# Molybdenum $\eta^3$-Allyl Dicarbonyl Complexes as a New Class of Precursors for Highly Reactive Epoxidation Catalysts with *tert*-Butyl Hydroperoxide

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New Mo(II) diimine derivatives of [Mo($\eta^3$-allyl)X(CO)$_2$(CH$_3$CN)$_2$] (allyl = $C_3H_5$ and $C_5H_5O$; X = Cl, Br) were prepared, and [Mo($\eta^3$-C$_3$H$_5$)Cl(CO)$_2$(BIAN)] (BIAN = 1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene) (**7**) was structurally characterized by single-crystal X-ray diffraction. This complex adopted an equatorial−axial arrangement of the bidentate ligand (axial isomer), in contrast with the precursors, found as the equatorial isomer in the solid and fluxional in solution. The new complexes of the type [Mo($\eta^3$-allyl)X(CO)$_2$(N−N)] (N−N is a bidentate chelating dinitrogen ligand) were tested for the catalytic epoxidation of cyclooctene using *tert*-butyl hydroperoxide as oxidant. All catalytic systems were 100% selective toward epoxide formation. While their turnover frequencies paralleled those of related Mo(II) carbonyl compounds or Mo(VI) compounds bearing similar N-donor ligands, they exhibited similar olefin conversions in consecutive catalytic runs. The acetonitrile precursors were generally more active than the diimine complexes, and the chloro derivatives more active than the bromo ones. Combined vibrational and NMR spectroscopy and computational studies (DFT) were used to investigate the nature of the molybdenum species formed in the catalytic system with [Mo($\eta^3$-C$_3$H$_5$)Cl(CO)$_2${1,4-(2,6-dimethyl)-phenyl-2,3-dimethyldiazabutadiene}] (**4**) and to propose that the resulting species may be dimeric bearing oxide bridges.

## Introduction

The synthesis of materials with controlled compositions, architectures, and functionalities is of great scientific interest in the field of catalysis. An important group of such versatile materials consists of organometallic complexes since their properties can be fine-tuned by changing the metal (electron configuration, oxidation state, coordination number, and geometry) and the ligands (binding mode and electronic and steric properties). Organometallic complexes have been used as homogeneous catalysts for the industrial production of chemicals for many years, and the future prospects seem quite promising.[1]

The availability of suitable starting materials has always been of considerable importance to the synthetic chemist. $\eta^3$-Allyl dicarbonyl complexes of Mo and W play an important role in both coordination chemistry[2−9] and catalytic organic transformations, and their reactivity depends on the nature of the ligands completing the coordination sphere.[10−17] Since the discovery of pseudooctahedral molybdenum(II) complexes of the type [Mo($\eta^3$-allyl)X(CO)$_2$(CH$_3$CN)$_2$] (X = halide) in 1968,[18] a series of derivatives containing the {Mo($\eta^3$-allyl)(CO)$_2$}$^+$ moiety has been easily prepared by substitution of the labile nitrile ligands and/or the anion X.[2,12,14,18,19−27] In particular, compounds of the type [Mo($\eta^3$-allyl)X(CO)$_2$(N−N)], where N−N = 2,2′-bipyri-

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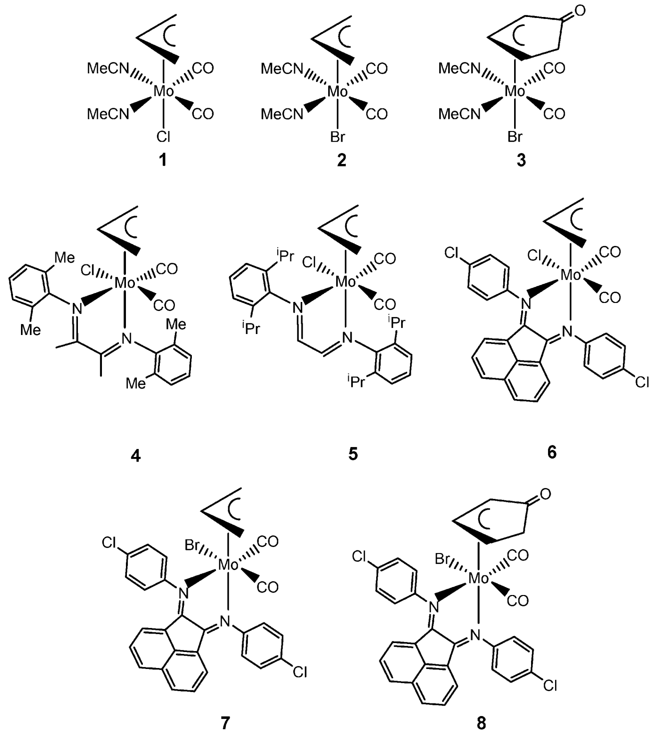
dine or 1,10-phenanthroline, were found to possess some air and water tolerance.[28,23] These compounds have been successfully used as catalyst precursors for imine aziridination,[29] oxidation of triphenylphosphine with molecular oxygen,[30] or as catalysts for allylic alkylations.[10−12] Recent studies have revealed that complexes [Mo($\eta^3$-$C_3H_5$)X(CO)$_2$($CH_3CN$)$_2$] act as single component initiators for ring-opening metathesis polymerization of norbornene and polymerization of terminal acetylenes[31] and catalyze the oligomerization of Ph(C≡C)$_n$Ph ($n$ = 1, 2).[20]

Olefin epoxidation with molybdenum complexes is a particularly relevant catalytic reaction since homogeneous molybdenum catalysts are the basis of important industrial processes, such as ARCO-Halcon, for epoxidation with alkyl hydroperoxides as oxidant.[32,33] Recently, it has been found that halocarbonyl Mo(II) complexes of the type MoCpCl(CO)$_3$ (Cp=$\eta^5$-cyclopentadienyl) react readily with *tert*-butyl hydroperoxide (TBHP) in decane to give the corresponding dioxomolybdenum(VI) complexes CpMoO$_2$Cl,[34] which in turn are active and selective catalysts for olefins epoxidation using alkyl hydroperoxides as oxidants.[35−37] Under certain reaction conditions, turnover frequencies of up to 21 000 mol mol$^{-1}_{\mathrm{Mo}}$ h$^{-1}$ were found that even surpass that of the well-known MeReO$_3$/H$_2$O$_2$ epoxidation system.[34] The carbonyl precursors were applied directly as catalyst precursors without isolation of the dioxo complexes (less stable than the former) prior to use, and by adjustment of the reaction conditions such as temperature, the oxidative decarbonylation of the catalyst precursor was not rate-determining in the epoxidation mechanism.[37]

1,4-Diaza-1,3-butadienes are favorable supporting ligands for complexes of the family [MoO$_2$X$_2$L] (L = Lewis base), enhancing catalyst stability and activity for olefin epoxidation with TBHP.[38−41] In this work, we set out to prepare complexes of the type [Mo($\eta^3$-allyl)X(CO)$_2$(N−N)] (X = Br, Cl) by reaction of the parent species [Mo($\eta^3$-$C_3H_5$)X(CO)$_2$($CH_3CN$)$_2$] with several bidentate chelating 1,4-diazabutadiene ligands and to examine, for the first time, how these Mo(II) $\eta^3$-allyl dicarbonyl complexes and their precursors perform as catalyst precursors for the epoxidation of olefins using TBHP. The different stereochemical and electronic characteristics of the X and N−N ligands may impart distinct reactivities. For comparison, congener organometallic complexes were prepared by modifying the allyl group from $\eta^3$-$C_3H_5$ to $\eta^3$-$C_5H_5O$.

**Chart 1**



## Results and Discussion

**Synthesis and Characterization.** Derivatives of the Mo$^{\mathrm{II}}$($\eta^3$-allyl)X(CO)$_2$ fragment with bidentate nitrogen ligands, namely, 1,4-(2,6-dimethyl)phenyl-2,3-dimethyldiazabutadiene, 1,4-(2,6-diisopropyl)phenyldiazabutadiene (DAB), or 1,4-(4-chloro)phenyl-2,3-(1,9-naphthalene)diazabutadiene (BIAN), were synthesized from the well-known precursors [Mo($\eta^3$-$C_3H_5$)Cl(CO)$_2$($CH_3CN$)$_2$] (**1**), [Mo($\eta^3$-$C_3H_5$)Br(CO)$_2$($CH_3CN$)$_2$] (**2**),[22] or [Mo($\eta^3$-$C_5H_5O$)Br(CO)$_2$($CH_3CN$)$_2$] (**3**).[42] All the complexes are depicted in Chart 1. The complexes **4**−**8** were obtained by displacement of the acetonitrile ligands of complexes **1**−**3** and subsequent coordination of the bidentate ligand to the molybdenum center.

Two stable isomers, axial and equatorial, are known for this family of complexes, as shown in Chart 2. The preferences between them are not clear, and often they interconvert in solution.[43] In many structurally characterized species, it has been observed that bulky ligands tend to favor the formation of the axial isomer.

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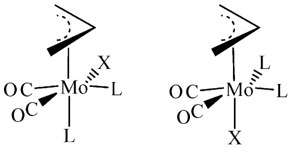
**Chart 2**



axial equatorial

**Table 1. FTIR Wavenumbers of $\nu_{C\equiv O}$ and $\nu_{C\equiv N}$ Modes for Complexes 1−8**

| complex | $\nu_{C\equiv O}$ (cm$^{-1}$) | $\nu_{C\equiv N}$ (cm$^{-1}$) |
|---|---|---|
| **1** | 1949, 1851 | 2320, 2287 |
| **2** | 1941, 1851 | 2316, 2284 |
| **3** | 1969, 1887[a] | 2312[a] |
| **4** | 1938, 1847 | |
| **5** | 1956, 1865 | |
| **6** | 1928, 1869 | |
| **7** | 1946, 1869 | |
| **8** | 1906, 1982 | |

[a] Taken from ref 44.

**Table 2. Selected Distances (Å) and Angles (deg) for the Molybdenum Coordination Sphere of Complex 7**

| | | | |
|---|---|---|---|
| Mo−C(100) | 1.957(6) | Mo−C(200) | 1.983(6) |
| Mo−N(11) | 2.277(4) | Mo−N(24) | 2.229(4) |
| Mo−Br | 2.6989(7) | | |
| C(100)−Mo−C(200) | 79.2(2) | N(24)−Mo−N(11) | 72.7(1) |
| C(100)−Mo−N(11) | 104.6(2) | C(200)−Mo−N(11) | 165.5(2) |
| C(100)−Mo−N(24) | 86.0(2) | C(200)−Mo−N(24) | 93.8(2) |
| N(11)−Mo−Br | 83.6(1) | N(24)−Mo−Br | 82.0(1) |
| C(100)−Mo−Br | 162.7(2) | C(200)−Mo−Br | 89.3(2) |
| Cent−Mo−O(100)[a] | 93.7 | Cent−Mo−O(200) | 96.6 |
| Cent−Mo−N(11) | 97.9 | Cent−Mo−N(24) | 170.2 |
| Cent−Mo−Br | 100.3 | | |

[a] Cent denotes the centroid defined by the three allylic carbon atoms.

Elemental analysis and FTIR and $^1$H and $^{13}$C NMR spectroscopy support the proposed structures. The FTIR spectra of **1**−**8** show the $\nu_{C\equiv O}$ stretching modes of the *cis*-C≡O groups in the expected range (1780−2000 cm$^{-1}$)[10] and the $\nu_{C\equiv N}$ of the precursors **1**−**3** (Table 1). A new band assigned to the $\nu_{C=N}$ mode of the nitrogen ligands and slightly deviated from those of the free ligands appears in the range 1600−1660 cm$^{-1}$. The vibrations assigned to the allyl group (∼3000 cm$^{-1}$ $\nu_{C-H}$ stretching, 1410−1420 cm$^{-1}$ $\delta_{C-H}$ in plane bending, 1000−1050 cm$^{-1}$ $\nu_{C-H}$ stretching, 950−900 cm$^{-1}$ $\delta_{C-H}$ out of plane bending) are always present, while the absence of the $\nu_{C\equiv N}$ stretching modes at ca. 2300 cm$^{-1}$ in **4**−**8** reflects the loss of the nitrile ligands from the precursors.

The $^1$H NMR spectroscopic data for all complexes show signals assigned to the corresponding bidentate nitrogen and allyl ligands. For example, the spectrum of [Mo($\eta^3$-C$_3$H$_5$)Cl(CO)$_2${1,4-(2,6-dimethyl)phenyl-2,3-dimethyldiazabutadiene}] (**4**) displays a multiplet in the range $7.50 < \delta < 7.24$ ppm, assigned to the protons of the aromatic rings, and signals at $\delta \approx 3.36$, 2.46, and 1.17 ppm, which are related to the meso, syn, and anti protons of the allyl group, respectively. The signals of the methyl protons are observed at 2.23 (CH$_3$Ph) and 2.13 ppm (CH$_3$-DAB).

The crystal structure of [Mo($\eta^3$-C$_3$H$_5$)Br(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (**7**) was determined by single-crystal X-ray diffraction. Selected bond distances and angles in the molybdenum coordination sphere, listed in Table 2, show that the metal center is surrounded by the ligands in a pseudooctahedral environment. The perspective view of **7** presented in Figure 1 confirms that the isomer found in the solid state is the axial one. The equatorial coordination plane is determined by the two carbonyls, bromine, and one nitrogen donor from 1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene, while the axial positions are occupied by the remaining nitrogen atom of this ligand and the centroid of $\eta^3$-C$_3$H$_5$ fragment.

This geometric arrangement is comparable to that found in related complexes.[43,45,46] The reported distances of the atom donors to the molybdenum center compare well with those quoted in Table 2 for **7**.

The two phenyl rings intersect the 2,3-naphthalenediazabutadiene fragment at interplanar angles of 88.8(2) and 79.0(1)°, indicating that they are almost perpendicular to this extended aromatic system.

Furthermore, in the unit cell, the naphthalenediazabutadiene aromatic rings from two molecules of **7** are at a distance of ca. 3.8 Å. This suggests that they are involved in $\pi-\pi$ stacking interactions, as shown in Figure 2.

**Catalytic Epoxidation of Olefins.** All complexes were tested as catalyst precursors for olefin epoxidation using *cis*-cyclooctene as a model substrate and *tert*-butyl hydroperoxide (TBHP in decane) as oxygen donor, without cosolvent, at 55 °C. Practically no olefin reacted without a catalyst, whereas the addition of a Mo complex led to a catalytically efficient process, yielding 88−100% 1,2-epoxycyclooctane as the only product within 24 h (Table 3).

The highest reaction rate was observed for **1**; nearly 90% cyclooctene conversion was achieved within ca. 10 min reaction, corresponding to a turnover frequency (TOF) of 472 mol mol$_{Mo}^{-1}$ h$^{-1}$ (Table 3). This is comparable to that reported in the literature for several halocarbonylmolybdenum(II) complexes of the type [MoCpCl(CO)$_3$] and dioxomolybdenum(VI) complexes of type [MoCpClO$_2$] (Cp = $\eta^5$-cyclopentadienyl)[34,37,47,48] and better than that reported for [Mo(O)$_2$(Cl)$_2$(CH$_3$CN)$_2$] used as catalyst precursors in the same reaction. In the case of the complexes **4**−**8**, the TOFs are comparable to some of the most active complexes of the type [MoCl$_2$O$_2$(DAB)] reported previously (using similar reaction conditions).[38,39,40] The highest TOF was observed for **6** (426 mol mol$_{Mo}^{-1}$ h$^{-1}$).

The ligand dependency of Mo-catalyzed epoxidation of olefins has been extensively investigated for complexes of the type [MoCpCl(CO)$_3$], [MoCpClO$_2$], and [MoX$_2$O$_2$L] (L = bidentate neutral N-ligand),[50,51] but to the best of our knowledge until now nothing has been reported for ($\eta^3$-allyl)dicarbonylmolybdenum(II) complexes. The initial rate of cyclooctene epoxidation in the presence of **1**−**8** is different depending on the nature of the X, N-donor ligands, and $\pi$-allyl ligands of the original compounds. Higher initial reaction rates are observed for the chloro complexes in comparison to their bromo congeners (compare couples **1**/**2** and **6**/**7**; Table 3). This is

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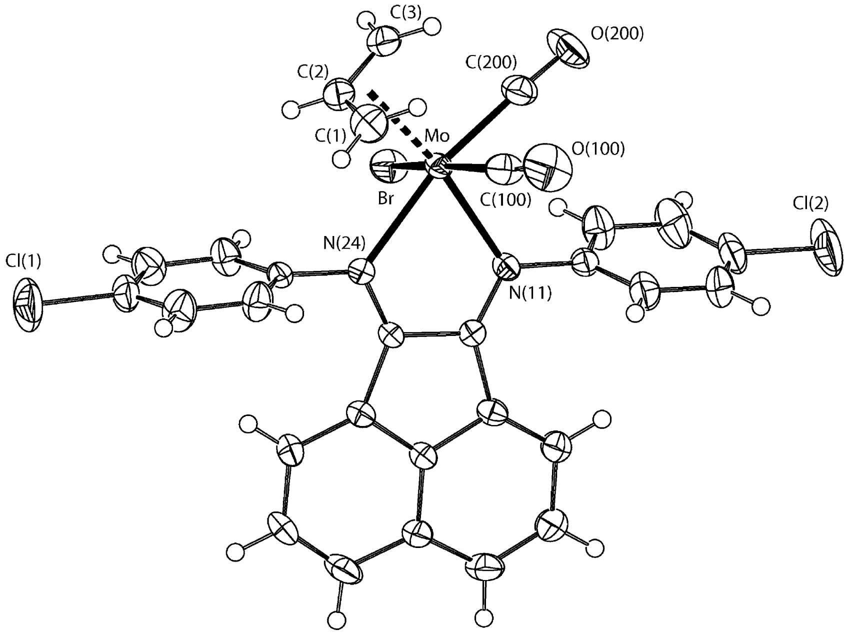

**Figure 1.** ORTEP diagram showing the molecular structure of [Mo($\eta^3$-$C_3H_5$)Br(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (**7**) with thermal ellipsoids drawn at 50% probability level.

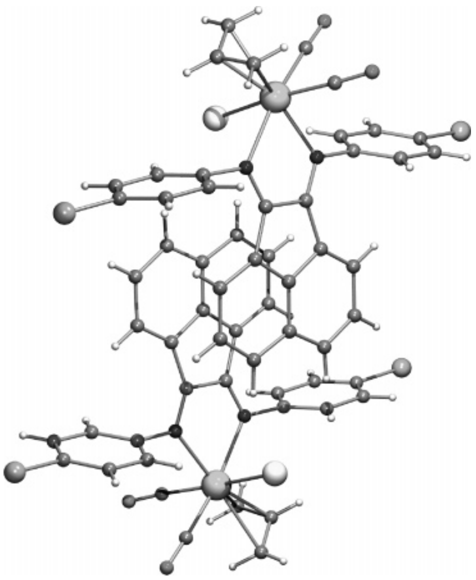

**Figure 2.** Crystal packing diagram illustrating the $\pi-\pi$ stacking in the unit cell of naphthalenediazabutadiene fragments of two molecules of **7**.

**Table 3. Olefin Epoxidation Using TBHP as Oxygen Donor in the Presence of Complexes 1−8**

| complex | substrate | TOF[a] (mol $\text{mol}_{\text{Mo}}^{-1}$ $h^{-1}$) | conv[b] (%) | conv[c] (%) run 1/run 2 |
|---|---|---|---|---|
| **1** | cyclooctene | 472 | 99/100 | 93/81 |
| **2** | cyclooctene | 222 | 99/100 | 88/91 |
| **3** | cyclooctene | 310 | 97/100 | |
| **4** | cyclooctene | 297 | 88/95 | 82/63 |
| **5** | cyclooctene | 305 | 68/88 | |
| **6** | cyclooctene | 426 | 99/100 | 93/84 |
| **7** | cyclooctene | 307 | 99/100 | 91/78 |
| **8** | cyclooctene | 284/265[d] | 97/100 | 88/83 |
| **8** | (*R*)-(+)-limonene | 287[d] | 100/100 | |
| **8** | cyclododecene | 100[d] | 82/94 | |
| **8** | *trans*-2-octene | 42[d] | 67/85 | |
| **8** | 1-octene | 2[d] | 22/40 | |

[a] Turnover frequency calculated at 10 min, at 55 °C. [b] Cyclooctene conversion after 6/24 h reaction in the first run, at 55 °C. [c] Cyclooctene conversion in the first/second runs, at 45 °C. [d] 1,2-Dichloroethane was used as cosolvent, at 55 °C.

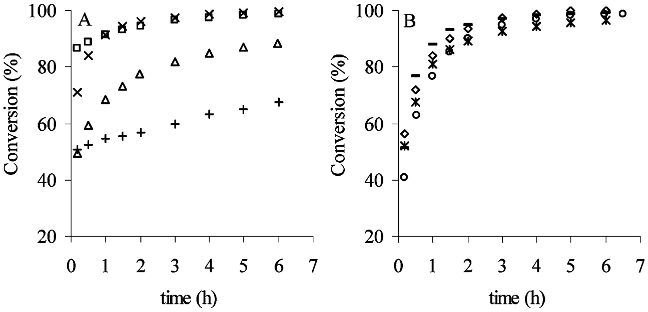

**Figure 3.** Cyclooctene epoxidation using TBHP as oxygen donor, without cosolvent, at 55 °C, in the presence of (A) [Mo($\eta^3$-allyl)-Cl(CO)$_2$(N−N)] (**1** (□); **4** (△); **5** (+); **6** (×)) or (B) [Mo($\eta^3$-allyl)-Br(CO)$_2$(N−N)] (**2** (○); **3** (◇); **7** (−); **8** (∗)).

typical of the [$MoX_2O_2L$]-type complexes with the same L and has been attributed to the enhanced Lewis acidity at the metal center in the case of X = Cl,[40,52−54] though this interpretation has not been confirmed.[54] In the case of the complexes with X = Cl, the epoxidation reaction is slower for **4-6** (bearing bidentate N-ligands) than for the corresponding precursor **1**: this effect is less pronounced for X = Br (Figure 3). A comparative study for couples **2**/**3** and **7**/**8** shows that the initial reaction rate is somewhat affected by the type of $\pi$-allyl ligand ($\eta^3$-$C_3H_5^-$ or $\eta^3$-$C_5H_5O^-$) present in the original compounds. The different catalytic activities are probably a consequence of the complex interplay of steric and electronic factors, which govern among others the type of isomers formed (Chart 2). The more labile solvent adducts **1**−**3** may exist as a mixture of isomers that interconvert, while the complexes bearing bulkier and bidentate N−N ligands may be less fluxional in solution,

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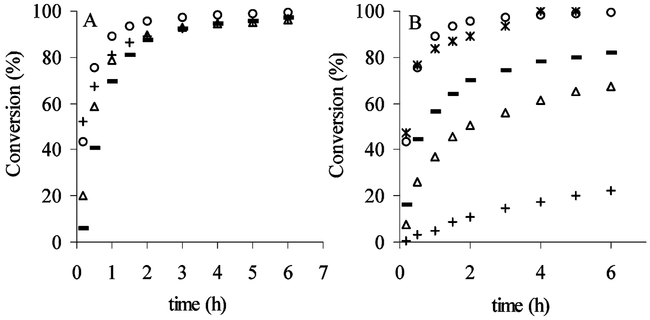

**Figure 4.** Olefins epoxidation using TBHP as oxygen donor in the presence of **8**, at 55 °C: (A) solvent effect on cyclooctene epoxidation without a cosolvent (+) or with 1,2-dichloroethane (○), toluene (△), or *n*-hexane (−), at 55 °C; (B) epoxidation of cyclooctene (○), (*R*)-(+)-limonene (∗), cyclododecene (−), *trans*-2-octene (△), or 1-octene (+), using 1,2-dichloroethane as cosolvent.

preferring the axial isomer, as attested for **7** by $^1$H NMR spectroscopy. The nature of the ligands may affect the electronic density of the metal center, accounting for different reactivity of the complexes with, for example, TBHP (a necessary step to originate active intermediate species, since no reaction occurs without TBHP). Differences in solubility are unlikely to be relevant, since the solubility of these compounds in the reaction medium is apparently similar.

The kinetic profiles of **1**−**8** display an initial abrupt increase in cyclooctene conversion (no induction periods were observed) after which the reaction slows down considerably with the course of time (Figure 3). This behavior has typically been found for cyclooctene epoxidation with complexes of the type MoCpCl(CO)$_3$ and MoCpClO$_2$,[34,36,37,48] as well as for several dioxomolybdenum(VI) complexes belonging to the [MoX$_2$O$_2$L] family, under similar reaction conditions.[51,53,54] Kinetic and DFT studies of molybdenum epoxidation reactions catalyzed by [MoX$_2$O$_2$L] complexes have led to the proposal that the TBHP first reacts with the metal species and afterward the olefin attacks the resulting intermediate Mo−alkyl(hydro)peroxo complex in a second step to give the corresponding epoxide and *tert*-butanol. The latter byproduct may compete with *t*-BuOOH for coordination to the metal center, gradually retarding the overall reaction.[53,54,55]

The catalyst reusability was examined at 45 °C, by initiating a second reaction cycle after 24 h, without catalyst separation and recharging equimolar amounts of cyclooctene and TBHP. In general, the catalytic performance was quite efficient in the second run (Table 3). The catalytic results obtained for **1** and **2** are outstanding compared to those found in the literature for solvent adducts of the type [MoX$_2$O$_2$(CH$_3$CN)$_2$], used as catalysts in the same reaction.[49] The latter undergo catalyst deactivation during a first catalytic run, accounting for a maximum of 65% cyclooctene conversion, at 55 °C. Compounds **1** and **2** gave 100% conversion, which decreased by a factor of only 0.13 and 0.03, respectively, from the first to the second run. Compounds **2** and **8** also gave approximately the same conversion in the first and second runs, and in the cases of **1**, **4**, **6**, and **7** conversions at 24 h decreased by a factor of 0.10−0.24.

Further tests to assess the influence of the solvent on the epoxidation of cyclooctene were carried out for **8**, using *n*-hexane, toluene, or 1,2-dichloroethane (DCE), at 55 °C. The type of solvent influences the reaction rate, mainly for the first 2 h reaction (Figure 4A), without affecting product selectivity. The addition of a cosolvent led to a drop in the initial reaction rate, which may be partly due to the decrease in catalyst concentration as a result of the dilution. Nevertheless, between 15 and 120 min reaction conversion follows the order DCE > none > toluene > hexane. Whereas the reaction system with DCE is homogeneous, for hexane a heterogeneous solid−liquid system is obtained, which may explain, at least in part, the observed differences in catalytic activity. Eventually, at 6 h, nearly quantitative epoxide yield is obtained for all solvents.

The catalytic performance of **8** was further investigated for the epoxidation of other olefins, namely, cyclododecene, *trans*-2-octene, 1-octene, and (*R*)-(+)-limonene, using DCE as solvent, at 55 °C. For all substrates, with the exception of limonene, the corresponding epoxide is the only product. The initial rate of olefin conversion decreases in the order cyclooctene ≅ limonene > cyclododecene > *trans*-2-octene > 1-octene (Table 3). The kinetic profiles are similar, suggesting that a similar reaction mechanism may be involved for all olefins (Figure 4B). In the case of limonene, 95% epoxide products are obtained at 24 h and byproducts include ca. 4% diols. Regioselectivity is high in favor of the epoxidation of the internal cyclic double bond, yielding limonene oxide and 1,2:8,9-diepoxy-*p*-menthane in a molar ratio of 7. These results are consistent with the mechanistic aspects mentioned above, since the higher electronic density of an internal olefinic double bond (compared with the terminal C═C bond) should favor nucleophilic attack on an electrophilic oxidizing specie. The slower reaction of cyclododecene in comparison to that of cyclooctene may be due to the larger molecular dimensions of the former substrate.

**Reaction Mechanism.** The clear understanding of the mechanism of olefin epoxidation using the previous compounds requires the elucidation of the nature of the active specie(s) involved. Joshi[30] proposed that the oxidation of [Mo($\pi$-allyl)-Cl(CO)$_2$L] (L = bis(3,5-dimethylpyrazolyl)methane) with molecular oxygen resulted in the loss of an allyl radical and formation of a dimeric Mo(V) oxo complex featuring the neutral bidentate chelate and the halide ligand. This dimeric complex efficiently catalyzed the oxidation of triphenylphosphine with O$_2$, possibly via a peroxo intermediate. Attempts at characterizing the metal complex after catalysis were made for **4**. After cooling of the sample to room temperature, a small amount (ca. 15 wt % of the initial amount of **4**) of solid compound (lighter in color than the original complex and hereafter denoted as **4***) could be separated from the reaction solution by centrifugation. Compound **4*** was thoroughly washed with *n*-hexane and dried at room temperature prior to characterization.

The FTIR and Raman spectra of **4*** were substantially different from that of the original compound. In contrast to that observed for **4**, the IR spectrum of **4*** did not show the $\nu_{C\equiv O}$ bands in the region 1780−2000 cm$^{-1}$ but contained two new strong $\nu_{Mo=O}$ bands at 920 and 956 cm$^{-1}$, characteristic of the asymmetric and symmetric stretching vibrations of the *cis*-[MoO$_2$]$^{2+}$ fragment.[53,54,56] In the Raman spectrum of **4*** the Mo═O stretching modes are observed in the range 880−980 cm$^{-1}$, whereas the bands in the range 430−510 cm$^{-1}$, assigned to Mo−C bonds, practically disappeared.[54] On the basis of these results, it seems possible that, under the reaction conditions, **4** undergoes complete oxidative decarbonylation in the presence of TBHP, to give a dioxomolybdenum complex. The IR spectrum of **4*** contained a broad band of strong intensity centered at 714 cm$^{-1}$, not present in the spectrum of the original

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compound, which may be assigned to Mo−O−Mo stretching vibrations.[56,57] Materials containing binuclear species with two Mo(VI) centers, each with two Mo═O groups and each linked by one or two oxo-bridges, have been identified as active species for olefin epoxidation and oxidation of alcohols with TBHP, under reaction conditions similar to those applied in this work.[56] The IR-absorption band at ca. 1646 cm$^{-1}$ assigned to the $\nu_{C=N}$ mode in the DAB group of **4** shifted to 1620 cm$^{-1}$ after catalysis, possibly due to changes in the oxidation state and first coordination sphere of Mo. Weak bands in the range 2850−3060 cm$^{-1}$ assigned to C−H bonds of the DAB ligand were present for both **4** and **4***. The Raman spectra of **4** and **4*** differed in the 190−240 cm$^{-1}$ range, possibly owing to changes in the Mo−N stretching vibrations, as would be expected from the discussion above.[54] After catalysis, the intensities of the Raman-absorption bands centered at ca. 250 and 360 cm$^{-1}$ assigned to Mo−Cl vibrations decreased drastically. The band at 1213 cm$^{-1}$, tentatively assigned to the $\pi$-allyl group of **4**, is no longer present after catalysis. The $^1$H NMR spectrum of **4*** in $CD_2Cl_2$ displayed signals in the range 7−8.0 ppm, assigned to the aromatic rings, as well as two methyl resonances at 1.96 and 1.60 ppm, but showed no signals of allyl groups. These results indicate that the Mo(II) complex reacts with TBHP to give the active oxidizing species for olefin epoxidation, which may be dimeric dioxomolybdenum(VI) complexes of the type $[\{MoXO_2(N-N)\}_2(\mu\text{-}O)]$ and/or $[\{MoO_2(N-N)\}_2(\mu\text{-}O)_2]$. The **4*** sample contains less than 1% Cl (ascertained by ionic chromatography), which is much lower than that expected for $[\{MoClO_2(N-N)\}_2(\mu\text{-}O)]$ (ca. 7.7% Cl). Hence, if species of the type $[\{MoClO_2(N-N)\}_2(\mu\text{-}O)]$ are formed during catalysis, they are not predominant. Elemental analysis of 4* gave 59.5% C, 3.2% N, and 5.4% H. The expected values for $[\{MoO_2(N-N)\}_2(\mu\text{-}O)_2]$ are 55.1% C, 6.4% N, and 5.5% H and for $[\{MoXO_2(N-N)\}_2(\mu\text{-}O)]$ are 51.8% C, 6.0% N, and 5.2% H. The relatively high carbon content of **4*** may be due to reaction products and/or solvent present in the recovered solid (the presence of decane and *tert*-butanol signals was detected in the $^1$H NMR). The ESI mass spectra of **4*** showed several ions, and above *m*/*z* 750, the spectrum was quite noisy, making it difficult to interpret. Three parts of the spectrum (*m*/*z* = 177, 487, 517) showed isotopic patterns corresponding to Mo species that were not identified. Degradation of the complex may occur to a certain extent under the conditions of the ESI source (350 °C).

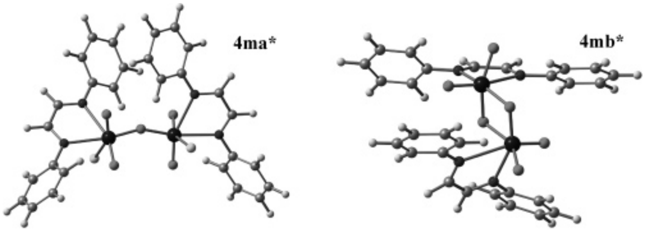

**Figure 5.** DFT-optimized geometries of two possible Mo(VI) dimers $[\{MoO_2Cl(N-N)\}_2(\mu\text{-}O)]$ (**4ma***) and $[\{MoO_2(N-N)\}_2(\mu\text{-}O)_2]$ (**4mb***).

DFT/B3PW91[58] calculations (Gaussian03 program; see Computational Details) were performed to try to identify the species **4***. Several models based on available oxide complexes of Mo(VI), including monomers and dimers, were built. 1,4-Phenyldiazabutadiene was taken as model for the DAB ligand in **4** (methyl groups were replaced by hydrogen atoms). The monomers did not converge easily, suggesting that they are not stable species in the absence of another coordinating ligand. Two model dimers, $[\{MoO_2Cl(N-N)\}_2(\mu\text{-}O)]$ (**4ma***) and $[\{MoO_2(N-N)\}_2(\mu\text{-}O)_2]$ (**4mb***), were studied. For $[\{MoO_2Cl(N-N)\}_2(\mu\text{-}O)]$ (**4ma***), the molybdenum is coordinated to three oxygen atoms, which can exhibit a facial or meridional arrangement. Structures available in the CSD[59] contain the *fac*-$Mo(O)_3$ group, and it was found that during the optimization procedure the meridional isomers converted into the facial ones. The structures of the two most likely optimized models of **4*** are shown in Figure 5.

The Mo−O−Mo angle was 156.6 and 102.6°/98.6° for **4ma*** and **4mb***, respectively, with Mo−O distances of 1.886 and 1.925/1.980 Å, in the same order. The terminal Mo═O bonds were slightly shorter for **4ma*** (1.676/1.706 Å) than for **4mb*** (1.690/1.717 Å). These values are in the range usually found for other Mo(VI) oxide complexes. The calculated $\nu_{Mo-O-Mo}$ stretching frequency was 798 and 661 cm$^{-1}$ for **4ma*** and **4mb***, respectively, compared to 714 cm$^{-1}$ for **4***. The Mo═O stretching frequencies appeared in the range 936−1012 cm$^{-1}$ for **4ma*** and 911−990 cm$^{-1}$ for **4mb***, the former being closer to the experimental values. Both models give for the C═N stretching vibrations (1595−1706 cm$^{-1}$) values similar to that observed experimentally for **4*** (1620 cm$^{-1}$). These results, together with the lack of clear evidence for Mo−Cl vibrations, suggest that the reaction of **4** with TBHP originates a complex of the type $[(MoO_2(N-N))_2(\mu\text{-}O)_2]$, though a mixture of the two dimeric species cannot be ruled out. If species of the type $[(MoO_2(N-N))_2(\mu\text{-}O)_2]$ were also formed from **6**−**8**, one could expect similar epoxidation rates for these three complexes, at least after an initial period of time. In fact, for **6**−**8**, cyclooctene conversions at 1 h differ only in 10%, tending to similar values (Figure 3A,B). Similarly, in the case of complexes **1**−**3**, conversions differ in 8% after 1.5 h reaction. When the solid is removed from the reaction mixture (using a Whatman 0.2 $\mu$m (PVDF w/GMF) membrane at the reaction temperature) after 30 min and the solution is left to react further 5.5 h, cyclooctene conversion is the same as that achieved when no solid is removed, suggesting that the reaction is homogeneous in nature. The recovered solid **4*** is active in a second reaction run, giving 75% conversion at 24 h compared to 95% when no solid is removed during the reaction.

A proposal of the catalytic cycle for olefin epoxidation is sketched in Scheme 1, based on our previous studies of similar reactions.[54,55] We assume that the precursor complex is converted by TBHP in the active species, the Mo(VI) dimer **4***. Another molecule of TBHP adds to the Mo═O bond to form the heptacoodinate environment of Mo(VI), with two new ligands, OH and OOR.

Notice that a similar reaction may happen in the second side of the molecule (not shown for clarity). The olefin then adds to the Mo−O bond, forming a large cycle with hydrogen bond assistance from the OH ligand. This hydrogen bond positions the reagents for the loss of alcohol in the final step, which takes place with formation of the epoxide and regeneration of the catalyst.

## Conclusions

Several new complexes of the Mo($\eta^3$-allyl)X(CO)$_2$ fragment with derivatives of diazabutadiene were synthesized and char-

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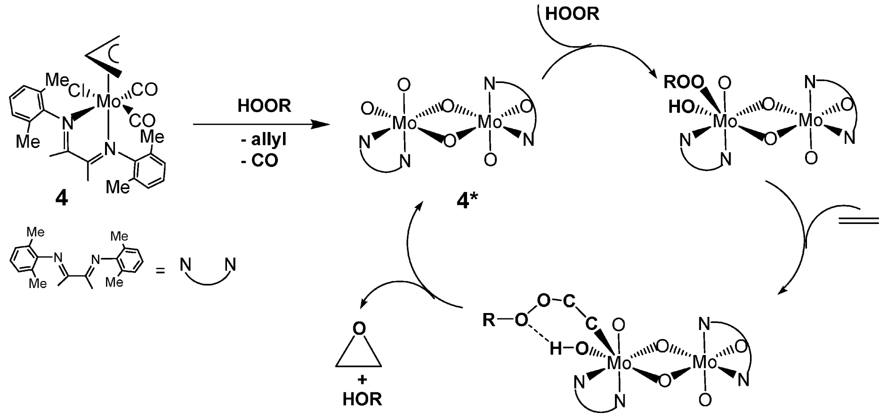
**Scheme 1**



acterized. The X-ray structure of [Mo($\eta^3$-$C_3H_5$)Br$(CO)_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (**7**) showed the formation of the axial isomer, and it was found by NMR spectroscopy that only one isomer exists in solution. The complexes were tested in the epoxidation of cyclooctene with TBHP, giving excellent epoxide selectivity and turnover frequencies, comparable to those reported previously for some well-known molybdenum(VI) catalysts but displaying as well an extremely efficient second run, not observed in any of the other Mo(VI) systems. To identify the active species, combined experimental (vibrational and NMR spectroscopy, analysis) and computational (DFT) studies were carried out for one of the diimine complexes. The probable active species is a dimer of the type $[\{MoO_2(N{-}N)\}_2(\mu\text{-}O)_2]$, which requires more TBHP to perform epoxidation and complete the catalytic cycle, as discussed in previous works for Mo(VI) catalysts. This formulation is also supported by the fact that similar olefin conversions are achieved after a relatively short period of time for complexes with the same N-donor ligands, independently of X and allyl ligands. More experimental work is being carried out to clarify the details of the mechanism. Probably, the dimeric framework of the active species is more stable under reaction conditions, contributing to the high catalytic activity after the first run. On the other hand, preliminary experiments carried out for **8** (which has no symmetry) showed no induction ability for enantioselective epoxidations with TBHP. This disappointing result is somewhat in agreement with the symmetric structure proposed for **4***.

## Experimental Section

**General Considerations.** All air-sensitive reactions and manipulations were performed using standard Schlenk techniques under an oxygen-free and water-free nitrogen atmosphere. Commercially available reagents and all solvents were purchased from standard chemical suppliers. Solvents were dried by standard procedures (THF, *n*-hexane, and $Et_2O$ over Na/benzophenone ketyl; $CH_2Cl_2$ and $CH_3CN$ over $CaH_2$), distilled under nitrogen, and kept over 4 Å molecular sieves (3 Å for $CH_3CN$).

Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer as KBr pellets. $^1H$ and $^{13}C$ solution NMR spectra were obtained with a Bruker Avance-400 spectrometer. Chemical shifts are quoted in parts per million (ppm) from TMS. Microanalyses for C, H, and N were performed at the Departments of Chemistry, Universities of Aveiro and Vigo. The ESI (in negative mode) mass spectral data were obtained at the Mass Spectrometry Center, University of Aveiro, using a Finnigan LXP (Thermo Electron Corp.) equipment operated at an acceleration voltage of 5 kV and ESI source temperature of 350 °C. Ionic chromatography was carried out on a DX100 equipment using a AG4ASC column and an aqueous solution composed of 1.7 mM $Na_2CO_3$ plus 1.8 mM $NaHCO_3$ as eluent.

Complexes [Mo($\eta^3$-$C_3H_5$)Cl$(CO)_2(CH_3CN)_2$] (**1**) and [Mo($\eta^3$-$C_3H_5$)Br$(CO)_2(CH_3CN)_2$] (**2**) were prepared by following the synthetic procedure reported in literature by tom Dieck et al.[22] [Mo($\eta^3$-$C_5H_5O$)Br$(CO)_2(CH_3CN)_2$] (**3**) was prepared as described by Liebeskind et al.,[42] and the ligands 1,4-(2,6-dimethyl)phenyl-2,3-dimethyldiazobutadiene, 1,4-(2,6-diisopropyl)phenyldiazabutadiene,[60] and 1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene were from literature procedures.[61]

**Preparation of [Mo($\eta^3$-$C_3H_5$)Cl$(CO)_2${1,4-(2,6-dimethyl)phenyl-2,3-dimethyldiazabutadiene}] (4).** 2,6-DimethylPh-DAB (2,6-$MeC_6H_3$)N=C($CH_3$)C($CH_3$)C=N(2,6-$MeC_6H_3$)) (0.5 mmol, 0.146 g) was added to a yellow solution of [Mo($\eta^3$-$C_3H_5$)Cl$(CO)_2(CH_3CN)_2$] (0.5 mmol, 0.155 g) in $CH_2Cl_2$ (20 mL), under $N_2$ and stirring, to give a dark blue solution. This solution was stirred for 2 h, and the volume was reduced under vacuum. After addition of *n*-hexane, the mixture was left in the fridge during 2 days and gave dark blue precipitate. It was washed with 3 × 5 mL of diethyl ether and dried under vacuum.

Anal. Calcd for **4**·1.5$CH_2Cl_2$: C, 49.10; H, 4.97; N, 4.32. Found: C, 48.86; H, 4.60; N, 4.53.

$^1H$ NMR (400 MHz, $CDCl_3$, room temperature, ppm): $\delta$ 7.24 (m, H3′−H5′, 6H), 3.36 (m, $H_{meso}$, 1H), 2.46 (br, $H_{syn}$ + $CH_3Ph$, 5H), 2.23 (br, $CH_3Ph$, 9H), 2.13 (s, $CH_3$-DAB, 6H), 1.17 (d, $H_{anti}$, 2H).

$^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, room temperature, ppm): $\delta$ 172.38 (C2/C3), 129.75 (C3′ or C5′), 129.48 (C1′), 128.78 (C3′ or C5′), 127.21 (C2′/C6′), 126.99 (C4′), 73.71 ($C_{meso}$), 63.08 ($C_{anti/syn}$), 20.43 ($CH_3Ph$), 18.52 ($CH_3$-DAB).

Selected IR (KBr pellets, $cm^{-1}$): 1938, 1847 ($\nu_{C\equiv O}$), 1630 ($\nu_{C=N}$), 1417 ($\delta_{p(C-H)allyl}$), 1210 ($\nu_{s(C-C}$−C)allyl), 983 ($\delta_{op(C-H)allyl}$).

**Preparation of [Mo($\eta^3$-$C_3H_5$)Cl$(CO)_2${1,4-(2,6-diisopropyl)phenyldiazabutadiene}] (5).** 2,6-DiisopropylPh-DAB [2,6-$^iPrC_6H_3$)N=C($CH_3$)C($CH_3$)C=N(2,6-$^iPrC_6H_3$)] (0.5 mmol, 0.188 g) was added to a yellow solution of [Mo($\eta^3$-$C_3H_5$)Cl$(CO)_2(CH_3CN)_2$] in $CH_2Cl_2$ (20 mL), under $N_2$ and stirring, to give a dark green solution. This solution was stirred for 2 h, and the volume was reduced by vacuum. After addition of *n*-hexane, the mixture was left in the fridge during several days and gave a dark green precipitate. It was washed three times with 5 mL of *n*-hexane and dried under vacuum.

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Anal. Calcd for **5**·1.5$C_6H_{14}$: C, 65.42; H, 8.51; N, 3.81. Found: C, 65.85; H, 7.61; N, 3.30. $^1H$ NMR (400 MHz, $CDCl_3$, room temperature, ppm): $\delta$ 8.02 (s, H-DAB, 2H), 7.30−7.20 (m, H3−H5, Ph, 6H), 3.67 (m, $H_{meso}$ + $CH^i$pr, 5H), 2.86 (br, $H_{syn}$, 2H), 1.44 (d, $H_{anti}$, 2H), 1.30 (d, $CH_3{}^i$pr, 6H), 1.23 (d, $CH_3{}^i$pr, 6H), 1.01 (d, $CH_3{}^i$pr, 6H), 0.93 (d, $CH_3{}^i$pr, 6H). $^{13}C\{^1H\}$ NMR (100.51 MHz, $CDCl_3$, room temperature, ppm): $\delta$ 159.88 (C2/C3), 141.10 (C2′, C6′), 139.48 (C1′), 128.34, 124.77 (C3′, C5′), 123.77 (C4′), 78.29 ($C_{meso}$), 65.26 ($C_{anti/syn}$), 26.47, 22.63 ($CH_3$ $^i$pr,), 28.16 ($CH^i$pr). Selected IR (KBr pellets, $cm^{-1}$): 1938, 1847 ($\nu_{C\equiv O}$).

**Preparation of [Mo($\eta^3$-$C_3H_5$)Cl(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (6).** To a yellow solution ($CH_2Cl_2$, 10 mL) of [Mo($\eta^3$-$C_3H_5$)Cl(CO)$_2$($CH_3CN$)$_2$] (1.0 mmol, 0.310 g) was added *N,N*'-bis(*p*-chlorophenylimino)acenaphthene (1 mmol, 0.396 g) under stirring and $N_2$. A dark green precipitate was formed. The stirring was continued overnight. The green precipitate was filtered off, washed with 3 × 10 mL of $CH_2Cl_2$, and dried under vacuum.

Anal. Calcd for **6**: C, 55.31; H, 3.04; N, 4.45. Found: C, 54.55; H, 3.06; N, 4.28. $^1H$ NMR (400 MHz, dmf-$d_7$, room temperature, ppm): $\delta$ 8.30 (d, H5/H6, 2H), 7.85 (d, H3′/H5′, 4H), 7.73 (t, H4/H7, 2H), 7.58 (d, H2′/H6′, 4H), (6.96 (br, H3/H8, 2H), 4.95 (m, $H_{meso}$, 1H), 2.98 ($H_{syn}$, overlapped with the solvent signal), 1.31 (d, $H_{anti}$, 2H). $^{13}C$ NMR (HMQC, dmf-$d_7$, ppm): $\delta$ 131.6 (C5/C6), 130.5 (C3′/C5′), 128.7 (C4/C7), 124.8 (C3/C8), 122.2 (C2′/C6′), 77.3 ($C_{meso}$), 56.2 ($C_{anti/syn}$). Selected IR (KBr pellets, $cm^{-1}$): 1928, 1869 ($\nu_{C\equiv O}$).

**Preparation of [Mo($\eta^3$-$C_3H_5$)Br(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (7).** *N,N*'-Bis(*p*-chlorophenylimino)acenaphthene (2.6 mmol, 1.027 g) was added to a yellow solution of [Mo($\eta^3$-$C_3H_5$)Br(CO)$_2$($CH_3CN$)$_2$] (2,0 mmol, 0.710 g) in ethanol (30 mL) under $N_2$ with stirring. The dark green solution formed was stirred for 2 days, and then the volume was reduced under vacuum. The mixture was left in the fridge during several days. The dark blue precipitate was filtered out, washed with 2 × 20 mL of *n*-hexane, and dried under vacuum. It was recrystallized by diffusion of *n*-hexane into a $CH_2Cl_2$ solution of the compound. Diffusion of *n*-hexane into a $CH_2Cl_2$ solution of the compound gave good crystals for single X-ray diffraction studies.

Anal. Calcd for **7**: C, 51.66; H, 2.84; N, 4.15. Found: C, 50.94; H, 3.08; N, 4.04. $^1H$ NMR ($CDCl_3$, room temperature, ppm): $\delta$ 7.96 (d, H5/H6, 2H), 7.61 (d, H3′/H5′, 4H), 7.59 (d, H2′/H6′, 4H), 7.4′), 7.46 (t, H4/H7, 2H), 6.63 (br, H3/H8, 2H), 3.72 (m, $H_{meso}$), 2.01 (d, $H_{syn}$, 2H), 1.18 (d, $H_{anti}$, 2H). $^{13}C$ NMR (dmf-$d_7$, ppm): $\delta$ 132.8 (C5/C6), 130.5 (C3′/C5′), 128.7 (C4/C7), 124.9 (C3/C8), 122.3 (C2′/C6′), 77.5 ($C_{meso}$), 55.6 ($C_{anti/syn}$). Selected IR (KBr pellets, $cm^{-1}$): 1946, 1869 ($\nu_{C\equiv O}$).

**Preparation of [Mo($\eta^3$-$C_5H_5O$)Br(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (8).** *N,N*'-Bis(*p*-chlorophenylimino)acenaphthene (3 mmol, 1.203 g) was added to a yellow solution of Mo($\eta^3$-$C_5H_5O$)Br(CO)$_2$($CH_3CN$)$_2$] (3.0 mmol, 1.184 g) in $CH_2Cl_2$ (20 mL) under $N_2$ with stirring. The dark green precipitate formed was filtered out, washed with 2 × 20 mL of *n*-hexane, and dried under vacuum.

Anal. Calcd for **8**·$CH_2Cl_2$: C, 48.09; H, 2.65; N, 3.51. Found: C, 48.17; H, 2.45; N, 3.56. $^1H$ NMR (dmso-$d_6$, ppm): 8.31 (dd, H5/H6, 2H), 7.80 (dd, H3′/H5′, 4H), 7.71 (t, H4/H7, 2H), 7.68-7.39 (m, H2′/H6′, 4H), (6.83 (d, H3/H8, 2H), 6.20 (t, H3-Cy, 1H), 3.64 (m, H2-Cy, 1H), 3.47 (t, H4-Cy, 1H), 2.88, 1.98 (d, H5-Cy, 2H). Selected IR (KBr pellets, $cm^{-1}$): 1906, 1982 ($\nu_{C\equiv O}$).

**Catalytic Reactions Using Compounds 1−8.** The liquid-phase catalytic epoxidations were carried out at atmospheric pressure in a reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath. Typically, 1% molar ratio of complex/substrate and a substrate/oxidant molar ratio of 0.63 were used. *tert*-Butyl hydroperoxide (TBHP) was used as the oxygen donor (5.5 M in decane), and different substrates were studied, namely cyclooctene, (*R*)-(+)-limonene, 1-octene, *trans*-2-octene, and cyclododecene. The reactions were carried out without additional solvent (other than the decane present in the TBHP solution) or using *n*-hexane, 1,2-dichloroethane, or toluene as cosolvent (2 mL solvent for 1.8 mmol substrate). The course of the reaction was monitored using a gas chromatograph (Varian 3800) equipped with a capillary column (DB-5, 30 m × 0.25 mm) and a flame ionization detector. The products were identified by gas chromatography−mass spectrometry (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas.

**Crystallography.** Crystals of [Mo($\eta^3$-$C_3H_5$)Br(CO)$_2${1,4-(4-chloro)phenyl-2,3-naphthalenediazabutadiene}] (**7**) with suitable quality for single-crystal X-ray determination were grown up from $CH_2Cl_2$/hexane solution. Crystal data: $C_{29}H_{19}BrCl_2MoO_2$, $M_r$ = 674.21; triclinic, space group $P\bar{1}$, $Z = 2$; $a = 9.705(12)$, $b = 10.499(17)$, $c = 13.612(17)$ Å; $V = 1335.2$ Å$^3$; $\alpha = 77.65(10)$, $\beta = 87.16(10)$, $\gamma = 80.25\ (10)°$; $\rho$(calcd) = 1.677 Mg $m^{-3}$, $\mu$(Mo K$\alpha$) = 2.218 $mm^{-1}$.

X-ray data were collected at room temperature on a MAR Research Image plate system using graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) at Reading University. The crystals were positioned at 50 mm from the detector, and the frames were measured using an appropriated counting. Data analysis was carried out with the XDS.[62] An empirical absorption correction was carried out using the DIFABS program.[63] A total of 6691 reflections collected were merged in $\bar{1}$ symmetry leading to 4539 unique data with a $R_{int}$ of 0.0308.

The structure was solved by direct methods and subsequent difference Fourier syntheses and refined by full matrix least-squares on $F^2$ using the SHELX-97 system programs.[64] Anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms bonded to carbon atoms were included in the refinement in calculated positions giving thermal parameters equivalent 1.2 times those of the atom to which were attached. The residual electronic density ranging from −0.49 to 0.67 e Å$^{-3}$ was within the expected values. The final refinement of 335 parameters converged to final R and $R_w$ indices $R_1 = 0.0514$ and $wR_2 = 0.0970$ for 3740 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0697$ and $wR_2 = 0.1031$ for all unique *hkl* data. Molecular diagrams were drawn with PLATON.[65]

**Computational Details.** DFT[58] calculations were performed using the Gaussian03 program (rev C.02)[66] with the B3PW91 hybrid functional. This functional includes a mixture of Hartree−Fock exchange with DFT exchange-correlation given by Becke's three-parameter hybrid functional[67] with Perdew and Wang's 1991

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gradient-corrected correlation functional.[68] The basis set for Mo consisted of the standard SDD basis set[69] augmented with a f polarization function in all calculations,[70] while the 6-311G** basis set[71] was used on all remaining atoms. Frequency calculations were performed at the same level of theory to confirm the nature (minima) of the stationary points determined.

The two models **4ma*** and **4mb*** were based on available structures of Mo(VI) oxide complexes taken from the CSD,[59] namely GODMIV, HUXMAD, ECOYAW, and FILYIL (see the structures in Figure 1S, Supporting Information) and the DAB ligand from the X-ray structure of complex **7** described above, and their structures were optimized under $C_2$ symmetry.

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**Supporting Information Available:** Figures giving available structures of Mo(VI) oxides from the CSD. This material is available free of charge via the Internet at http://pubs.acs.org.

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