Electronic Supplementary Information

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

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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 $^1$H, 75.5 MHz for $^{13}$C, 59.6 MHz for $^{29}$Si and 121.5 MHz for $^{31}$P). The $^1$H 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% $\text{H}_3\text{PO}_4$ 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 El, 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 °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 (~ 2 ·10⁻² mbar). The crude mixture was extracted with n-pentane and the solvent was removed in vacuo (~ 2 ·10⁻² mbar) to yield 6a as yellow oil.

Complex 6a: Yield: (0.624 g, 0.91 mmol, 91%). $^1$H NMR (300.1 MHz, CDCl₃, 25 °C): δ = 0.22 (s, 9 H, SiMe₃), 0.30 (s, 9 H, SiMe₃), 0.95 (s, 1 H, P-CH), 3.30 (dd, 2 H, $^3$JH,H = 6.0 Hz, $^3$JH,H = 6.0 Hz, CH₂-I), 3.73 – 3.91 (m, 1 H, P-OCH₂), 4.00 – 4.18 (m, 1 H, P-O-CH₂), 7.96 (dd, 1 H,
\( ^{1}J_{P,H} = 321.4 \text{ Hz}, \quad ^{3}J_{H,H} = 1.20 \text{ Hz, P-H}. \quad ^{13}\text{C}\left(^{1}\text{H}\right) \text{ NMR (75.5 MHz, CDCl}_{3}, \text{ 25 }^\circ\text{C}}:\ \delta = 0.4 \quad (d, \quad ^{3}J_{P,C} = 2.3 \text{ Hz, SiMe}_{3}), \quad 1.3 \quad (d, \quad ^{3}J_{P,C} = 9.1 \text{ Hz, CH}_{2}-), \quad 2.4 \quad (d, \quad ^{3}J_{P,C} = 3.2 \text{ Hz, SiMe}_{3}), \quad 23.7 \quad (d, \quad ^{1}J_{P,C} = 13.6 \text{ Hz, P-CH}_{2}), \quad 70.0 \quad (d, \quad ^{2}J_{P,C} = 2.6 \text{ Hz, P-OCH}_{2}), \quad 196.6 \quad (d_{\text{sat}}, \quad ^{1}J_{W,C} = 125.1 \text{ Hz}, \quad ^{2}J_{P,C} = 7.4 \text{ Hz, cis-CO}), \quad 199.1 \quad (d, \quad ^{2}J_{P,C} = 25.2 \text{ Hz, trans-CO}).^{29}\text{Si} \text{ (59.6 MHz, CDCl}_{3}, \text{ 25 }^\circ\text{C}}:\ \delta = 0.89 \quad (d, \quad ^{2}J_{P,\text{Si}} = 5.8 \text{ Hz}), \quad 2.61 \quad (d, \quad ^{2}J_{P,\text{Si}} = 9.2 \text{ Hz}). \quad ^{31}\text{P} \text{ NMR (121.5 MHz, CDCl}_{3}, \text{ 25 }^\circ\text{C}}:\ \delta = 106.7 \quad (d_{\text{sat}}, \quad ^{1}J_{W,P} = 270.3 \text{ Hz}, \quad ^{2}J_{P,H} = 321.4 \text{ Hz}). \quad \text{IR} \quad (\text{ATR, } \ddot{\nu} \text{ [cm}^{-1}]): \ddot{\nu} = 2263 \quad (w, \quad v(\text{PH})), \quad 2071 \quad (s, \quad v(\text{CO})), \quad 1981 \quad (s, \quad v(\text{CO})), \quad 1904 \quad (vs, \quad v(\text{CO})). \quad \text{MS (EI, 70 eV)}: \quad \text{m/z (})%\text{) = 686.0 (15) \quad [M^+]^{+}, \quad 657.9 \quad (10) \quad [M-CO]^+, \quad 602.0 \quad (20) \quad [M-3CO]^+, \quad 574.0 \quad (30) \quad [M-4CO]^+, \quad 546.0 \quad (25) \quad [M-5CO]^+, \quad 73.1 \quad (100) \quad [\text{SiMe}_{3}]^{+}.

![Diagram](https://example.com/diagram.png)

**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* (~2 ·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 (~2 ·10^{-2} mbar).

**Complex 7a: Yield:** (0.457 g, 0.819 mmol, 65 %), melting point: 77 °C. \(^{1}\text{H} \text{ NMR (300.1 MHz, C}_{6}\text{D}_{6}, \text{ 25 }^\circ\text{C}}): \delta = 0.08 \quad (d, \quad ^{4}J_{P,H} = 0.4 \text{ Hz, 9H, SiMe}_{3}), \quad 0.16 \quad (s, \quad 9 \text{ H, SiMe}_{3}), \quad 2.00 \quad (d, \quad 1 \text{ H, } ^{2}J_{P,H} = 8.8 \text{ Hz, PCH}), \quad 2.64 \quad (\text{ddd}, \quad 1 \text{ H}, \quad ^{2}J_{H,H} = 13.3 \text{ Hz}), \quad 3.37 \quad (d_{\text{sat}}, \quad ^{1}J_{H,H} = 8.2 \text{ Hz, } ^{3}J_{H,H} = 5.0 \text{ Hz, CH}_{2}), \quad 2.98 \quad (\text{ddd}, \quad 1 \text{ H}, \quad ^{2}J_{P,H} = 13.0 \text{ Hz, } ^{2}J_{H,H} = 13.3 \text{ Hz}), \quad 3.17 \quad (d_{\text{sat}}, \quad ^{1}J_{H,H} = 10.2 \text{ Hz, } ^{3}J_{H,H} = 8.2 \text{ Hz, CH}_{2}, \quad 4.04 \quad (\text{dddd}, \quad 1 \text{ H}, \quad ^{3}J_{P,H} = 4.5 \text{ Hz, } ^{3}J_{H,H} = 10.2 \text{ Hz, } ^{2}J_{H,H} = 7.5 \text{ Hz, } ^{1}J_{H,H} = 5.0 \text{ Hz, CH}_{2}), \quad 4.48 \quad (\text{ddd}, \quad 1 \text{ H}, \quad ^{3}J_{P,H} = 4.5 \text{ Hz, } ^{3}J_{H,H} = 10.2 \text{ Hz, } ^{2}J_{H,H} = 7.5 \text{ Hz, } ^{1}J_{H,H} = 5.0 \text{ Hz, CH}_{2}), \quad 8.2 \quad (d, \quad ^{2}J_{P,H} = 8.2 \text{ Hz, } ^{2}J_{H,H} = 7.5 \text{ Hz, CH}_{2}). \quad ^{13}\text{C}(^{1}\text{H}) \text{ NMR (75.5 MHz, C}_{6}\text{D}_{6}, \text{ 25 }^\circ\text{C}}: \delta = 1.7 \quad (d, \quad ^{3}J_{P,C} = 4.2 \text{ Hz, SiMe}_{3}), \quad 2.1 \quad (d, \quad ^{3}J_{P,C} = 2.6 \text{ Hz, SiMe}_{3}), \quad 35.4 \quad (d_{\text{iso}}, \quad \text{CH}_{2}, \quad 38.5 \quad (d, \quad ^{1}J_{P,C} = 14.6 \text{ Hz, PCH}), \quad 68.9 \quad (d, \quad ^{2}J_{P,C} = 15.2 \text{ Hz, PCH}_{2}), \quad 197.5 \quad (d_{\text{sat}}, \quad ^{1}J_{W,C} = 125.8 \text{ Hz}, \quad ^{2}J_{P,C} = 7.8 \text{ Hz, cis-CO}), \quad 200.7 \quad (d, \quad ^{2}J_{P,C} = 25.2 \text{ Hz, trans-CO}).^{29}\text{Si} \text{ (59.6 MHz, C}_{6}\text{D}_{6}, \text{ 25 }^\circ\text{C}}: \delta = 0.05 \quad (d, \quad ^{2}J_{P,\text{Si}} = 6.0 \text{ Hz), } -2.52 \quad (s). \quad ^{31}\text{P}(^{1}\text{H}) \text{ NMR (121.5 MHz, C}_{6}\text{D}_{6}, \text{ 25 }^\circ\text{C}}: \delta = 190.3 \quad (p_{\text{sat}}, \quad ^{1}J_{W,P} = 267.7 \text{ Hz}). \quad \text{IR} \quad (\text{ATR, } \ddot{\nu} \text{ [cm}^{-1}]): \ddot{\nu} = 2071 \quad (s, \quad v(\text{CO})), \quad 1992 \quad (s, \quad v(\text{CO})), \quad 1908 \quad (s, \quad v(\text{CO})). \quad \text{MS (EI, 70 eV)}: \quad \text{m/z (})%\text{) = 558.1 (50) \quad [M]^+, \quad 502.1 \quad (20) \quad [M-2CO]^+, \quad 474.1 \quad (30) \quad [M-3CO]^+, \quad 446.0 \quad (20) \quad [M-4CO]^+, \quad 418.0 \quad (40) \quad [M-5CO]^+, \quad 390.0 \quad (100) \quad [M-5CO-C_{2}H_{4}]^+, \quad 73.1 \quad (70) \quad [\text{SiMe}_{3}]^+. \quad \text{EA: calc. for C}_{14}\text{H}_{23}\text{O}_{5}\text{P}_{2}\text{Si}_{2}\text{W}: \quad C \quad 30.12, \quad H \quad 4.15 \quad \text{found: } C \quad 30.28, \quad H \quad 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 (~ 2 ·10⁻² mbar). The crude mixture was purified by low temperature column chromatography (ø = 2cm, h = 5 cm, PE, SiO₂, -20 °C) and obtained, after a first yellow fraction was separated with pure petroleum ether, an orange fraction using petroleum ether and diethyl ether (ratio 50 : 0.5). After removing of all volatiles in vacuo (~ 2 ·10⁻² mbar), the product was sublimed (1 h, 110° C, 2.6 ·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. $^1$H NMR (300.1 MHz, CDCl₃, 25 °C): $\delta = 1.74$ (d, $J_{P,H} = 11.0$ Hz, 3 H, C₅Me₅), $1.75$ (s, 3 H, C₅Me₅), $1.80$ (dq, $J_{P,H} = 5.0$ Hz, $J_{H,H} = 1$Hz, 3 H, C₅Me₅), $1.82$ (dq, $J_{P,H} = 4.3$ Hz, $J_{H,H} = 1.0$ Hz, 3 H, C₅Me₅), $1.93$ (s, 3 H, C₅Me₅), $3.34$ (ddd, 1 H, $J_{P,H} = 0.4$ Hz, $J_{H,P} = 13.8$ Hz, $J_{H,H} = 9.2$ Hz, $J_{H,P} = 6.6$ Hz, CH₂), $3.63$ (ddd, 1 H, $J_{H,H} = 5.3$ Hz, $J_{H,P} = 13.8$ Hz, $J_{H,P} = 9.7$ Hz, $J_{H,H} = 6.5$ Hz, CH₂), $5.05$ (ddd, 1 H, $J_{H,P} = 2.2$ Hz, $J_{H,H} = 7.1$ Hz, $J_{H,P} = 9.7$ Hz, $J_{H,H} = 6.6$ Hz, CH₂), $5.16$ (ddd, 1 H, $J_{H,P} = 3.3$ Hz, $J_{H,H} = 7.1$ Hz, $J_{H,H} = 9.2$ Hz, $J_{H,P} = 6.5$ Hz, CH₂). $^{13}$C($^1$H) NMR (75.5 MHz, CDCl₃, 25 °C): $\delta = 11.5$ (d, $J_{P,C} = 2.8$ Hz, C₅Me₅), $11.5$ (d, $J_{P,C} = 1.5$ Hz, C₅Me₅), $11.7$ (d, $J_{P,C} = 1.5$ Hz, C₅Me₅), $11.8$ (d, $J_{P,C} = 2.0$ Hz, C₅Me₅), $13.2$ (d, $J_{P,C} = 4.8$ Hz, C₅Me₅), $32.2$ (d, $J_{P,C} = 23.5$ Hz, P-CH₂), $65.4$ (d, $J_{P,C} = 2.9$ Hz, P-C₅Me₅), $73.1$ (d, $J_{P,C} = 13.7$ Hz, P-CH₂), $132.7$ (d, $J_{P,C} = 7.3$ Hz, C₅Me₅), $138.9$ (d, $J_{P,C} = 1.7$ Hz, C₅Me₅), $141.4$ (d, $J_{P,C} = 5.9$ Hz, C₅Me₅), $143.4$ (d, $J_{P,C} = 7.0$ Hz, C₅Me₅), $196.1$ (d, $J_{P,C} = 125.6$ Hz, $J_{W,C} = 7.8$ Hz, cis-CO), $199.4$ (d, $J_{W,C} = 139.2$ Hz, $J_{P,W,C} = 28.0$ Hz, trans-CO). $^{31}$P($^1$H) NMR (121.5 MHz, CDCl₃, 25 °C): $\delta = 208.4$ ppm ($\delta_{sat} = 119.2$ Hz, $\delta_{sat} = 275.5$ Hz). IR (ATR, ü [cm⁻¹]): ü = 2069 (s, v(CO)), 1977 (w, v(CO)), 1896 (vs, v(CO)). MS (EI, 70 eV): m/z (%) = 534.0 (35) $^{[M]^+}$, 450.0 (5) $^{[M-CO]^+}$, 398.8 (65) $^{[M-C₅Me₅]^+}$, 370.8 (100) $^{[M-C₅Me₅-CO]^+}$, 342.8 (30) $^{[M-C₅Me₅-2CO]^+}$, 314.8 (15) $^{[M-C₅Me₅-3CO]^+}$, 286.8 (15) $^{[M-C₅Me₅-4CO]^+}$, 258.9 (10) $^{[M-C₅Me₅-5CO]^+}$, 135.0 (70) $^{[C₅Me₅]^+}$, 119.0 (55) $^{[C₅Me₅-C₅H₅]^+}$, 105.0 (35) $^{[C₅Me₅-C₅H₅]^+}$, 91.0 (25) $^{[C₅Me₅-C₅H₅]^+}$. HR-MS: found 532.0404, calculated value for $C_{75}H_{138}O_{50}P$: 532.0402. EA: calc. for $C_{75}H_{138}O_{50}P$: 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 \( ^{31} \)P NMR), all volatiles were removed in vacuo (\( \sim 2 \cdot 10^{-2} \) mbar). The crude mixture was purified by washing it three times with 5 mL of n-pentane and drying it in vacuo (\( \sim 2 \cdot 10^{-2} \) 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. \( ^{31} \)P\( ^{1} \)H NMR (121.5 MHz, [D8]THF, 25 °C): \( \delta = 46.0 \), \( (s\text{, sat}, \ J_{W,P} = 244.1 \) Hz, \( \ J_{P,H} = 302.6 \) 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-bromopropane-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 \( ^{31} \)P NMR), all volatiles were removed in vacuo (\( \sim 2 \cdot 10^{-2} \) mbar). The crude mixture was extracted with n-pentane (3 times 40 mL) and the solvent was removed in vacuo (\( \sim 2 \cdot 10^{-2} \) mbar). The material was subsequently placed in a sublimation flask and heated for 1.5 h (130 °C, \( \sim 2 \cdot 10^{-2} \) 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 %). \( ^{1} \)H NMR (300.1 MHz, CDCl₃, 25 °C): \( \delta = 0.21 \) (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, \( \ J_{P,H} = 321.5 \) Hz, \( \ J_{P,H} = 0.8 \) Hz, P-H). \( ^{13} \)C\( ^{1} \)H NMR (75.5 MHz, CDCl₃, 25 °C): \( \delta = 0.3 \) (d, \( \ J_{P,C} = 2.2 \) Hz, SiMe₃), 2.2 (d, \( \ J_{P,C} = 3.3 \) Hz, SiMe₃), 23.5 (d, \( \ J_{P,C} = 13.1 \) Hz, P-CH), 29.4 (s, CH₂), 33.3 (d, \( \ J_{P,C} = 8.7 \) Hz, CH₂), 67.1 (d, \( \ J_{P,C} = 3.5 \) Hz, P-OC₂H), 196.7 (d, \( \ J_{W,C} = 125.6 \) Hz, \( \ J_{P,C} = 7.4 \) Hz, cis-CO), 199.3 (d, \( \ J_{W,C} = 140.3 \) Hz, \( \ J_{P,C} = 25.1 \) Hz, trans-CO). \( ^{29} \)Si (59.6 MHz, CDCl₃, 25°C) \( \delta = 1.12 \) (d, \( \ J_{P,Si} = 5.5 \) Hz), 2.97 (d, \( \ J_{P,Si} = 9.1 \) Hz). \( ^{31} \)P\( ^{1} \)H NMR (121.5 MHz, CDCl₃, 25 °C): \( \delta = 104.7 \) ppm (d, \( \ J_{W,P} = 8.7 \) Hz, \( \ J_{P,H} = 302.6 \) Hz). \(^{2}\)
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 (~ 2 ·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 (~ 2 ·10⁻² mbar).

Complex 12: Yield: (0.1025 g, 0.18 mmol, 23 %), melting point: 85 °C. ¹H NMR (300.1 MHz, CDCl₃, 25 °C): δ = 0.24 (s, 9 H, SiMe₃), 0.28 (s, 9 H, SiMe₃), 1.64 (d, J_P,H = 12.8 Hz, 1 H, PCH), 2.05 – 2.25 (m, 2 H, CH₂), 2.50 – 2.64 (m, 2 H, CH₂), 4.01 – 4.10 (m, 1 H, CH₂), 4.11 – 4.20 (m, 1 H, CH₂). ¹³C({¹H}) NMR (75.5 MHz, CDCl₃, 25 °C): δ = 2.6 (d, ³J_P,C = 3.3 Hz, SiMe₃), 2.8 (d, ³J_P,C = 2.2 Hz, SiMe₃), 25.3 (s, CH₂), 31.7 (s_{br}, P-CH), 37.2 (s_{br}, P-CH₂), 70.9 (d, ²J_P,C = 5.7 Hz, P-OCH₂), 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). ³¹P({¹H}) NMR (121.5 MHz, CDCl₃, 25 °C): δ = 139.5 ppm (s_{br}, full-width at half-intensity (FWHI, h₁/₂) = 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, ῦ [cm⁻¹]): ῦ = 2262 (w, ν(PH)), 2071 (s, ν(CO)), 1981 (w, ν(CO)), 1906 (vs, ν(CO)). ESI-MS: C₁₅H₂₆O₆BrPSi₂W calc. 651.969, found: 651.946 [M⁺].

Crystal data and summary of data collection and refinement
**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 with a Bruker X8-Kappa ApexII diffractometer equipped with a low-temperature device at 100 K by using graphite monochromated Mo Kα radiation (λ = 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\(_{24}\)O\(_6\)PSi\(_2\)W, M = 686.23, crystal dimensions 0.11 × 0.1 × 0.03 mm\(^3\), triclinic, space group P -1, Z = 2, a = 9.179(3) Å, b = 10.433(4) Å, c = 14.066(5) Å, α = 86.293(10)°, β = 81.810(10)°, γ = 71.584(9)°, V = 1214.0(7) Å\(^3\), d\(_m\) = 1.877 g cm\(^{-3}\), μ = 6.216 mm\(^{-1}\), T = 100 K, transmission factors (min./max.) 0.3610/ 0.7459, empirical absorption correction, 2θmax= 50.5°, no. of unique data 5889, Rint = 0.0751, R1 (for I > 2σ(I)) = 0.1405, wR2 (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 with a Bruker X8-Kappa ApexII diffractometer equipped with a low-temperature device at 100 K by using graphite monochromated Mo Kα radiation (λ = 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\(_5\)PSi\(_2\)W, M = 558.32, crystal dimensions 0.12 × 0.09 × 0.04 mm\(^3\), orthorhombic, space group P\(_2_1\)\(_2_1\)\(_2\), Z = 4, a = 9.7786(5) Å, b = 9.9521(4) Å, c = 21.9977(10) Å, α = 90°, β = 90°, γ = 90°, V = 2140.76(17) Å\(^3\), d\(_m\) = 1.732 g cm\(^{-3}\), μ = 5.606 mm\(^{-1}\), T = 100 K, transmission factors (min./max.) 0.5298/ 0.7460, empirical absorption correction, 2θmax= 55.972°, no. of unique data 5137, Rint = 0.0371, R1 (for I > 2σ(I)) = 0.0230, wR2 (for all data) = 0.0398, final R = 0.0252, goodness of fit 0.940, ΔF(max./min.) = 0.44/ -0.38e 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 with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 123 K by using graphite monochromated Mo Kα radiation (λ = 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\(_6\)PSi\(_2\)W, M = 572.35, crystal dimensions 0.26 × 0.14 × 0.05 mm\(^3\), orthorhombic, space group P\(_2_1\)\(_2_1\)\(_2\), Z = 4, a = 9.2343(4) Å, b = 10.3502(4) Å, c = 23.1652(11) Å, α = 90°, β = 90°, γ = 90°, V = 2214.06(17) Å\(^3\), d\(_m\) = 1.717 g cm\(^{-3}\), μ = 5.422 mm\(^{-1}\), T = 123 K, transmission factors (min./max.) 0.4738/ 0.7459, empirical absorption correction, 2θmax= 55.994°, no. of unique data 5344, Rint = 0.0633, R1 (for I > 2σ(I)) = 0.0367, wR2 (for all data) = 0.0584, final R = 0.0535, goodness of fit 0.999, ΔF(max./min.) = 0.89/ -1.02e Å\(^{-3}\).
Literature


(b) Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.