Supporting Information for

Oxygen-transfer Reactions of Molybdenum- and Tungstendioxo Complexes Containing η^2-Pyrazolate Ligands

Kerstin Most, Jens Hoßbach, Denis Vidovic, Jörg Magull, Nadia C. Mösch-Zanetti*

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, D-37077 Göttingen/Germany

Fax: (+49) 551 39 3373; e-mail: **nmoesch@gwdg.de**

Characterisation data for compounds 1 – 5.

[$MoO_2Cl(\eta^2$-*t*-$Bu_2pz)$] (1): 0.3 g (1.51 mmol) of [MO_2Cl_2] and 0.33 g (1.51 mmol) of *t*-Bu_2pzK gave 0.45 g (87%) of the yellow product. mp 125 °C. ^{1}H NMR (C_6D_6,δ) 1.12 (s, 18 H, *t*-Bu*H*), 6.09 (s, 1 H, ring-*H*). ^{13}C NMR (C_6D_6, δ) 160.94 (s, 4 C, α-*C*), 112.46 (s, 2 C, β-*C*), 32.09 (s, 4 C, *C*$(CH_3)_3$), 30.05 (s, 12 C, C(*C*$H_3)_3$). IR (KCl, cm^{-1}) 971, 941. MS-EI (m/z): 344 (M^+), 329 (M^+ - Me), 165 (*t*-Bu_2pz - Me). Found: C, 38.3; H, 5.9; N, 8.3. Calc. for $C_{11}H_{19}ClMoN_2O_2$: C, 38.56; H, 5.59; N, 8.17.

[$MoO_2(\eta^2$-*t*-$Bu_2pz)_2$] (2): 0.6 g (3.02 mmol) of [MO_2Cl_2] and 1.31 g (6.04 mmol) of *t*-Bu_2pzK gave 1.31 g (89%) of the slightly yellow product. mp 115 °C. ^{1}H NMR (C_6D_6, δ) 1.20 (s, 18 H, *t*-Bu*H*), 6.21 (s, 1 H, ring-*H*). ^{13}C NMR (C_6D_6, δ) 162.30 (s, 4 C, α-*C*), 107.08 (s, 2 C, β-*C*), 32.37 (s, 4 C, *C*$(CH_3)_3$), 30.20 (s, 12 C, C(*C*$H_3)_3$). IR (KCl, cm^{-1}) 951, 922. MS-EI (m/z): 488 (M^+), 473 (M^+ - Me), 165 (*t*-Bu_2pz - Me). Found: C, 54.7; H, 8.0; N, 11.5. Calc. for $C_{22}H_{38}MoN_4O_2$: C, 54.31; H, 7.87; N, 11.52.

[$MoO_2(\eta^2$-*t*-Bu_2-4-Br$pz)_2$] (3): 0.33 (1.68 mmol) of [MoO_2Cl_2] and 1.0 g (3.36 mmol) of *t*-Bu_2-4-BrpzK yielded 1.08 g (87 %) of slightly yellow crystals. 160 °C. ^{1}H NMR (C_6D_6, δ) 1.30 (s, 18 H, *t*-Bu*H*), ^{13}C NMR (C_6D_6, δ) 157.47 (s, 4 C, α-*C*), 98.51 (s, 2 C, β-*C*), 33.47 (s, 4 C, *C*$(CH_3)_3$), 28.35 (s, 12 C, C(*C*$H_3)_3$). IR (KCl, cm^{-1}) 985, 951, 924. MS-EI (m/z): 646 (M^+), 631 (M+ - Me), 588 (M^+ - *t*-Bu - H). Found: C, 40.6; H, 5.6; N, 8.6. Calc. for $C_{22}H_{36}Br_2MoN_4O_2$: C, 41.01; H, 5.63; N, 8.70.

[$WO_2(\eta^2$-*t*-$Bu_2pz)_2$] (4): 0.5 g (1.45 mmol) of [WO_2Cl_2(dme)] and 0.63 (2.9 mmol) of *t*-Bu_2pzK gave 0.69 g (83%) of yellow crystals. mp 125 °C. ^{1}H NMR (C_6D_6, δ) 1.18 (s, 18 H, *t*-Bu*H*), 6.44 (s, 1 H, ring-*H*). ^{13}C NMR (C_6D_6, δ) 162.15 (s, 4 C, α-*C*), 108.57 (s, 2 C, β-*C*), 32.44 (s, 4 C, *C*$(CH_3)_3$), 30.05 (s, 12 C, C(*C*$H_3)_3$). IR (KCl, cm^{-1}) 996, 960. MS-EI (m/z): 574 (M^+), 559 (M^+ - Me), 516 (M^+ - *t*-Bu), 165 (*t*-Bu_2pz - Me). Found: C, 45.8; H, 6.6; N, 9.6. Calc. for $C_{22}H_{38}N_4O_2W$: C, 46.00; H, 6.67; N, 9.75.

[WO_2(η^2-*t*-Bu_2-4-Brpz)$_2$] (5): 0.63 g (1.68 mmol) of [WO_2Cl_2(dme)] and 1 g (3.36 mmol) of *t*-Bu_2-4-BrpzK yielded 1.0 g (83%) of slightly yellow crystals. 150 °C. ^{1}H NMR (C_6D_6, δ) 1.28 (s, 18 H, *t*-Bu*H*), 6.44 (s, 1 H, ring-*H*). ^{13}C NMR (C_6D_6, δ) 157.47 (s, 4 C, α-*C*), 100.73 (s, 2 C, β-*C*), 33.61 (s, 4 C, *C*(CH_3)$_3$), 28.25 (s, 12 C, C(*C*H_3)$_3$). IR (Nujol mull, KCl, cm^{-1}) 967, 801, 726. MS-EI (m/z): 732 (M^+), 717 (M^+ - Me), 635 (M^+-Br -Me -2 H), 259 ([*t*-Bu_2-4-BrPzH]$^+$). Found: C, 35.85; H, 4.90; N, 7.44. Calc. for $C_{22}H_{36}N_4Br_2O_2W$: C, 36.09; H, 4.96; N, 7.65.

X-ray crystallography

Crystals of *t*-Bu_2-4-BrpzH and the complexes **3** and **6** were taken from the solution, cover with oil and mounted on glass fibres at room temperature. Data were collected on a Stoe IPDS II-array detector system instrument with graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

[1] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 1990, *46*, 467-473.

[2] G. M. Sheldrick, University Göttingen

Table 1. Selected bond lengths [Å] and angles [°] for **3** and **6**

3		**6**, molecule 1		**6**, molecule 2	
Mo(1)-O(1)	1.685(3)	Mo(1)-O(1)	1.656(2)	Mo(2)-O(2)	1.642(2)
Mo(1)-O(2)	1.686(3)	Mo(1)-N(1)	2.337(3)	Mo(2)-N(5)	2.313(3)
Mo(1)-N(1)	2.050(3)	Mo(1)-N(2)	2.183(3)	Mo(2)-N(6)	2.188(3)
Mo(1)-N(2)	2.214(3)	Mo(1)-N(3)	2.143(3)	Mo(2)-N(7)	2.139(3)
Mo(1)-N(3)	2.206(3)	Mo(1)-P(1)	2.539(1)	Mo(2)-P(3)	2.547(1)
Mo(1)-N(4)	2.032(3)	Mo(1)-P(2)	2.549(1)	Mo(2)-P(4)	2.555(1)
O(1)-Mo(1)-O(2)	105.22(17)	P(1)-Mo(1)-P(2)	172.09(3)	P(3)-Mo(2)-P(3)	172.85(3)
O(1)-Mo(1)-N(2)	140.07(14)	N(1)-Mo(1)-P(1)	83.46(8)	N(5)-Mo(2)-P(3)	83.97(8)
O(2)-Mo1-N(3)	140.35(15)	N(1)-Mo(1)-P(2)	90.17(8)	N(5)-Mo(2)-P(4)	91.11(8)
O(1)-Mo(1)-N(4)	107.85(15)	N(2)-Mo(1)-P(1)	86.84(8)	N(6)-Mo(2)-P(3)	87.41(8)
O(2)-Mo(1)-N(4)	103.89(15)	N(2)-Mo(1)-P(2)	90.67(8)	N(6)-Mo(2)-P(4)	91.57(8)
O(1)-Mo(1)-N(1)	102.87(14)	N(1)-Mo(1)-N(3)	118.79(10)	N(5)-Mo(2)-N(7)	119.00(10)
O(2)-Mo(1)-N(1)	109.79(15)	N(1)-Mo(1)-O(1)	138.04(10)	N(5)-Mo(1)-O(2)	137.86(10)
O(1)-Mo(1)-N(3)	98.23(14)	N(3-Mo(1)-O(1)	103.12(11)	N(7)-Mo(1)-O(2)	103.08(11)
O(2)-Mo(1)-N(2)	95.83(13)				
N(1)-Mo(1)-N(3)	95.20(13)				
N(4)-Mo(1)-N(2)	99.22(14)				
N(1)-Mo(1)-N(2)	37.37(12)				
N(3)-Mo(1)-N(4)	37.52(13)				

Table 2. Crystallographic data and structure refinement

	3	**6**
M	604.16	1413.61
Formula	$C_{20}H_{20}Br_2MoN_4O_2$	$C_{68}H_{136}Mo_2N_8O_2P_4$
T/K	133(2)	133(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*P*na2_1	*P*2_1/*c*
a/Å	17.9568(11	19.960(4)
b/Å	15.4586(14)	21.596(4)
c/Å	10.0275(6)	20.531(4)
α/°	90	90
β/°	90	116.65(3)
γ/°	90	90
U/Å^3	2783.5(3)	7910(3)
Z	4	4
D_c/ mg m^{-3}	1.442	1.187
μ/mm^{-1}	3.361	0.441
F(000)	1184	3040
2θ/Range/°	1.74 to 24.77	1.89 to 24.81
hkl Ranges	-20 to 21, -17 to 18, -11 to 10	-23 to 23, -25 to 25, -24 to 24
Measured reflections	15505	84117
Unique reflections	4342 (R_{int} = 0.0394)	13544 (R_{int} = 0.1083)
Observed reflections [$I > 2\sigma(I)$]	3628	7706
Data/restraints/parameters	4342/1/292	13544/0/793
Goodness-of-fit on F^2	0.962	0.732
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0258	*R*1 = 0.0319
	*wR*2 = 0.0417	*wR*2 = 0.0586
R indices (all data)	*R*1 = 0.0350	*R*1 = 0.0737
	*wR*2 = 0.0427	*wR*2 = 0.0646
Largest diff. peak, hole/e Å^{-3}	0.564 and –0.477	0.414 and –0.369