Supplementary Information

General Considerations. All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under nitrogen and used immediately. TBHP (*tert*-butyl hydrogen peroxide, ~5.5 M in decane over molecular sieve 4Å and 5.0-6.0 M in decane) was purchased from Sigma-Aldrich. Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. ^{1}H and ^{13}C NMR were measured in CD_3CN at room temperature unless stated otherwise with AMX500 500 MHz FT NMR spectrometer. IR spectra were recorded on a Shimadzu IR-470 spectrometer using KBr pellets as IR matrix. ESI-MS was performed on a Brucker amaZon X ion trap mass spectrometer. Sample was introduced into the ESI-source using a syringe pump.

Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(IBz)(CH_3CN)][BF_4]$ (1b)

$AgBF_4$ (0.19 g, 1 mmol) was added to a solution of compound $CpMo(CO)_2(IBz)Br$[1] (1 mmol) in CH_3CN (20 mL). After stirring for 6 h at room temperature, the color of solution changed from purple to red. The reaction mixture was filtered through Celite, and the filtrate was dried under vacuum. The resulting dark red solid was recrystallized from acetonitrile and diethyl ether twice, yielding red crystals as the product. (Yield: 80%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 7.44 -7.15 (m, 10H, CH_2*Ph*), 7.31 (s, 2H, =C*H*), 5.59 (s, 5H, *Cp*), 5.38-5.18 (q, 4H, NCH_2Ph, *J*=15.75Hz). ^{13}C NMR (125.77 MHz, CD_3CN): δ (ppm) = 248.29 (s, Mo-*C*O), 246.08 (s, Mo-*C*O) 182.04 (s, N*C*N), 137.44, 129.87, 128.90, 127.75 (phenyl), 125.78 (s, =*C*H), 95.96 (s, *Cp*), 55.89 (s, Ph*C*H_2N). IR (KBr)/cm^{-1}: ν_{sym}(CO) = 1972 (vs) , ν_{asym} (CO) = 1879, I_{asym}/I_{sym} = 1.30 (predicted OC-Mo-CO angle 96°), ν (BF_4) = 1084. ESI-MS (in CH_3CN, *m/z* (%)): M^+ = $[(\eta^5$-

$C_5H_5)Mo(CO)_2(IBz)]^+$ = 467 (100). Anal. Calcd for $C_{26}H_{24}BF_4MoN_3O_2$: C, 52.64; H, 4.08; N, 7.08. Found: C, 52.66; H, 4.09; N, 7.38.

Synthesis of $[(\eta^5\text{-}C_5H_5)MoO_2(IBz)][BF_4]$ (2b).

TBHP (5.5M in decane, 2.5mmol) (0.45 mL) was introduced to the the solution of compound **2b** (0.5 mmol) in CH_3CN (15 mL) and the reaction mixture was stirred for 6 h at r.t.. Then MnO_2 was added to destroy the remained TBHP. After filtration and removing the solvent, the resulted oily crude product was washed with Et_2O and THF, giving greenish yellow solid as final product. (Yield: 80%). ^1H NMR (500MHz, CD_3CN): δ (ppm) = 7.58 (s, 2H, =C*H*), 7.45-7.18 (m, 10H, *Ph*), 6.50 (s, 5H, *Cp*), 5.17 (s, 4H, NCH_2Ph). ^{13}C NMR (125.77MHz, CD_3CN): δ (ppm) = 164.23 (s, N*C*N), 135.16, 130.24, 129.91, 128.95 (phenyl), 128.35 (s, =*C*H), 115.91 (s, *Cp*), 56.43 (s, $PhCH_2N$). IR (KBr)/cm^{-1} : ν(Mo=O) = 929 (s), 898 (s). ESI-MS (in CH_3CN, *m/z* (%)): $M^+ = [(\eta^5\text{-}C_5H_5)MoO_2(IBz)]^+$ = 443 (100). Anal. Calcd for $C_{22}H_{21}BF_4MoN_2O_2$: C, 50.03; H, 4.01; N, 5.30. Found: C, 50.18; H, 4.23; N, 5.84.

X-ray Crystallography

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.[2] Structure solutions and refinements were performed by using the programs SHELXS-97[3a] and SHELXL-97[3b]. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically.

Compound **1b**: The crystal is triclinic, space group P-1. The asymmetric unit contains two cations $C_{26}H_{24}N_3O_2Mo$ and two BF_4^-. A small cell was tried and the cations were disordered.

Compound **3**: The crystal is monoclinic, space group P2(1)/c. The asymmetric unit contains one cation $C_{21}H_{25}N_2$, half an anion Mo_6O_{19} and half a CH_3CN which was disordered into two positions with occupancy 50:50 related by the centre of symmetry. The whole anion and the other half of the CH_3CN are generated by the inversion through the centre of symmetry. Compound **4**: The crystal is monoclinic, space group P2(1)/c. The asymmetric unit contains cation $C_{22}H_{21}N_2O_2Mo$ and half an anion Mo_6O_{19}. The whole anion is generated by the inversion through the centre of symmetry.

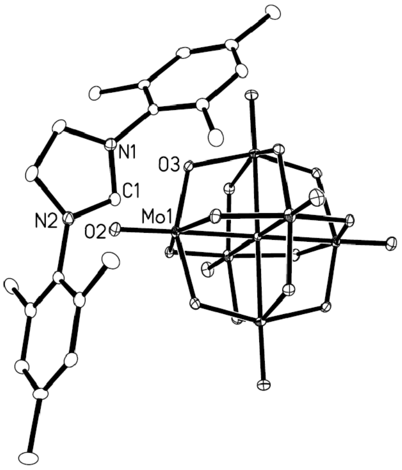

Fig. 1 ORTEP diagram of $\{[IMesH][Mo_6O_{19}]\}^-$ in **3** (30% probability ellipsoids). Hydrogen atoms are omitted.

Catalytic reactions.

Cyclooctene (0.4 g, 3.6 mmol), mesitylene (1 g, internal standard) and catalysts (1 mol%, 0.036 mmol) were added to the reaction vessel under an air atmosphere at 55°C. The reaction was started by the addition of TBHP (5.0-6.0 M in decane) (~7.2 mmol, 1.31 mL). The course of the reactions was monitored by quantitative GC analysis. The samples were taken in regular time intervals, diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into the GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

References:

1. S. Li, C. W. Kee, K.-W. Huang, T. S. A. Hor and J. Zhao, *Organometallics,* 2010, **29**, 1924.

2. SADABS: Area-Detection Absorption Correction: Bruker AXS Inc., Madison, WI, 1995.

3. (a) G. M. Sheldrick, SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.