Supporting Information

Experimental

General

All manipulations were carried out under dry nitrogen using standard Schlenk line or glove box techniques. All solvents were purified by standard methods and distilled under a nitrogen atmosphere immediately prior to use. 4-(2,6-Dimethyl-phenylimino)-pent-2-en-ol[1] and $[MoO_2Cl_2]$[2] were prepared according to literature procedures. Toluene for spectroscopy (conform to ACS) was ordered form Acros and distilled over Na/benzophenone. All other chemicals mentioned were used as purchased from commercial sources (Aldrich, Merck, Strem).
Samples for mass spectrometry were measured on a BIO-RAD Digilab FTS-7 mass spectrometer with a Finnigan MAT 95 and all NMR spectra on a Bruker Avance 500 or 200 MHz. Elemental analyses were performed by the Analytisches-Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen and Analytisches-Chemisches Laboratorium des Technisches Instituts für Anorganische Chemie, Graz. IR spectra were recorded on Perkin Elmer Ft-IR spectrometer 1725X as nujol mull between KBr plates. UV/Vis spectra were recorded on Varian Cary UV-Vis-NIR spectrophotometer.

X-ray crystallographic determinations

Crystals of compound **3** were taken from the solution, covered with oil, mounted on glass fibres and placed immediately in a protective stream of cold nitrogen (100 K). Crystallographic data (excluding structure factors) for compound **3** has been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 618904 (**3**) Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html or on application to CCDC, 12 union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).
Crystal data for **3**: $C_{26}H_{32}MoN_2O_5 \cdot 1.5\ C_7H_8$, M_w = 686.68, triclinic, space group $P\bar{1}$, a = 11.700(2), b = 12.012(2), c = 12.815(2) Å, α = 77.95(3)°, β = 73.18(3)°, γ = 78.95(3)° V = 1669.3(5) Å^3, Z = 2, ρ_{calc} = 1.366 Mg m^{-3}, F(000) = 718, λ = 1.54178 Å, T = 100(2) K, $\mu(Cu_{K\alpha})$ = 3.567 mm^{-1}. Data for the structure were collected on a Bruker three-circle diffractometer equipped with Smart 6000 CCD area detector using mirror-monochromated $Cu_{K\alpha}$ radiation. The structure was solved by direct methods using SHELXS-97[3] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[3] All non-hydrogen were refined anisotropically, while all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model with U_{ij} tied to the parent atom. Intensity measurements were performed on a rapidly cooled crystal in a range $3.65 \leq \theta \leq 58.75$. Of the 11416 measured reflections 4347 were independent (R_{int} = 0.0319). The oxo und the peroxo group were disordered. For ca. 10% of the crystal the oxo group is lying on the position of the peroxo group and vice versa. A toluene molecule lying on the inversion center and a further toluene molecule were also disordered. All disordered groups were refined with distant restraints and restraints for the anisotropic displacement parameters. The final refinements converged at $R1$ = 0.0256 for $I>2\sigma(I)$, $wR2$ = 0.0673 for all data. The final difference Fourier synthesis gave a min/max residual electron density −0.374/+0.361 e Å^3. CCDC-618904 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk(conts/retrieving.html (or from the Cambrige Crystallographic Data Centre, 12, Union Road, Cambrige CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Syntheses

[MoO_2L_2] (1): The ligand 4-(2,6-dimethyl-phenylimino)-pent-2-en-ol[1] (400 mg, 2 mmol) was dissolved in 20 ml of toluene and a three-fold excess of triethylamine was added. The solution was cooled to -20 °C and added dropwise to a precooled suspension of [MoO_2Cl_2][2] in toluene (200 mg, 1 mmol). The bright-yellow mixture was left to stir at room temperature for 2 h, than filtered over celites, concentrated to 10 ml and left at -35 °C overnight. Yellow crystals were collected, rinsed with cold pentane and dried *in vacuo* giving 280 mg of **1** (47 %). ^{1}H NMR (500 MHz, C_6D_6): δ 1.3 (s, 3H, H_3C-C=NAr), 1.85 (s, 3H, H_3C-C-O), 2.22 (s, 3H, H_3C-Ar), 2.51 (s, 3H, H_3C-Ar), 5.16 (s, 1H, *γ-H*), 6.88-7.11 (m, 3H, *H*-Ar) ppm. ^{13}C NMR (500 MHz, C_6D_6): δ 18.4 (CH_3-CO), 18.8 (CH_3-C-N), 23.4 (CH_3-Ar), 25.6 (CH_3-Ar), 102.7 (-CH), 125.4 (*C*-Ar), 129.3 (*C*-Ar), 131.8 (*C*-Ar), 151.8 (N-*C*-Ar), 170.7 (N-*C*-CH_3), 183.1 (O-*C*-CH_3) ppm. MS (EI): *m/z* 534 (100%) [MoO_2L_2]$^+$; Anal. Calc. for $C_{26}H_{32}MoN_2O_4$: C, 58.64; H, 6.00; N, 5.20. Found: C, 58.97; H, 6.19; N, 4.65%; IR (KBr, cm $^{-1}$): 919m, 885s, 849m, 814m.

[$MoOL_2(PMe_3)$] (2): Yellow **1** (300 mg, 0.5 mmol) was suspended in 80 ml of pentane and five-fold excess of trimethylphosphine (0.025 ml) was added *via* microsyringe and stirred for 2 h at room temperature. The obtained green solution was filtered over celites, concentrated to 15 ml and placed at -80 °C. After 2 days shiny green crystals were collected and dried *in vacuo* giving 142 mg of **2** (48 %). ^{1}H NMR (300 MHz, toluene-d_8): δ 0.73 (d, 9H, P(CH_3)$_3$, $^3J_{PH}$ = 8.7 Hz), 1.44 (s, 3H, H_3C), 1.68 (s, 3H, H_3C), 1.81 (s, 3H, H_3C),1.91 (s, 3H, H_3C), 2.40 (s, 3H, H_3C), 2.49 (s, 3H, H_3C), 2.51 (s, 3H, H_3C), 2.66 (s, 3H, H_3C), 4.91 (s, 1H, *γ-H*), 5.05 (s, 1H, *γ-H*), 6.93-7.00 (m, 6H, *H*-Ar) ppm. ^{31}P NMR (500 MHz, C_6D_6): -5.7 ppm. MS (EI): *m/z* 518 (100%) [$MoOL_2$]$^+$; Anal. Calc. for $C_{29}H_{41}MoN_2O_3P$: C, 58.78; H, 6.97; N, 4.73. Found: C, 57.66; H, 6.77; N, 4.71%; IR (KBr, cm $^{-1}$): 956m, 942m, 924m, 767s.

[$MoO(O_2)L_2$] (3): To a suspension of **1** (300 mg, 0.5 mmol) in 80 ml pentane 0.025 ml (2.5 mmol) of PMe_3 was added *via* microsyringe and stirred for 2 h at room temperature. After filtration over celites dry molecular oxygen was bubbled through a green pentane solution of **2** within few minutes. Rapid color change to orange was observed. The volume of the solution was reduced to 10 ml and bright-yellow **3** crystallized at room temperature. Following filtration and drying *in vacuo* gave 297 mg of **3** (54 %). ^{1}H NMR (200 MHz, C_6D_6): δ 1.42 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 5.13 (s, 1H, *γ-H*), 5.16 (s, 1H, *γ-H*), 6.95-7.10 (m, 6H, *H*-Ar) ppm. ^{13}C NMR (200 MHz, C_6D_6): δ 18.5, 19.1, 20.0, 24.5, 24.6, 25.0, 102.8, 103.0, 126.1, 126.2, 127.8, 128.4, 128.5, 128.8, 129.1, 131.8, 132.0, 133.0, 133.4, 133.7, 134.2 ppm. MS (EI): *m/z* 550 (100%) [$MoO(O_2)L_2$]$^+$; Anal. Calc. for $C_{26}H_{32}MoN_2O_5$: C, 56.93; H, 5.88; N, 5.11. Found: C, 56.64; H, 6.19; N, 4.91%; IR (KBr, cm $^{-1}$): 1144s, 948m, 895w, 864s.

Visible optical spectroscopy

Visible absorption spectra were recorded in 1 cm quartz cells at 25 °C. The trimethylphosphine solution (2.8 10^{-3} M) was mixed with a solution of **1** (5.6 10^{-5} M) in the glove box, sealed and immediately measured. The spectrophotometric data were analyzed by the programm ORIGIN 5.0.

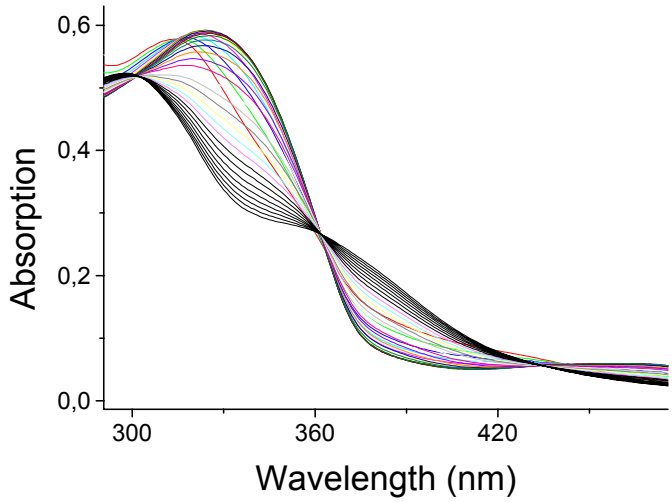

Fig. 1 Reduction of **1** in toluene at rt. Spectra from t = 3 to 90 minutes

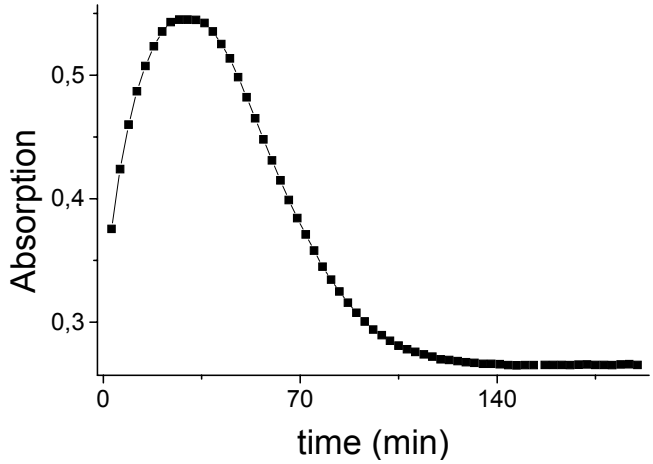

Fig. 2 Dependance of the absorption from time at λ = 339 nm for reaction time t = 3 to 175 minutes

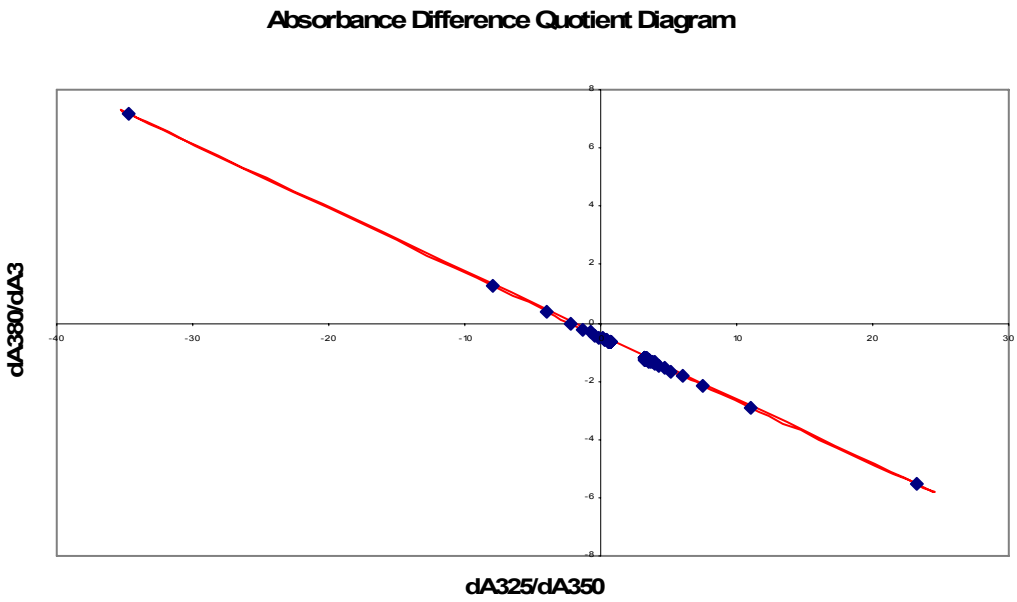

Fig. 3 Absorbance difference quotient (ADQ) diagrams[4]

References:

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