Electronic Supplementary Information for

Reactions of O-protonated oxaphosphirane complexes: formation of a η^2-Wittig ylide complex and a 1,3-oxaphospholane complex

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Analytical details of complexes 3, 5 and 7:

All reactions were carried out in an inert atmosphere using purified and dried argon and standard Schlenk techniques. Solvents were dried over sodium wire or CaH₂ (CH₂Cl₂) and distilled under argon. NMR data were recorded on a Bruker DMX 300 spectrometer at 30 °C using CDCl₃ and C₆D₆ as solvent and internal standard; shifts are given relative to tetramethylsilane (13C: 75.5 MHz) and 85% H₃PO₄ (31P: 121.5 MHz). Mass spectra were recorded on a a Kratos MS 50 spectrometer (EI, 70 eV). UV/vis absorption spectra were measured with a Shimadzu UV-1650PC spectrometer, and IR spectra were recorded by using a Nicolet 380 FTIR spectrometer in the ν = 4000–450 cm⁻¹ range spectrometer.

Complex 3:
δ_H (300 MHz; CDCl₃; 30 °C) 0.3 (9 H, s, Si(CH₃)₃), 0.4 (9 H, d, 4_J_{F,H} 1.1, Si(CH₃)₃), 1.8 (1 H, d, 2_J_{P,H} 15.7, CH(SiMe₃)₂), 2.3 (1 H, d, br, 3_J_{P,H} 24.0, OH), 5.3 (1 H, d, 2_J_{F,H} 6.6, C(OH)), 7.4 (5 H, m, Ph); δ_P (121.5 MHz; CDCl₃; 30 °C; 85%H₃PO₄) 198.1 (dd sat, 1_J_{W,P} 296.3, 1_J_{P,F} 826.0); δ_F (282.4 MHz; CDCl₃; 30 °C; CFCI₃) -123.1 (d, 1_J_{P,F} 851.9); ν_max/cm⁻¹ 3585m (OH), 2075m (CO), 1987s (CO), 1930s (CO), 2023s (CO); m/z (EI) 640 (M +, 60%), 612 (20), 556 (10), 316.1 (10), 179 (100), 73 (80).

Complex 5:
δ_H (300 MHz; CDCl₃; 30 °C) 0.2 (9 H, s, Si(CH₃)₃), 0.3 (9 H, d, 4_J_{F,H} 1.1, Si(CH₃)₃), 0.85 (1 H, d, 2_J_{P,H} 20.0, CH(SiMe₃)₂), 3.4 (1 H, d, 2_J_{F,H} 17.4, CHPh), 7.45 (5 H, m, Ph); δ_P (121.5 MHz; CDCl₃; 30 °C; 85%H₃PO₄) 143.5 (ddd sat, 1_J_{W,P} 144.0, 1_J_{P,F} 1043.0, 2_J_{P,H} 20.6, 2_J{(P,H)} 16.8); δ_F (282.4 MHz; CDCl₃; 30 °C; CFCI₃) -71.5 (d, 1_J_{P,F} 1059.7); ν_max/cm⁻¹ 3373br (OH), 2076m (CO), 1982s (CO), 1942s (CO).

Complex 7:
δ_H (300 MHz; CDCl₃; 25 °C) 1.15 (3 H, d, 3_J_{H,H} 7.1, CH-C₃H₃), 1.34 (3 H, dd, 2_J_{P,H} 12.8, 1_J{P,H} 3.5, PC-C₃H₃), 1.45 (3 H, s, OC-C₃H₃), 1.59 (3 H, „sext“ , J_{H,H} 8.6, C-C₃H₃), 1.71 („quint“ , J_{H,H} 0.8 Hz, C-C₃H₃), 2.99 (1 H, dq, 3_J_{P,H} 22.9, J_{H,H} 7.6, CH-C₃H₃), 4.34 (1 H, dd, 2_J_{F,H} 29.1, 1_J{F,H} 16.6, PCH-Ph), 7.34-7.41 (3 H, m, Ph), 7.46-7.51 (2 H, m, Ph); δ_P (121.5 MHz; CDCl₃; 25 °C; 85%H₃PO₄) 215.6 (d sat, 1_J_{W,P} 898.3, 1_J_{P,F} 892.6); δ_F (282.4 MHz; CDCl₃; 25 °C; CFCI₃) -149.7 (d, J_{C,F} = 12.3 Hz); ν_max/cm⁻¹ 2970w (C=C), 2079m (CO), 1982s (CO), 1918s (CO); m/z (EI) 616.1 (M⁺, 5 %), 532 (1), 510 (8), 426 (3), 396 (2), 368 (2), 340 (2), 136 (100), 121 (20).

Further computational details:
R = CH(SiMe₃)₂
R = C₅Me₅

**Fig. 2** Calculated structures of reactive intermediates 8a and 8b (most hydrogen atoms omitted; bond distances in Å).

DFT calculations were carried out with the TURBOMOLE V5.9.1 program package. For optimizations, the gradient corrected exchange functional by Becke (B88) in combination with the gradient corrected correlation functional by Lee, Yang and Parr (LYP) with the RI approximation and the valence-double-ζ basis set SV(P) was used. For the oxaphosphirane oxygen the basis was augmented with uncontracted gaussian functions having an exponent of 0.0845 (one of each type). For tungsten the effective core potential ECP-60-MWB was employed. The influence of the polar solvent was taken into account by employing the COSMO approach with ε = 8.93. For cavity construction the atomic radii of Bondi, obtained from crystallographic data, were used; the atomic radius of tungsten was set to 2.2230 Å. Transition states were located by using a TRIM algorithm. Excellent initial guesses were obtained through relaxed surface scans along the major reaction coordinates. All stationary points were characterized by numerical vibrational frequencies calculations. Single point calculations were carried out using the Three Parameter Hybrid Functional Becke (B3) in combination with the correlation functional LYP using the valence-triple-ζ basis set TZVP, which was augmented as specified above, and ECP-60-MWB for tungsten. The COSMO approach was employed with the same parameters as used for optimizations. Zero point corrections and thermal corrections to free energies were adopted from frequencies calculations on the optimization level (RI-BLYP/aug-SV(P)/ECP-60-MWB(W), COSMO). It has been shown that this approach is appropriate for reactions of epoxide, aziridine and thiirane with methanethiolate.