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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:

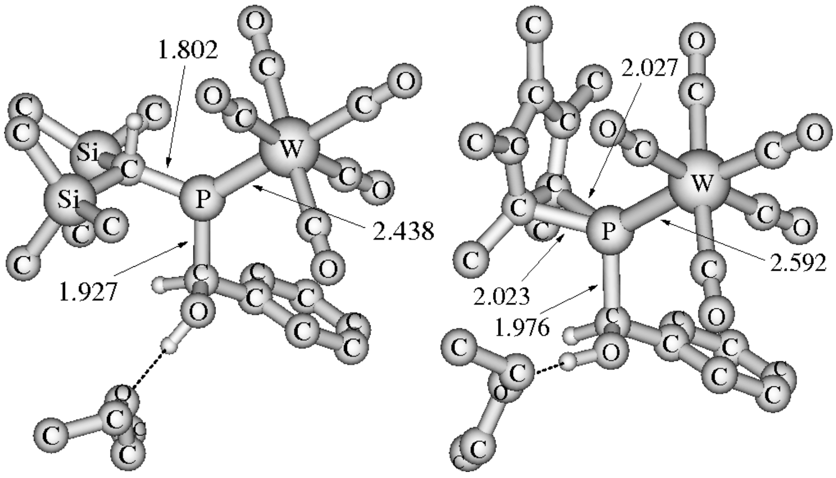
All reactions were carried out in an inert atmosphere using purified and dried argon and standard Schlenk techniques. Solvents were dried over sodium wire or CaH_2 (CH_2Cl_2) and distilled under argon. NMR data were recorded on a Bruker DMX 300 spectrometer at 30 °C using $CDCl_3$ and C_6D_6 as solvent and internal standard; shifts are given relative to tetramethylsilane (^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 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 ῦ̣ = 4000–450 cm^{-1} range spectrometer.

Complex **3**:
δ_H (300 MHz; $CDCl_3$; 30 °C) 0.3 (9 H, s, Si(C*H*$_3$)$_3$), 0.4 (9 H, d, $^4J_{F,H}$ 1.1, Si(C*H*$_3$)$_3$), 1.8 (1 H, d, $^2J_{P,H}$ 15.7, C*H*(SiMe$_3$)$_2$), 2.3 (1 H, d, br, $^3J_{P,H}$ 24.0, O*H*), 5.3 (1 H, d, $^2J_{F,H}$ 6.6, C*H*OH), 7.4 (5 H, m$_c$, Ph); δ_P(121.5 MHz; $CDCl_3$; 30°C; 85%H_3PO_4) 198.1 (dd$_{sat}$, $^1J_{W,P}$ 296.3, $^1J_{P,F}$ 826.0); δ_F (282.4 MHz; $CDCl_3$; 30°C; $CFCl_3$) -123.1 (d, $^1J_{P,F}$ 851.9); ν_{max}/cm^{-1} 3585m (OH), 2075m (CO), 1987s (CO), 1930s (CO), 2023s (CO), 1992m (CO); *m/z* (EI) 640 (M$^+$, 60 %), 612 (20), 556 (10), 316.1 (10), 179 (100), 73 (80).

Complex **5**: δ_H (300 MHz; $CDCl_3$, 30°C) 0.2 (9 H, s, Si(C*H*$_3$)$_3$), 0.3 (9 H, d, $^4J_{F,H}$ 1.1, Si(C*H*$_3$)$_3$), 0.85 (1 H, d, $^2J_{P,H}$ 20.0, C*H*(SiMe$_3$)$_2$), 3.4 (1 H, d, $^2J_{P,H}$ 17.4, C*H*Ph), 7.45 (m$_c$, 5H; Ph); δ_P (121.5 MHz; $CDCl_3$; 30°C; 85%H_3PO_4) 143.5 (ddd$_{sat}$, $^1J_{W,P}$ 144.0, $^1J_{P,F}$ 1043.0, $^2J_{P,H}$ 20.6, ^2J(P,H) 16.8); δ_F(282.4 MHz, $CDCl_3$; 30°C; $CFCl_3$) -71.5 (d, $^1J_{P,F}$ 1059.7; ν_{max}/cm^{-1} 3373br (OH), 2076m (CO), 1980s (CO), 1942s (CO).

Complex **7**: mp 110-112 °C (decomp); δ_H (300 MHz; $CDCl_3$; 25 °C) 1.15 (3 H, d, $J_{H,H}$ 7.1, CH-C*H*$_3$), 1.34 (3 H, dd, $^3J_{P,H}$ 12.8, $^4J_{F,H}$ 3.5, PC-C*H*$_3$)), 1.45 (3 H, s, OC-C*H*$_3$), 1.59 (3 H, „sext", $J_{H,H}$ 0.86, C-C*H*$_3$), 1.71 („quint", $J_{H,H}$ 0.8 Hz, C-C*H*$_3$), 2.99 (1 H, dq, $^3J_{P,H}$ 22.9, $J_{H,H}$ 7.6, C*H*-CH$_3$), 4.34 (1 H, dd, $^2J_{P,H}$ 29.1, $^3J_{F,H}$ 16.6, PC*H*-Ph), 7.34-7.41 (3 H, m, Ph), 7.46-7.51 (2 H, m, Ph); δ_P (121.5 MHz; $CDCl_3$; 25°C; 85% H_3PO_4) 215.6 (d$_{sat}$, $^1J_{W,P}$ 289.3, $^1J_{P,F}$ 892.6; δ_F (282.4 MHz; $CDCl_3$; 25 °C; $CFCl_3$) - 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:



8a: R = $CH(SiMe_3)_2$ **8b**: R = C_5Me_5

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.[1a] For optimizations[1b] the gradient corrected exchange functional by Becke[2] (B88) in combination with the gradient corrected correlation functional by Lee, Yang and Parr[3] (LYP) with the RI approximation[4] and the valence-double-ζ basis set SV(P)[5] 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[6] was employed. The influence of the polar solvent was taken into account by employing the COSMO approach[7] with $\varepsilon = 8.93$. For cavity construction the atomic radii of Bondi,[8] obtained from cystallographic data, were used; the atomic radius of tungsten was set to 2.2230 Å. Transition states were located by using a TRIM algorithm.[9] Excellent initial guesses were obtained through relaxed surface scans along the major reaction coordinates. All stationary points were characterized by numerical vibrational frequencies calculations.[10] Single point calculations were carried out using the Three Parameter Hybrid Functional Becke3[11] (B3) in combination with the correlation functional LYP[3] using the valence-triple-ζ basis set TZVP,[12] which was augmented as specified above, and ECP-60-MWB[6] for tungsten. The COSMO approach[7] 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.[13]

1 R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* 1989, **162**, 165–169; M. v. Arnim, R. Ahlrichs, *J. Chem. Phys.* 1999, **111**, 9183–9190.
2 A. D. Becke, *Phys. Rev., A.* 1988, **38**, 3098–3100.
3 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785–789.
4 K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 1995, **240**, 283–290; K.Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 1995, **242**, 652–660; K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theo. Chem. Acc.* 1997, **97**, 119–124.
5 A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* 1992, **97**, 2571–2577.
6 D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* 1990, **77**, 123–141.
7 A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* 1993, 799–805.
8 A. Bondi, *J. Phys. Chem.* 1964, **68**, 441–451.
9 T. Helgaker, *Chem. Phys. Lett.* 1991, **182**, 503−510.
10 P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* 2002, **362**, 511−518; P. Deglmann, F. Furche, *J. Chem. Phys.* 2002, **117**, 9535−9538; P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* 2004, **384**, 103−107.
11 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.
12 A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 1994, **100**, 5829–5835.
13 H. Helten, T. Schirmeister, B. Engels, *J. Phys. Chem. A* 2004, **108**, 7691–7701; H. Helten, T. Schirmeister, B. Engels, *J. Org. Chem.* 2005, **70**, 233–237; c) R. Vicik, H. Helten, T. Schirmeister, B. Engels, *Chem. Med. Chem.* 2006, **1**, 1021–1028.