Electronic Supplementary Information (ESI)

Influence of N-donor bases and the solvent in oxodiperoxomolybdenum catalysed olefin epoxidation in ionic liquids

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Table S1. Comparing the effect of imidazole additives in the molybdenum catalysed epoxidation of *cis*-cyclooctene in IL solvents over 2 h.[a]

Entry	Base Additive [pK_a]	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	Imidazole [6.95]	C_8mim-PF_6	48	48	100
2		C_{12}mim-PF_6	43	43	100
3	1-Methylimidazole [6.95]	C_8mim-PF_6	48	48	100
4		C_{12}mim-PF_6	44	44	100
5	4-Methylimidazole [7.40]	C_8mim-PF_6	45	45	100
6		C_{12}mim-PF_6	44	44	100

[a] Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, base additive 0.10 mmol, 30 % aqueous H_2O_2 3.0 mmol, *cis*-cyclooctene 1.0 mmol, solvent 2.0 mL, T = 60 ºC, t = 2 h. Extraction with pentane (3 x 3 mL), yields and conversions calculated by GC.

Scheme S1. Oxidative decomposition of 4-methylimidazole.

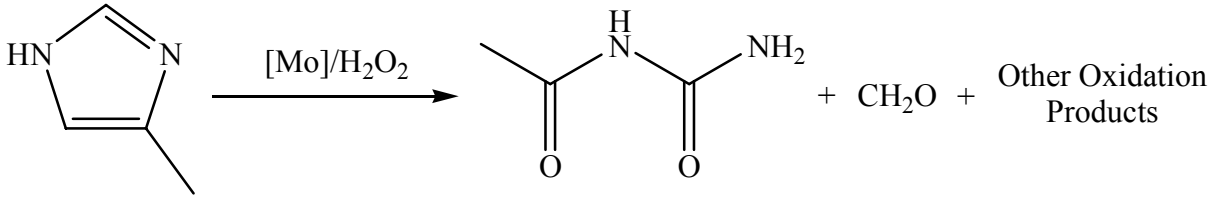

Table S2. Epoxide yields for ten catalytic cycles in C_8mim-PF_6 as solvent in the presence of $[Mo(O)(O_2)_2(H_2O)_n]$/dmpz (dmpz = 3,5-dimethylpyrazole).[a]

Catalytic cycle	Yields (%)			
	Time = 4h		Time = 2h	
	With added dmpz [b]	Without dmpz [c]	With added dmpz [b]	Without dmpz [c]
1	89.3	86.0	95	95
2	71.8	78.5	99	97
3	84.8	77.8	96	93
4	77.1	69.6	97	86
5	70.6	55.8	97	77
6	73.1	58.2	96	70
7	81.8	61.2	95	70
8	83.4	36.4	98	67
9	79.4	34.4	96	66
10	82.3	25.8	99	62

Initially: Aqueous $[Mo(O)(O_2)_2(H_2O)_n]$ 0.025 mmol, 3,5-dimethylpyrazole 0.1 mmol, 30 % aqueous H_2O_2 3.0 mmol, cis-cyclooctene 1.0 mmol, C_8mim-PF_6 2.0 mL. Extraction with petroleum ether (3 x 3 mL) after each cycle, yields calculated by GC. T = 60 ºC, t_{run} = 2 h. [b] 30 % $H_2O_{2\,(aq)}$ 3.0 mmol, *cis*-cyclooctene 1.0 mmol, 3,5-dimethylpyrazole 0.1 mmol added prior to each successive run. [c] 30 % $H_2O_{2\,(aq)}$ 3.0 mmol, *cis*-cyclooctene 1.0 mmol added prior to each successive run.

Table S3. Crystal data and structure refinement for $[MoO(O_2)_2(3\text{-Mepz})_2]$.

Empirical formula	$C_8H_{12}MoN_4O_5$	
Formula weight	340.16	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.4740(3) Å	α = 90°.
	b = 13.3115(4) Å	β = 104.148(2)°.
	c = 8.5537(3) Å	γ = 90°.
Volume	1266.83(7) Å3	
Z	4	
Density (calculated)	1.783 Mg/m3	
Absorption coefficient	1.055 mm-1	
F(000)	680	
Crystal size	0.47 x 0.32 x 0.13 mm3	
Theta range for data collection	4.17 to 30.62°.	
Index ranges	$-15 \le h \le 16$, $-19 \le k \le 19$, $-12 \le l \le 11$	
Reflections collected	39044	
Independent reflections	3882 [R(int) = 0.0300]	
Completeness to theta = 30.62°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8751 and 0.6770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3882 / 2 / 171	
Goodness-of-fit on F^2	1.066	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0190, wR2 = 0.0507	
R indices (all data)	R1 = 0.0219, wR2 = 0.0515	
Largest diff. peak and hole	0.370 and -0.619 $eÅ^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $[MoO(O_2)_2(3\text{-Mepz})_2]$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	2852(1)	193(1)	10128(1)	17(1)
O(1)	3759(1)	-803(1)	10690(1)	26(1)
O(2)	3469(1)	1163(1)	11783(1)	28(1)
O(3)	4031(1)	1287(1)	10420(1)	26(1)
O(4)	1528(1)	-61(1)	11094(1)	24(1)
O(5)	1285(1)	-461(1)	9442(1)	23(1)
N(1)	3024(1)	-23(1)	7673(1)	22(1)
N(2)	3831(1)	-680(1)	7325(1)	21(1)
N(3)	1636(1)	1523(1)	8900(1)	21(1)
N(4)	429(1)	1496(1)	8682(2)	23(1)
C(1)	3660(1)	-814(1)	5733(2)	26(1)
C(2)	2689(2)	-226(1)	5008(2)	36(1)
C(3)	2326(2)	253(1)	6251(2)	33(1)
C(4)	4414(2)	-1498(2)	5016(2)	38(1)
C(5)	-95(1)	2369(1)	8127(2)	24(1)
C(6)	813(1)	2993(1)	7927(2)	34(1)
C(7)	1866(1)	2437(1)	8432(2)	31(1)
C(8)	-1422(1)	2524(1)	7835(2)	38(1)

Table S5. Bond lengths [Å] and angles [°] for $[MoO(O_2)_2(3\text{-}Mepz)_2]$.

Mo(1)-O(1)	1.6818(10)	C(1)-C(2)	1.379(2)
Mo(1)-O(2)	1.9192(10)	C(1)-C(4)	1.488(2)
Mo(1)-O(4)	1.9280(10)	C(2)-C(3)	1.388(2)
Mo(1)-O(5)	1.9540(10)	C(2)-H(2)	0.9500
Mo(1)-O(3)	1.9622(10)	C(3)-H(3)	0.9500
Mo(1)-N(1)	2.1754(12)	C(4)-H(4A)	0.9800
Mo(1)-N(3)	2.3387(11)	C(4)-H(4B)	0.9800
O(2)-O(3)	1.4734(15)	C(4)-H(4C)	0.9800
O(4)-O(5)	1.4714(14)	C(5)-C(6)	1.375(2)
N(1)-C(3)	1.3343(19)	C(5)-C(8)	1.496(2)
N(1)-N(2)	1.3588(16)	C(6)-C(7)	1.392(2)
N(2)-C(1)	1.3395(17)	C(6)-H(6)	0.9500
N(2)-H(2N)	0.827(14)	C(7)-H(7)	0.9500
N(3)-C(7)	1.3261(18)	C(8)-H(8A)	0.9800
N(3)-N(4)	1.3526(15)	C(8)-H(8B)	0.9800
N(4)-C(5)	1.3408(17)	C(8)-H(8C)	0.9800
N(4)-H(4N)	0.833(14)		

O(1)-Mo(1)-O(2)	103.21(5)	O(3)-Mo(1)-N(1)	89.90(5)
O(1)-Mo(1)-O(4)	103.69(5)	O(1)-Mo(1)-N(3)	170.08(5)
O(2)-Mo(1)-O(4)	89.37(5)	O(2)-Mo(1)-N(3)	83.90(4)
O(1)-Mo(1)-O(5)	101.21(5)	O(4)-Mo(1)-N(3)	83.07(4)
O(2)-Mo(1)-O(5)	131.88(4)	O(5)-Mo(1)-N(3)	78.38(4)
O(4)-Mo(1)-O(5)	44.54(4)	O(3)-Mo(1)-N(3)	79.16(4)
O(1)-Mo(1)-O(3)	100.92(5)	N(1)-Mo(1)-N(3)	81.45(4)
O(2)-Mo(1)-O(3)	44.60(4)	O(3)-O(2)-Mo(1)	69.25(6)
O(4)-Mo(1)-O(3)	131.80(4)	O(2)-O(3)-Mo(1)	66.15(6)
O(5)-Mo(1)-O(3)	157.55(4)	O(5)-O(4)-Mo(1)	68.67(6)
O(1)-Mo(1)-N(1)	88.63(5)	O(4)-O(5)-Mo(1)	66.79(6)
O(2)-Mo(1)-N(1)	134.15(5)	C(3)-N(1)-N(2)	105.49(12)
O(4)-Mo(1)-N(1)	131.10(5)	C(3)-N(1)-Mo(1)	131.88(11)
O(5)-Mo(1)-N(1)	86.87(5)	N(2)-N(1)-Mo(1)	121.61(9)

C(1)-N(2)-N(1)	111.72(12)	H(4A)-C(4)-H(4B)	109.5
C(1)-N(2)-H(2N)	128.3(13)	C(1)-C(4)-H(4C)	109.5
N(1)-N(2)-H(2N)	119.9(13)	H(4A)-C(4)-H(4C)	109.5
C(7)-N(3)-N(4)	104.78(11)	H(4B)-C(4)-H(4C)	109.5
C(7)-N(3)-Mo(1)	133.58(10)	N(4)-C(5)-C(6)	106.24(13)
N(4)-N(3)-Mo(1)	121.32(8)	N(4)-C(5)-C(8)	121.85(13)
C(5)-N(4)-N(3)	112.38(11)	C(6)-C(5)-C(8)	131.91(13)
C(5)-N(4)-H(4N)	128.0(13)	C(5)-C(6)-C(7)	105.47(13)
N(3)-N(4)-H(4N)	119.5(13)	C(5)-C(6)-H(6)	127.3
N(2)-C(1)-C(2)	106.46(13)	C(7)-C(6)-H(6)	127.3
N(2)-C(1)-C(4)	123.03(14)	N(3)-C(7)-C(6)	111.11(13)
C(2)-C(1)-C(4)	130.50(14)	N(3)-C(7)-H(7)	124.4
C(1)-C(2)-C(3)	106.07(14)	C(6)-C(7)-H(7)	124.4
C(1)-C(2)-H(2)	127.0	C(5)-C(8)-H(8A)	109.5
C(3)-C(2)-H(2)	127.0	C(5)-C(8)-H(8B)	109.5
N(1)-C(3)-C(2)	110.25(14)	H(8A)-C(8)-H(8B)	109.5
N(1)-C(3)-H(3)	124.9	C(5)-C(8)-H(8C)	109.5
C(2)-C(3)-H(3)	124.9	H(8A)-C(8)-H(8C)	109.5
C(1)-C(4)-H(4A)	109.5	H(8B)-C(8)-H(8C)	109.5
C(1)-C(4)-H(4B)	109.5		

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[MoO(O_2)_2(3\text{-Mepz})_2]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U11	U22	U33	U23	U13	U12
Mo(1)	14(1)	20(1)	17(1)	1(1)	5(1)	2(1)
O(1)	24(1)	29(1)	26(1)	4(1)	6(1)	9(1)
O(2)	21(1)	37(1)	25(1)	-10(1)	7(1)	-1(1)
O(3)	17(1)	30(1)	30(1)	-2(1)	8(1)	-3(1)
O(4)	22(1)	28(1)	25(1)	2(1)	11(1)	-1(1)
O(5)	21(1)	22(1)	25(1)	-1(1)	5(1)	-3(1)
N(1)	21(1)	26(1)	19(1)	1(1)	6(1)	4(1)
N(2)	17(1)	27(1)	19(1)	-2(1)	5(1)	2(1)
N(3)	15(1)	21(1)	28(1)	4(1)	6(1)	0(1)
N(4)	16(1)	20(1)	35(1)	8(1)	8(1)	0(1)
C(1)	24(1)	34(1)	21(1)	-5(1)	7(1)	-2(1)
C(2)	41(1)	48(1)	19(1)	0(1)	5(1)	10(1)
C(3)	34(1)	42(1)	22(1)	3(1)	4(1)	13(1)
C(4)	32(1)	52(1)	29(1)	-15(1)	9(1)	3(1)
C(5)	23(1)	21(1)	29(1)	7(1)	5(1)	3(1)
C(6)	27(1)	23(1)	48(1)	14(1)	5(1)	-1(1)
C(7)	21(1)	27(1)	45(1)	13(1)	7(1)	-4(1)
C(8)	23(1)	32(1)	58(1)	16(1)	10(1)	8(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[MoO(O_2)_2(3\text{-Mepz})_2]$.

	x	y	z	U(eq)
H(2N)	4369(15)	-914(13)	8060(20)	26
H(4N)	108(16)	988(12)	8960(20)	28
H(2)	2339	-161	3885	44
H(3)	1674	712	6110	39
H(4A)	5253	-1275	5330	56
H(4B)	4132	-1485	3838	56
H(4C)	4356	-2184	5406	56
H(6)	738	3662	7529	40
H(7)	2646	2680	8441	38
H(8A)	-1787	1930	8198	56
H(8B)	-1769	2628	6681	56
H(8C)	-1580	3114	8436	56

Table S8. Torsion angles [°] for $[MoO(O_2)_2(3\text{-Mepz})_2]$.

O(1)-Mo(1)-O(2)-O(3)	92.24(7)
O(4)-Mo(1)-O(2)-O(3)	-163.84(6)
O(5)-Mo(1)-O(2)-O(3)	-149.16(6)
N(1)-Mo(1)-O(2)-O(3)	-8.94(9)
N(3)-Mo(1)-O(2)-O(3)	-80.74(6)
O(1)-Mo(1)-O(3)-O(2)	-97.81(7)
O(4)-Mo(1)-O(3)-O(2)	21.92(9)
O(5)-Mo(1)-O(3)-O(2)	92.05(12)
N(1)-Mo(1)-O(3)-O(2)	173.60(6)
N(3)-Mo(1)-O(3)-O(2)	92.29(6)
O(1)-Mo(1)-O(4)-O(5)	-92.16(7)
O(2)-Mo(1)-O(4)-O(5)	164.39(6)
O(3)-Mo(1)-O(4)-O(5)	149.20(6)
N(1)-Mo(1)-O(4)-O(5)	8.21(8)
N(3)-Mo(1)-O(4)-O(5)	80.47(6)
O(1)-Mo(1)-O(5)-O(4)	98.20(7)
O(2)-Mo(1)-O(5)-O(4)	-21.18(9)
O(3)-Mo(1)-O(5)-O(4)	-91.66(12)
N(1)-Mo(1)-O(5)-O(4)	-173.81(6)
N(3)-Mo(1)-O(5)-O(4)	-91.90(6)
O(1)-Mo(1)-N(1)-C(3)	157.10(15)
O(2)-Mo(1)-N(1)-C(3)	-95.71(16)
O(4)-Mo(1)-N(1)-C(3)	50.04(17)
O(5)-Mo(1)-N(1)-C(3)	55.80(15)
O(3)-Mo(1)-N(1)-C(3)	-101.97(15)
N(3)-Mo(1)-N(1)-C(3)	-22.92(15)
O(1)-Mo(1)-N(1)-N(2)	-9.53(11)
O(2)-Mo(1)-N(1)-N(2)	97.66(11)
O(4)-Mo(1)-N(1)-N(2)	-116.59(10)
O(5)-Mo(1)-N(1)-N(2)	-110.84(11)
O(3)-Mo(1)-N(1)-N(2)	91.40(11)
N(3)-Mo(1)-N(1)-N(2)	170.45(11)

C(3)-N(1)-N(2)-C(1)	0.40(17)
Mo(1)-N(1)-N(2)-C(1)	170.11(10)
O(2)-Mo(1)-N(3)-C(7)	57.60(15)
O(4)-Mo(1)-N(3)-C(7)	147.70(16)
O(5)-Mo(1)-N(3)-C(7)	-167.38(16)
O(3)-Mo(1)-N(3)-C(7)	12.72(15)
N(1)-Mo(1)-N(3)-C(7)	-78.83(15)
O(2)-Mo(1)-N(3)-N(4)	-114.75(11)
O(4)-Mo(1)-N(3)-N(4)	-24.64(11)
O(5)-Mo(1)-N(3)-N(4)	20.28(10)
O(3)-Mo(1)-N(3)-N(4)	-159.62(11)
N(1)-Mo(1)-N(3)-N(4)	108.83(11)
C(7)-N(3)-N(4)-C(5)	-1.26(18)
Mo(1)-N(3)-N(4)-C(5)	173.01(10)
N(1)-N(2)-C(1)-C(2)	-0.60(18)
N(1)-N(2)-C(1)-C(4)	-179.78(14)
N(2)-C(1)-C(2)-C(3)	0.5(2)
C(4)-C(1)-C(2)-C(3)	179.64(18)
N(2)-N(1)-C(3)-C(2)	-0.03(19)
Mo(1)-N(1)-C(3)-C(2)	-168.24(12)
C(1)-C(2)-C(3)-N(1)	-0.3(2)
N(3)-N(4)-C(5)-C(6)	1.69(18)
N(3)-N(4)-C(5)-C(8)	-178.41(15)
N(4)-C(5)-C(6)-C(7)	-1.38(19)
C(8)-C(5)-C(6)-C(7)	178.73(19)
N(4)-N(3)-C(7)-C(6)	0.32(19)
Mo(1)-N(3)-C(7)-C(6)	-172.92(12)
C(5)-C(6)-C(7)-N(3)	0.7(2)

Table S9. Hydrogen bonds for $[MoO(O_2)_2(3\text{-Mepz})_2]$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...O(3)#1	0.827(14)	2.035(15)	2.8421(16)	165.3(18)
N(2)-H(2N)...O(2)#1	0.827(14)	2.474(17)	3.0720(15)	130.1(16)
N(4)-H(4N)...O(4)#2	0.833(14)	2.238(16)	2.9901(16)	150.4(17)
N(4)-H(4N)...O(5)	0.833(14)	2.332(18)	2.8041(15)	116.5(16)
N(4)-H(4N)...O(5)#2	0.833(14)	2.446(17)	3.1438(15)	142.0(17)
N(4)-H(4N)...O(4)	0.833(14)	2.545(18)	2.9781(16)	113.6(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 -x,-y,-z+2

Figure 1. Intra and intermolecular hydrogen bonds for $[MoO(O_2)_2(3\text{-Mepz})_2]$.

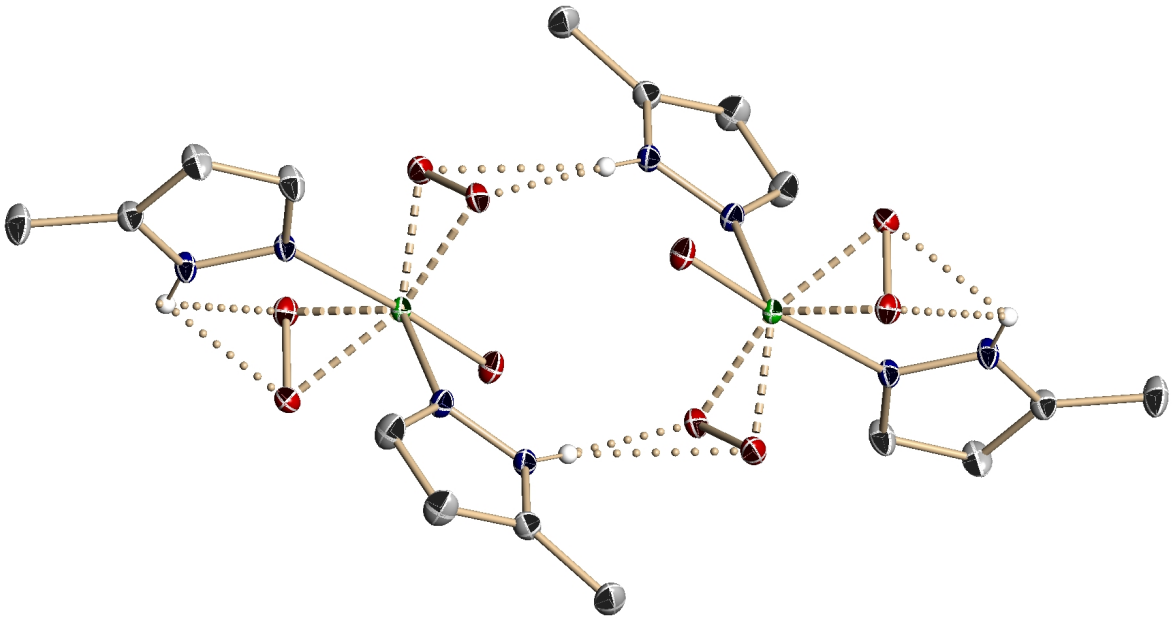

Figure 2. Crystal packing for $[MoO(O_2)_2(3\text{-Mepz})_2]$.