 1.7 M in *n*-hexane) of *t*-BuLi was added upon which a change to a light yellow color was observed. It was kept on stirring for 10 minutes. Subsequently 1.6 mmol of 3-bromopropan-1-ol (0.14 ml, 1.06 eq) was added and the mixture was stirred while slowly warming up to room temperature. After the reaction was completed (checked by ³¹P NMR), all volatiles were removed in vacuo (~ 2 · 10⁻² mbar). The crude mixture was extracted with *n*-pentane (3 times 40 mL) and the solvent was removed *in vacuo* (~ 2 · 10⁻² mbar). The material was subsequently placed in a sublimation flask and heated for 1.5 h (130 °C, ~ 2 · 10⁻² mbar) to remove all volatile material. Complex **11** was obtained as a yellow-brownish oil.

Complex 11: Yield: (0.604 g, 0.924 mmol, 62 %). ¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ = 0.21 (*s*, 9 H, SiMe₃), 0.27 (*s*, 9 H, SiMe₃), 0.93 (*s*, 1 H PCH), 2.12 – 2.56 (*m*, 2 H, CH₂), 3.46 – 3.51 (*m*, 2 H, CH₂), 3.66 – 3.74 (*m*, 1 H, CH₂), 3.87 – 3.96 (*m*, 1 H, CH₂) 7.87 (*dd*, ¹J_{P,H} = 321.5 Hz, ³J_{P,H} = 0.8 Hz, P-H). ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25 °C): δ = 0.3 (*d*, ³J_{P,C} = 2.2 Hz, SiMe₃), 2.2 (*d*, ³J_{P,C} = 3.3 Hz, SiMe₃), 23.5 (*d*, ¹J_{P,C} = 13.1 Hz, P-CH), 29.4 (*s*, CH₂), 33.3 (*d*, ¹J_{P,C} = 8.7 Hz, CH₂), 67.1 (*d*, ²J_{P,C} = 3.5 Hz, P-OCH₂), 196.7 (*d*_{sat}, ¹J_{W,C} = 125.6 Hz, ²J_{P,C} = 7.4 Hz, *cis*-CO), 199.3 (*d*_{sat}, ¹J_{W,C} = 140.3 Hz, ²J_{P,C} = 25.1 Hz, *trans*-CO). ²⁹Si (59.6 MHz, CDCl₃, 25 °C) δ = 1.12 (*d*, ²J_{P,Si} = 5.5 Hz), 2.97 (*d*, ²J_{P,Si} = 9.1 Hz). ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25 °C): δ = 104.7 ppm (*d*_{sat}, ¹J_{W,P}

= 268.1 Hz, $^1J_{P,H} = 321.5$ Hz). IR (ATR, $\tilde{\nu}$ [cm^{-1}]): $\tilde{\nu} = 2262$ (w, $\nu(\text{PH})$), 2071 (s, $\nu(\text{CO})$), 1981 (w, $\nu(\text{CO})$), 1906 (vs, $\nu(\text{CO})$). ESI-MS: $\text{C}_{15}\text{H}_{26}\text{O}_6\text{BrPSi}_2\text{W}$ calc. 651.969, found: 651.946 [M] $^+$.



Preparation of 12. In a Schlenk tube, 514 mg (0.787 mmol) of complex **11** were dissolved in 25 mL of THF and 164 mg (0.82 mmol) of potassium hexamethyldisilazide in 10 mL THF were added dropwise at room temperature; the solution was kept stirring for 1h. During the addition a rapid formation of precipitate and a change of the colour to yellow-orange was observed. After 1h all volatiles were removed *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar). The product was purified by extraction with *n*-pentane (4 times 20 mL) and subsequent precipitation from and washing with *n*-pentane at -100 °C (1 time 5 mL and 3 times 2 mL). Complex **12** was obtained as white powder after drying *in vacuo* ($\sim 2 \cdot 10^{-2}$ mbar).

Complex 12: Yield: (0.1025 g, 0.18 mmol, 23 %), melting point: 85 °C. ^1H NMR (300.1 MHz, CDCl_3 , 25 °C): $\delta = 0.24$ (s, 9 H, SiMe_3), 0.28 (s, 9 H, SiMe_3), 1.64 (d, $^2J_{P,H} = 12.8$ Hz, 1 H, PCH), 2.05 – 2.25 (m, 2 H, CH_2), 2.50 – 2.64 (m, 2 H, CH_2), 4.01 – 4.10 (m, 1 H, CH_2), 4.11 – 4.20 (m, 1 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 25 °C): $\delta = 2.6$ (d, $^3J_{P,C} = 3.3$ Hz, SiMe_3), 2.8 (d, $^3J_{P,C} = 2.2$ Hz, SiMe_3), 25.3 (s, CH_2), 31.7 (s_{br} , P-CH), 37.2 (s_{br} , CH_2), 70.9 (d, $^2J_{P,C} = 5.7$ Hz, P-OCH $_2$), 197.6 (d_{sat} , $^1J_{W,C} = 126.2$ Hz, $^2J_{P,C} = 8.2$ Hz, *cis*-CO), 200.3 (d, $^2J_{P,C} = 24.8$ Hz, *trans*-CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , 25 °C): $\delta = 139.5$ ppm (s_{br} , full-width at half-intensity (FWHI, $h_{1/2}$) = 760 Hz), a second isomer was observed in very small amount (ratio 99.5:0.5): 125.2 ppm (s_{sat} , $^1J_{P,W} = 267.1$ Hz). IR (ATR, $\tilde{\nu}$ [cm^{-1}]): $\tilde{\nu} = 2066$ (s, $\nu(\text{CO})$), 1981 (w, $\nu(\text{CO})$), 1898 (vs, $\nu(\text{CO})$). Pos. ESI-MS: $\text{C}_{15}\text{H}_{25}\text{O}_6\text{PSi}_2\text{W}$ calc. 572.047, found: 572.03 [M] $^+$, 265287.110 [$\text{M}-\text{W}(\text{CO})_5 + \text{Na} + \text{O}$] $^+$, 265.130 [$\text{M}-\text{W}(\text{CO})_5 + \text{H} + \text{O}$] $^+$, 249.136 [$\text{M}-\text{W}(\text{CO})_5 + \text{H}$] $^+$. EA: calc. for $\text{C}_{15}\text{H}_{25}\text{O}_6\text{PSi}_2\text{W}$: C 31.48, H 4.40 found: C 31.42, H 4.34.

Crystal data and summary of data collection and refinement

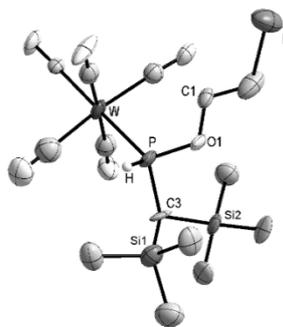


Fig. 1 Molecular structure of phosphinite complex **6a**. Ellipsoids are set at 50 % probability and hydrogen atoms (except the one directly bonded to phosphorus) are omitted for clarity. Selected bond lengths [Å] and angles [°]: W–P 2.486(8), P–C3 1.79(3), P–O1 1.63(2), W–P–C3 122.5(12), W–P–O1 120.0(10).

Crystal Data for 6a: Suitable single-crystals of **6a** were obtained from a concentrated *n*-pentane solution at 4 °C. Data were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by Patterson methods (SHELXS-97)^[1] and refined by full-matrix least-squares on F^2 (SHELXL-97)^[1] $C_{14}H_{24}IO_6PSi_2W$, $M = 686.23$, crystal dimensions $0.11 \times 0.1 \times 0.03$ mm³, triclinic, space group $P-1$, $Z = 2$, $a = 9.179(3)$ Å, $b = 10.433(4)$ Å, $c = 14.066(5)$ Å, $\alpha = 86.293(10)^\circ$, $\beta = 81.810(10)^\circ$, $\gamma = 65.584(9)^\circ$, $V = 1214.0(7)$ Å³, $d_c = 1.877$ g cm⁻³, $\mu = 6.216$ mm⁻¹, $T = 100$ K, transmission factors (min./max.) 0.3610/ 0.7459, empirical absorption correction, $2\theta_{max} = 50.5^\circ$, no. of unique data 5889, $R_{int} = 0.0751$, R_1 (for $I > 2\sigma(I)$) = 0.1405, wR_2 (for all data) = 0.3359, final $R = 0.1918$, goodness of fit 1.231, ΔF (max./min.) = 5.69/ -4.76 e Å⁻³.

Crystal Data for 7a: Suitable single-crystals of **7a** were obtained from a concentrated *n*-pentane solution at 4 °C. Data were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by Patterson methods (SHELXS-97)^[1] and refined by full-matrix least-squares on F^2 (SHELXL-97)^[1] $C_{14}H_{23}O_6PSi_2W$, $M = 558.32$, crystal dimensions $0.12 \times 0.09 \times 0.04$ mm³, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 9.7786(5)$ Å, $b = 9.9521(4)$ Å, $c = 21.9977(10)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2140.76(17)$ Å³, $d_c = 1.732$ g cm⁻³, $\mu = 5.606$ mm⁻¹, $T = 100$ K, transmission factors (min./max.) 0.5298/ 0.7460, empirical absorption correction, $2\theta_{max} = 55.972^\circ$, no. of unique data 5137, $R_{int} = 0.0371$, R_1 (for $I > 2\sigma(I)$) = 0.0230, wR_2 (for all data) = 0.0398, final $R = 0.0252$, goodness of fit 0.940, ΔF (max./min.) = 0.44/ -0.38 e Å⁻³.

Crystal Data for 12: Suitable single-crystals of **12** were obtained from a concentrated *n*-pentane solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 123 K by using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by Patterson methods (SHELXS-97)^[1] and refined by full-matrix least-squares on F^2 (SHELXL-97)^[1] $C_{15}H_{25}O_6PSi_2W$, $M = 572.35$, crystal dimensions $0.26 \times 0.14 \times 0.05$ mm³, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 9.2343(4)$ Å, $b = 10.3502(4)$ Å, $c = 23.1652(11)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2214.06(17)$ Å³, $d_c = 1.717$ g cm⁻³, $\mu = 5.422$ mm⁻¹, $T = 123$ K, transmission factors (min./max.) 0.4738/ 0.7459, empirical absorption correction, $2\theta_{max} = 55.994^\circ$, no. of unique data 5344, $R_{int} = 0.0633$, R_1 (for $I > 2\sigma(I)$) = 0.0367, wR_2 (for all data) = 0.0584, final $R = 0.0535$, goodness of fit 0.999, ΔF (max./min.) = 0.89/ -1.02 e Å⁻³.

Literature

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