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Article

Molybdenum(II) Complexes Containing Cyclopentadienyl-Functionalized N-Heterocyclic Carbenes: Synthesis, Structure, and Application in Olefin Epoxidation

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A set of four different (Cp^x-NHC)$Mo(CO)_2I$ (Cp^x = Cp, Cp*, and Cp^{Bz}, NHC = N-heterocyclic carbenes) complexes has been prepared from the one-pot reaction of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ and the corresponding lithium NHC-cyclopentadienides. The modification of the Cp^x-NHC affords a smooth way to tune the stereoelectronic properties of these new molybdenum complexes. These compounds are air stable both in solution and in the solid state. Preliminary studies on the catalytic epoxidation with *cis*-cyclooctene and TBHP as oxidant show that the activity of the catalysts clearly depends on the nature of the Cp^x-NHC ligand. The reaction proceeds smoothly toward epoxide; no diols or any other byproduct was detected along the reaction course.

Introduction

Due to their ability to stabilize a wide range of metal fragments, anionic tethered N-heterocyclic carbenes have been of increasing interest in recent years.[1] A large set of ligands has been prepared, in which the NHC is combined with alkoxide, phenoxide, or amido groups, to potentially afford chelating coordination forms.[1,2] Their initial use in early transition metals has now been widened across both d-block and f-block metals. Recently, the first indenyl- and fluorenyl-NHCs were disclosed by Danopoulos and Downing.[3] Their coordination to a variety of transition metals such as Ti, Zr, V, Cr, Ni, Y, Ir, and Rh has demonstrated the scope of this type of ligand.[4−7] Due to the excellent catalytic properties provided by the combination of Cp* and NHC ligands in Ir(III) complexes,[8−11] we soon became interested in a new class of NHCs tethered to a tetramethylcyclopentadienyl through a two-carbon-atom aliphatic linker that we coordinated to Ir and Rh.[12,13]

On the basis of our previous experience in molybdenum chemistry,[14−16] and attending to the excellent catalytic properties of molybdenum cyclopentadienyls in the oxidation of unsaturated substrates,[14,17−19] we decided to expand our studies to the coordination of a series of Cp^x-NHC ligands to molybdenum. We believed that the presence of the tethered ligand may help to stabilize species not reachable by the combination of other monodentate ligands and also provide interesting catalytic applications. In this work we describe

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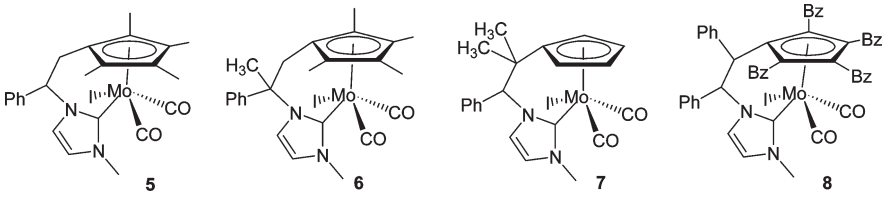
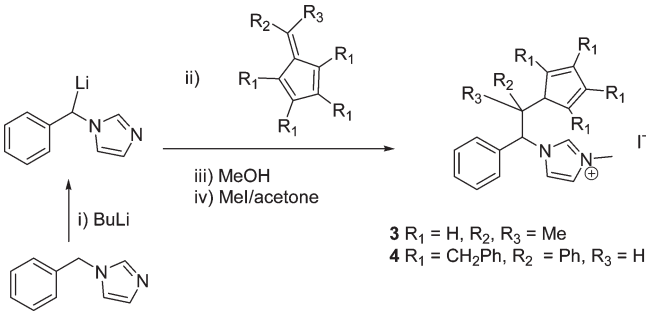
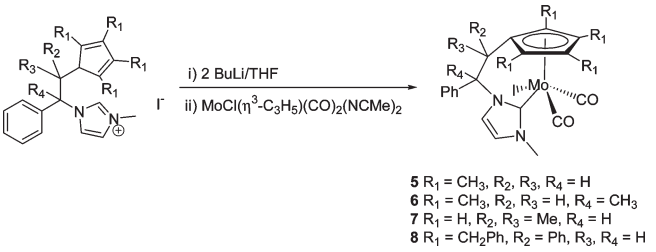
Chart 1



Scheme 1



Scheme 2



the preparation of a new set of Cp^x-NHC ligands and a general and straightforward method for the synthesis of molybdenum carbonyl complexes of general formula (Cp^x-NHC)Mo(CO)$_2$I. A preliminary study of the catalytic properties of these novel complexes in the epoxidation of *cis*-cyclooctene is discussed.

Results and Discussion

Synthesis and Characterization of *cis*-(Cp^x-NHC)Mo(CO)$_2$I Compounds. The new imidazolium pro-ligands Cp-NHC^{Me} (**3**) and Cp^{Bz}-NHC^{Me} (**4**) were prepared following a similar method to that described for the synthesis of the tetramethylcyclopentadienyl-imidazolylidenes Cp*-CHPh-NHC^{Me} (**1**) and Cp*-CMePh-NHC^{Me} (**2**), previously reported by us.[12,13] With the preparation of these two new species, we intend to increase the number of Cp^x-NHC ligands available, so that a controlled modification of their steric demand and electronic properties can be achieved. Deprotonation at the methylene group of benzylimidazole with *n*-BuLi, followed by reaction with the appropriate fulvene, treatment with MeOH, and subsequent reaction with MeI, afforded **1**−**4** as a mixture of isomers that result from the different position of the double bonds in the cyclopentadienyl ring (Scheme 1). The imidazolium salts **3** and **4** were isolated as yellow solids and were characterized by elemental analysis, mass spectrometry, and NMR (^{1}H and ^{13}C) spectroscopy.

Cyclopentadienyl-NHC molybdenum(II) compounds of general formula [(Cp^x-NHC)Mo(CO)$_2$I] [Cp^x-NHC = η^5-C$_5$Me$_4$-CH$_2$-CHPh-NHC^{Me} (**5**), η^5-C$_5$Me$_4$-CH$_2$-CMePh-NHC^{Me} (**6**), η^5-C$_5$H$_4$-CMe$_2$-CHPh-NHC^{Me} (**7**), and η^5-C$_5$(CH$_2$Ph)$_4$-CHPh-CHPh-NHC^{Me} (**8**)] (Chart 1) were prepared from the allyl precursor [MoCl(η^3-C$_3$H$_5$)(CO)$_2$-(NCMe)$_2$] and the appropriate NHC-cyclopentadienide lithium salt, (Cp^x-NHC)Li, previously formed *in situ* by deprotonation of **1**−**4** with 2 equiv of *n*-BuLi in THF (Scheme 2). The reactions were carried out without the need to isolate the NHC-deprotonated cyclopentadienides, (Cp^x-NHC)Li, by adding the molybdenum-allyl precursor to the THF reaction mixture. Subsequent workup furnished complexes **5**−**8** as red crystalline solids in high to moderate yield (77% for **5**, ca. 50% for **6**−**8**). Complexes **5**−**8** are perfectly stable in the solid state and could be easily handled in air. They are also rather stable in solution. In CD_2Cl_2 traces of degradation were observed after 24 h. All complexes are soluble in polar and nonpolar solvents such as NCMe, THF, ether, dichloromethane, methanol, and toluene and insoluble in hexane and pentane.

Complexes **5**−**8** have been characterized by IR, NMR spectroscopy (^{1}H, ^{13}C, ^{95}Mo), mass spectrometry, and elemental analysis. The crystal structure of **5** was determined by X-ray diffraction analysis. The ^{13}C NMR spectra provide the clearest indication that the metalation has occurred, with resonances at δ 187 (**5**), 188 (**6**), and 185 (**7**) assigned to the C$_{carbene}$. For complex **8**, the ^{13}C{^{1}H} NMR spectrum shows two C$_{carbene}$ resonances at δ 186.5 and 184.6 indicating the presence of two diastereoisomers (ratio 1:1) due to the existence of two asymmetric carbons in the molecule. For complexes **5**−**7** two diastereomers can be expected if we consider the chirality arising from the backbone and the chirality at the metal center,[20] but we found that only one of the diastereomers is obtained.

Compounds **5** and **8** were obtained as the *cis* isomers (relative to the disposition of the two CO ligands), while compounds **6** and **7** were isolated as a mixture of the *cis* and *trans* isomers. *trans*-**6** converted to *cis*-**6** in refluxing dichloromethane (4 h), as shown in Scheme 3. In the preparation of **7**, a mixture of *cis*-**7** and *trans*-**7** (*cis:trans* = 3:1) was obtained after being heated in similar conditions. The formation of the two isomers contrasts with the previously reported [CpMo(CO)$_2$(NHC^{Mes})H] (NHC^{Mes} = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, Cp = η^5-C$_5$H$_5$) complex, in which the *cis* isomer is clearly favored.[21] The IR spectra of the *cis* and *trans* isomers are easily distinguished by the relative intensities of the two ν(CO) absorptions. In the *cis* isomer the band due to the symmetric CO stretching vibration is more intense than the antisymmetric one, while in the *trans* isomer the antisymmetric CO stretching vibration is the most intense.[22]

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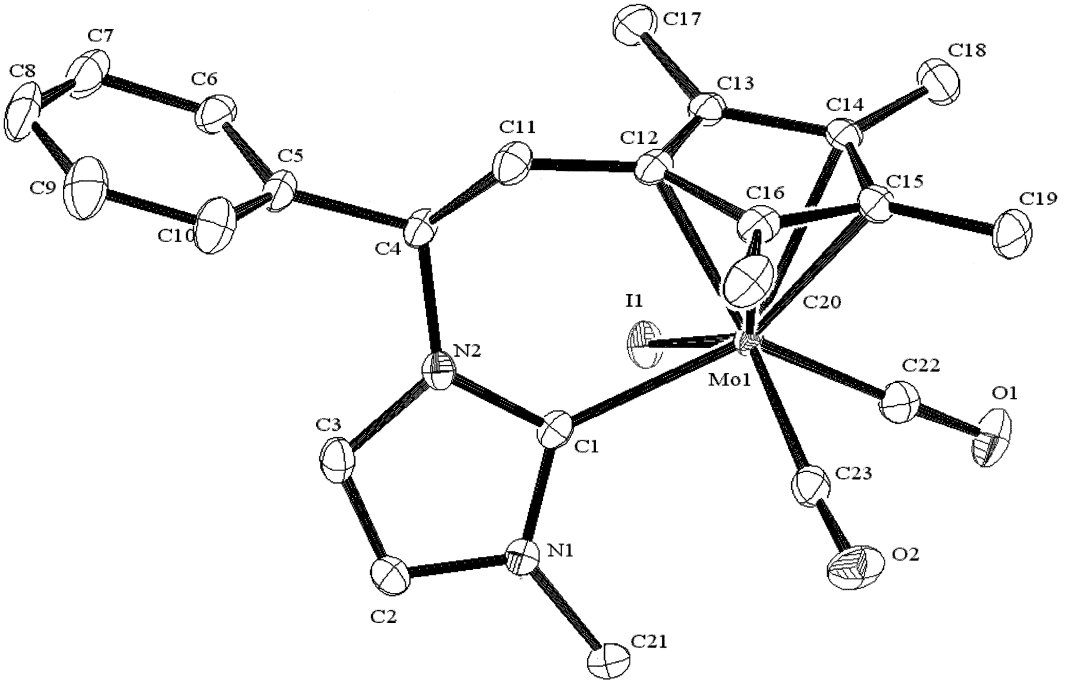
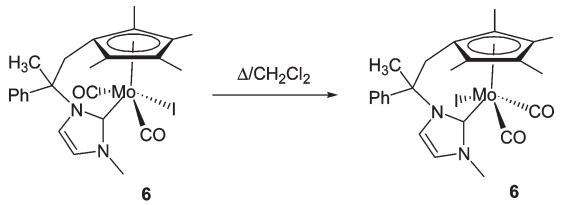


Figure 1. Molecular diagram of **5**. Selected bond distances (Å) and angles (deg): Mo(1)−C(1) 2.207(3), Mo(1)−I(1) 2.8635(3), Mo(1)−C(22) 1.978(3), Mo(1)−C(23) 1.939(3), Mo(1)−C(12) 2.360(3), Mo(1)−C(13) 2.413(3), Mo(1)−C(14) 2.322(3), Mo(1)−C(15) 2.269(3), Mo(1)−C(16) 2.288(3), C(1)−Mo(1)−I(1) 76.91(7), C(23)−Mo(1)−C(1) 84.19(11), C(22)−Mo(1)−I(1) 77.81(8), C(23)−Mo(1)−C(22) 76.16(12), N(2)−C(1)−Mo(1) 128.0(2).

Scheme 3



trans isomer *cis* isomer

The IR spectra of **5**−**8** show ν(CO) absorptions of the Cp derivatives at higher frequencies than those of Cp* and Cp^{Bz} derivatives, indicating the weaker electron-donating properties of the Cp ring compared to Cp* and Cp^{Bz}. The presence of the NHC fragment has also a clear influence on the frequency of the band, as can be seen if we compare the bands shown by **7** and **8** with the bands shown by CpMo(CO)$_3$I [ν(CO) 2055, 1983 cm^{-1}][23] and Cp^{Bz}Mo(CO)$_3$I [ν(CO) 2024, 1950 cm^{-1}],[24] as a clear consequence of the strong σ-donating character of the NHC.

The ^{13}C NMR spectra are also a clear indication of the configuration of both isomers. The two CO ligands are inequivalent in the *cis* isomer, appearing at δ 260 and 251 for **5**, 260 and 251 for **6**, and 259.6, 247.7, 259.5, and 247.6 for the two diastereoisomers of **8**. *trans*-**7** displays a single resonance at δ 257.6 for the two inequivalent CO carbons probably due to accidental degeneration, while two resonances at δ 247.3 and 247.1 are found for the *cis*-**7** (a doublet at δ 243.3 has been reported for *cis*-[CpMo(CO)$_2$(NHC^{Mes})H]).[21]

The ^{95}Mo NMR shifts for compounds **5**, **7**, and **8** are δ −741 (**5**), −810 (**7**), and −686, −759 (**8**), respectively. The ^{95}Mo NMR of **8** shows two resonances due to the presence of two diastereoisomers, as observed in its ^{1}H and ^{13}C NMR spectra. Given the structural similarity of the three complexes, we can conclude that the electronic richness around the metal is lower in **7**, as should be expected for the unsubstituted Cp being higher field shifted than the molybdenum cyclopentadienyl-NHCs **5** and **8**. The compounds studied in this work exhibited very different ^{95}Mo NMR signals than those of previously examined CpMo(CO)$_3$X (X = Me, Et, Cp = η^5-C$_5$Me$_5$, η^5-C$_5$H$_5$) and *ansa*-bridged CpMo(CO)$_3$ derivatives, which display their ^{95}Mo NMR signals in the region δ −1750 to −1590.[25,26]

The crystal structure of **5** was determined by X-ray diffraction analysis. The molecular structure and selected bond lengths and angles are depicted in Figure 1. The structure can be described as a distorted four-legged pianostool. The angles between contiguous legs range from 76.16(12)° to 84.19(11)°, typical values for this type of structure. The cyclopentadienyl ligand is bound in pentahapto fashion, as inferred from the total value of the angles at the ring (540°) and the metal ring−carbon distances, which range from 2.269(3) to 2.329(3) Å. The Mo−C$_{carbene}$ bond distance of 2.207(3) Å is in good agreement with the Mo−C$_{carbene}$ bond distances reported for related complexes, which are in the range from 2.152(5) to 2.35(1) Å.[27−29] The bond angles at the lateral four-atom chain show no ring tension of the

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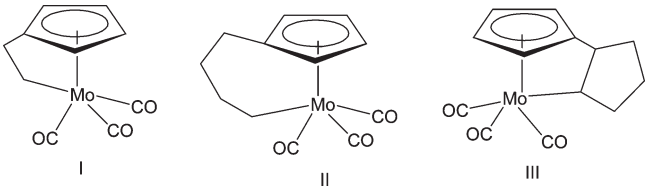
Scheme 4



six-membered ring. These values are in the range of those observed in the four-membered *ansa*-bridged [(η^5-$C_5H_4(CH_2)_3$-η^1-CH_2)$M(CO)_3$] derivatives (ranging from 114.1(3)° to 116.1(2)°).[30]

Catalytic Studies on Cyclooctene Epoxidation. The excellent catalytic performance of (η^5-C_5R_5)MoO_2X derivatives in the epoxidation of olefins is well established.[17−19] To avoid storage problems of the sensitive dioxo complexes, Romão, Kühn, Poli, and their respective co-workers showed that carbonyl precursors of general formula (η^5-C_5R_5)$Mo(CO)_3Cl$ can be directly used as catalyst precursors in olefin epoxidation, without isolation of the dioxo complexes prior to application.[17,18,25,31,32] Recently, Kühn and co-workers used *ansa*-bridged derivatives of the type *ansa*-$CpMo(CO)_3R$ (Scheme 4) to introduce chirality in the system by transforming the bridging C atoms into chiral centers.[26] However, it turned out that *ansa*-bridges with two carbon atoms in the bridge (type I, Scheme 4) were not sufficiently stable under oxidative conditions. Four-membered *ansa*-bridged complexes of the type [(η^5-$C_5H_4(CH_2)_3$-η^1-CH_2)-$Mo(CO)_3$] (type II, Scheme 4) and *ansa*-compounds with cycloalkyl moieties as bridging units (type III, Scheme 4) displayed greater stability and were successfully applied as catalysts in olefin epoxidation reactions without noticeable catalyst decomposition or cleavage of the M−C bridge during the reaction.[30] One of the purposes of our studies was to explore both the stability of our Cp-functionalized NHC molybdenum complexes under oxidative conditions and the catalytic activity of these novel complexes in olefin epoxidation. We consider that the strength of the NHC−metal bond could improve the stability of the chelated cyclopentadienyls, avoiding the breaking of the carbon−metal bond observed in some *ansa*-cyclopentadienyls of molybdenum and tungsten.[33] Also, the use of N-heterocyclic carbenes as ligands in oxidation chemistry is an area that remains in the early stages of development, although the preliminary results shown by some authors indicate that these ligands may provide very promising properties.[34]

For comparative purposes, we performed the catalytic experiments in similar conditions to those reported for $CpMo(CO)_3Cl$ complexes. The reactions were carried out with *tert*-butylhydroperoxide (TBHP) as oxidant at 55 °C in $CHCl_3$, using the precatalysts **5**, **7**, and **8**. Blank reactions showed that no significant amount of epoxide was formed in the absence of catalyst. The values measured for *cis*-cyclooctene conversion to its epoxide as a function of time are given in Table 1. As can be seen from these results, complexes **5** and **7** display very low catalytic activity. Only a 25% (**5**) and 11% (**6**) yield of the epoxide was obtained after 20 h. Complex **8** was the most active catalyst, affording a 91% yield of the corresponding epoxide after 20 h. The reaction was entirely selective for epoxidation with no byproduct observed (in all cases the conversion of *cis*-cyclooctene gave similar values to the yield of the epoxide). The reaction proceeded relatively slowly with a large induction period; the carbonyl complexes are first oxidized to the catalytically active compounds. In accordance with these results, it has been described that the replacement of the Cp or Cp* ligands by pentabenzylcyclopentadiene (Cp^{Bz}) in $CpMo(CO)_3Cl$ and $Cp^*Mo(CO)_3Cl$ provides a clear improvement of the catalytic activity.[17] Compound **8** and $Cp^{Bz}Mo(CO)_3Me$ afford different catalytic behaviors in terms of reaction rates and conversions. While $Cp^{Bz}Mo(CO)_3Me$ provides a maximum conversion of 82% after 30 min,[19] **8** yields 91% of the final product after 20 h. This result indicates that complex **8** is rather stable under oxidative conditions.

Table 1. Cyclooctene Epoxide Yields Reached with (Cp^x-NHC)$Mo(CO)_2I$ Complexes 5, 7, and 8[a]

complex	yield 5 h (%)	yield 8 h (%)	yield 20 h (%)
5	0	19	25
7	0	5	11
8	26	51	91

[a] Reaction conditions: 55 °C in $CHCl_3$ with a catalyst:cyclooctene:TBHP ratio of 1:100:300.

Conclusions

In this work we have extended the synthetic pathway for the preparation of Cp*-NHC (Cp* = η^5-C_5Me_4), previously reported by us, to the synthesis of novel unsubstituted and sterically demanding cyclopentadienyl-NHCs. In a clear illustration of the chemical versatility of these Cp-NHC ligands, we prepared (Cp^x-NHC)$Mo(CO)_2I$ compounds **5**−**8**. The chelating coordination of the ligand results in an improvement of the stability of these species, compared to other known $CpMo(NHC^{Mes})(CO)_2X$ complexes.[20] The preparation of the Cp, Cp*, and Cp^{Bz} derivatives provides a smooth change in the electronic properties of the complexes, which has a clear influence on their catalytic outputs. The studies on the catalytic epoxidation of *cis*-cyclooctene with TBHP as oxidant show that all complexes are active, but **8** is the most efficient one. The reaction selectively proceeds toward the epoxide, without any formation of diols or any other overoxidation byproduct. Compared to similar complexes reported in the literature, compound **8** is rather slow, but its stability under oxidative conditions allows its activity for longer reaction times, which in turn results in higher conversions to the final products than those provided by other known catalysts. Studies in order to increase the reaction rates by activating the catalyst are underway.

Experimental Section

General Procedures. All experiments were performed using standard Schlenk techniques. The starting materials dimethylfulvene,[35] pentabenzylcyclopentadiene,[36] Cp^*-CH_2-CHPh-NHC^{Me},[12]

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Cp*-CH_2-CMePh-NHC^{Me},[13] and [MoCl(η^3-C_3H_5)(CO)$_2$(NCMe)][37] were prepared according to literature procedures. All other reagents are commercially available and were used as received.

^{1}H and ^{13}C NMR NMR spectra were recorded on Bruker Avance III 400 MHz and Bruker Avance 500 MHz spectrometers at room temperature. ^{95}Mo NMR spectra were acquired on a Bruker Avance II spectrometer equipped with a 5 mm z-gradient TXO probe. The ^{95}Mo chemical shift was referenced to 1 M Na_2MoO_4 in D_2O (pH = 11). The spectra were recorded at 298 K. The ^{95}Mo NMR experiments were done at University Paul Sabatier in Toulouse following the method developed by S. Massou.[38] Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson 7000 FT-IR spectrometer. Elemental analyses and mass spectrometric analyses were performed in our laboratories at ITQB. Electrospray ionization mass spectra (ESI-MS) were recorded on an API-Ion trap (PO 03 MS). Samples were measured in NCMe solutions.

Synthesis of Cp-CMe$_2$-CHPh-NHC^{Me}I, 3. *n*-BuLi (14.14 mL of 1.6 M in hexane, 22.60 mmol) was added dropwise to a solution of benzylimidazole (2.98 g, 18.84 mmol) in THF (25 mL) at −60 °C and stirred for 20 min followed by addition of dimethylfulvene (2.0 g, 18.84 mmol) previously dissolved in 5 mL of THF. The reaction mixture was then allowed to reach room temperature and stirred for 1 h. Methanol was added to the reaction mixture, and the volatiles were removed under vacuum. The crude oily product was purified by flash chromatography (hexane/ethyl acetate, 1:4), affording a yellow solid of Cp-CMe$_2$-CHPh-NHC (3.0 g, 11.34 mmol, 60%). The yellow solid (1.93 g, 7.31 mmol) was redissolved in 30 mL of acetone, and iodomethane (2.29 mL, 36.57 mmol) was added at once to the solution. After stirring for 12 h at room temperature, all the volatiles were removed under vacuum, yielding a yellow solid of **3**, which was washed several times with diethyl ether. Yield: 2.94 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, 1H, NC*H*N), 7.47−7.20 (m, 7H, CH_{Ph}+CH_{imid}), 6.43−6.06 (m, 4H, CH_{Cp}), 5.94 (s, 1H, C*H*Ph$_{linker}$), 4.02 (s, 3H, NCH_3), 2.98−2.96 (m, 1H, CH_{Cp}), 1.40 (s, 3H, C$H_{3linker}$), 1.38 (s, 3H, C$H_{3linker}$). {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.7, 150.1 (C_{Phenyl}), 134.7, 133.0 (CH_{Imid}), 134.6, 134.3 (C_{Cp}), 132−128 (CH_{Phenyl} + CH_{Cp}), 122.8, 122.7 (CH_{Imid}, 122.4, 122.3CH_{Imid}, 72.96, 7265 (*C*HPh$_{linker}$), 42.06, 41.41 (*C*(CH$_3$)$_{2linker}$), 41.57, 40.64 (CH_{Cp}), 37.09, 37.02 (NCH_3), 27.39, 26.88 (C(*C*H$_3$)$_{2linker}$), 25.38, 24.93 (C(*C*H$_3$)$_{2linker}$). Anal. Calcd for $C_{19}H_{23}N_2I$: C, 56.16; H, 5.70; N, 6.89. Found: C, 56.27; H, 5.78; N, 6.55. MS (ESI): *m*/*z* 279 (100, M$^+$ − I).

Synthesis of Pentabenzylfulvene. *n*-BuLi (6.04 mL of 1.6 M in hexane, 9.66 mmol) was added dropwise to a solution of pentabenzylcyclopentadiene (3.60 g, 8.05 mmol) in THF (20 mL) at −60 °C. After being stirred for 20 min the reaction mixture was allowed to warm to room temperature, and it was further stirred for 1 h. Triphenylmethyl chloride (2.69 g, 9.66 mmol) was then added to the reaction mixture at 0 °C, and stirring was continued for 16 h at 4 °C. The crude product was used for the preparation of the proligand **4** without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−6.95 (m, 30H, CH_{Ph}), 6.64 (s, 1H, C*H*Ph), 3.85 (s, 2H, CH_2Ph), 3.52 (s, 2H, CH_2Ph), 3.50 (s, 2H, CH_2Ph), 3.39 (s, 2H, CH_2Ph). {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$, δ): 145−126 (C_{Ph}), 31.9 (*C*H$_2$Ph), 31.8 (*C*H$_2$Ph), 30.5 (*C*H$_2$Ph).

Synthesis of Cp^{Bz}-CHPh-CHPh-NHC^{Me}I, 4. *n*-BuLi (9.84 mL of 1.6 M in hexane, 15.16 mmol) was added dropwise to a solution of benzylimidazole (1.99 g, 12.64 mmol) in THF (20 mL) at −60 °C and stirred for 20 min followed by addition of pentabenzylfulvene (6.50 g, 12.64 mmol). The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. Methanol was added to the reaction mixture, and all volatiles were removed under vacuum. The crude oily product was purified by flash chromatography (hexane/ethyl acetate, 1:4), affording a yellow solid of Cp^{Bz}H-CHPh-CHPh-NHC (1.7 g, 25%). The yellow solid was redissolved in 5 mL of acetone, and iodomethane (0.51 mL, 8.19 mmol) was added at once to the solution. After stirring for 12 h at room temperature, all the volatiles were removed under vacuum, and the solid was thoroughly washed with diethyl ether. Compound **4** was obtained as a yellow solid. Yield: 1.08 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.0 (s, 1H, NC*H*N), 7.6−6.3 (m, 32H, CH_{Ph}+CH_{imid}+CH*Ph*$_{linker}$), 5.06 (d, 1H, NC*H*Ph$_{linker}$), 4.92 (d, 1H, NC*H*Ph$_{linker}$), 3.70−3.30 (m, 9H, CH_{Cp}+CH_{imid}+CH$_2$Ph$_{Cp}$), 3.19 (s, 3H, C$H_{3linker}$). {^{1}H}^{13}C NMR (100 MHz, $CDCl_3$): 146−134 (C_{Phenyl}), 130−125 (CH_{Phenyl}+CH_{Imid}), 65.6−64.2 (N*C*HPh$_{linker}$), 52.5−48.0 (CHPh*C*HPh$_{linker}$), 36.2, 36.1, 35.8 (N*C*H$_3$), 35.3−31.2 (*C*H$_2$Ph). Anal. Calcd for $C_{51}H_{47}N_2I$: C, 75.17; H, 5.81; N, 3.44. Found: C, 75.26; H, 5.92; N, 3.33. MS (ESI): *m*/*z* 687 (M$^+$ − I, 100%).

Synthesis of (Cp*NHC^{Me})Mo(CO)$_2$I, 5. *n*-BuLi (1.30 mL of 1.6 M in hexane, 2.08 mmol) was added to a solution of **1** (450 mg, 1.04 mmol) in THF (15 mL) at −60 °C and stirred for 1 h at ambient temperature followed by addition of [MoCl(η^3-C_3H_5)(CO)$_2$(NCMe)$_2$] (320 mg, 1.04 mmol) previously dissolved in THF (5 mL). The reaction mixture was then stirred for a further 12 h. The THF solvent was removed under vacuum, and the remaining solid was extracted with diethyl ether, yielding **5** as a red solid. Yield: 470 mg (77%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50−7.13 (m, 5H, CH_{Ph}), 6.89 (s, 1H, CH_{Imid}), 6.36 (s, 1H, CH_{Imid}), 4.97−4.94 (dd, 1H, C*H*Ph$_{linker}$), 3.69 (s, 3H, NCH_3), 3.08−2.83 (m, 2H, C$H_{2linker}$), 2.43 (s, 3H, CH_{3Cp*}), 1.97 (s, 3H, CH_{3Cp*}), 1.93 (s, 3H, CH_{3Cp*}), 1.73 (s, 3H, CH_{3Cp*}). {^{1}H}^{13}C NMR (125 MHz, $CDCl_3$): 260 (CO), 251 (CO), 187 ($C_{carbene}$-Mo), 139 (C_{ipso}phenyl), 130−128 (CH_{phenyl}), 123 (CH_{Imid}), 122 (CH_{Imid}), 116 (C_{Cp*}), 105 (C_{Cp*}), 102 (C_{Cp*}), 100 (C_{Cp*}), 99 (C_{Cp*}), 66 (*C*HPh$_{linker}$), 41 (N*C*H$_3$), 31 (*C*H$_{2linker}$), 13 (*C*H$_{3Cp*}$), 11.3 (*C*H$_{3Cp*}$), 11.2 (*C*H$_{3Cp*}$), 11 (*C*H$_{3Cp*}$). ^{95}Mo NMR (CD_2Cl_2, 26 MHz, δ ppm): −741. IR (KBr): ν(Mo−CO), cm^{-1} 1933 (vs), 1834 (s). Anal. Calcd for $C_{23}H_{25}N_2O_2MoI(OC_4H_8)_3$: C, 52.50; H, 6.17; N, 3.50. Found: C, 52.33; H, 6.24; N, 3.71. MS (ESI): *m*/*z* 459 (100, M$^+$ − I).

Synthesis of (Cp*-CH$_2$-CMePh-NHC^{Me})Mo(CO)$_2$I, 6. The title compound was synthesized similarly to **5** from **2** (230 mg, 0.52 mmol). Yield: red solid, 120 mg (55%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50−7.47 (m, 5H, Ph), 6.94 (s, 1H, CH_{Imid}), 6.48 (s, 1H, CH_{Imid}), 3.68 (s, 3H, NCH_3), 3.12−2.87 (m, 2H, C$H_{2linker}$), 2.34 (s, 3H, CH_{3Cp*}), 1.96 (s, 3H, CH_{3Cp*}), 1.92 (s, 3H, CH_{3Cp*}), 1.77 (s, 3H, CH_{3Cp*}), 1.81 (s, 3H, C*Me*-Ph$_{linker}$). {^{1}H}^{13}C NMR (125 MHz, CD_2Cl_2): 260 (CO), 251 (CO), 188 ($C_{carbene}$-Mo), 147 (C_{ipso}phenyl), 130−129 (CH_{phenyl}), 123.5 (CH_{Imid}), 123.2 (CH_{Imid}), 117 (C_{Cp*}), 103 (C_{Cp*}), 102 (C_{Cp*}), 100 (C_{Cp*}), 98 (C_{Cp*}), 73 (*C*(CH$_3$)Ph$_{linker}$), 42 (N*C*H$_3$), 30 (*C*H$_{2\ linker}$), 38 (C(*C*H$_3$)Ph$_{linker}$), 13 (*C*H$_{3Cp*}$), 12 (*C*H$_{3\ Cp*}$), 11.5 (*C*H$_{3Cp*}$), 11.2 (*C*H$_{3Cp*}$). IR (KBr): ν(Mo−CO), cm^{-1} 1935 (vs), 1832 (s). Anal. Calcd for $C_{24}H_{27}N_2O_2MoI(OC_4H_8)_2$: C, 51.76; H, 5.84; N, 3.77. Found: C, 51.37; H, 5.96; N, 3.83. MS (ESI): *m*/*z* 473 (100, M$^+$ − I).

Synthesis of (Cp-CMe$_2$-CHPh-NHC^{Me})Mo(CO)$_2$I, 7. The title compound was synthesized similarly to **5** from **3** (430 mg, 1.07 mmol). Yield: red solid, 240 mg (48%). Characterization of *cis* isomer: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.46−7.39 (m, 5H, CH_{Ph}), 7.07 (s, 1H, CH_{Imid}), 6.87 (s, 1H, CH_{Imid}), 5.92 (s, 1H, CH_{Cp}), 5.58 (s, 1H, CH_{Cp}), 5.27 (s, 1H, CH_{Cp}), 5.16−5.10 (m, 1H, C*H*Ph$_{linker}$), 4.71 (s, 1H, CH_{Cp}), 3.76 (s, 3H, NCH_3), 1.41 (s, 3H, C(CH_3)$_2$), 1.38 (s, 3H, C(CH_3)$_2$). {^{1}H}^{13}C NMR (100 MHz, CD_2Cl_2): δ 247.3, 247.1 (*C*O), 186.3 ($C_{carbene}$-Mo), 136.2 (C_{phenyl}), 130.8−128.6 (CH_{phenyl}), 124.5 (CH_{Imid}), 122.8 (CH_{Imid}), 87.1 (C_{Cp}), 84.2 (C_{Cp}), 83.0 (C_{Cp}), 68.6 (*C*HPh$_{linker}$), 41.9 (N*C*H$_3$), 37.3 (*C*(CH$_3$)Ph$_{linker}$), 14.2 (C(*C*H$_3$)Ph$_{linker}$). IR (KBr): ν(Mo−CO), cm^{-1} 1945 (vs), 1851(s). ^{95}Mo NMR

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(CD_2Cl_2, 26 MHz, δ ppm): −810. Anal. Calcd for $C_{21}H_{21}N_2O_2MoI(OC_4H_8)$: C, 47.78; H, 4.65; N, 4.45. Found: C, 47.85; H, 4.68; N, 4.45. MS (ESI): m/z 431 (100, $M^+ - I$).

Synthesis of (Cp^{Bz}-CHPh-CHPh-NHC^{Me})$Mo(CO)_2I$, 8. The title compound was synthesized similarly to **5** from **4** (570 mg, 0.70 mmol). Yield: red solid, 430 mg (63%). $\{^1H\}^{13}C$ NMR (100 MHz, CD_2Cl_2): δ 259.58, 259.55 (*C*O), 247.69, 247.63 (*C*O), 186.50, 184.67 ($C_{carbene}$-Mo), 141.55, 140.74, 140.64, 140.63, 140.25, 140.08, 140.00, 139.87, 139.62, 139.53, 138.60, 138.10 (C_{ipsoPh}), 132.54−122.88 (CH_{Ph}+CH_{Imid}), 120.91, 118.27, 113.02, 109.70, 109.61, 106.72, 106.48, 104.40, 103.22, 102.17 (C_{Cp}), 69.83, 68.90 (N*C*HPh$_{linker}$), 48.98, 46.07 (CHPh-*C*HPh$_{linker}$), 41.62, 41.47 (N*C*H$_3$), 36.68, 35.96, 34.66, 33.61, 33.48, 33.32, 33.28, 33.16 (CH_2Ph_{Cp}). The ^1H NMR of **8** was not informative and has not been included. IR (KBr): ν(Mo−CO), cm^{-1} 1941 (vs), 1883 (sh), 1860 (s), 1819 (sh). ^{95}Mo NMR (CD_2Cl_2, 26 MHz, δ ppm): −686, −759. Anal. Calcd for $C_{53}H_{45}N_2O_2MoI$: C, 65.98; H, 4.70; N 2.90. Found: C, 65.72; H, 5.01; N, 2.66. MS (ESI): m/z 840 (100, $M^+ - I$).

Catalytic Epoxidation of *cis*-Cyclooctene. The catalytic reactions were performed in air, within a reaction vessel equipped with a magnetic stirrer and immersed in an oil bath at 55 °C. A 1% molar ratio of catalyst:cyclooctene and a *tert*-butylhydroperoxide:substrate molar ratio of 3:1 were used with 3 mL of $CHCl_3$. *cis*-Cyclooctene, chloroform, mesitylene (as internal standard), and the catalysts were placed into the reaction vessel, and TBHP was added to the mixture. The course of the reaction was monitored by quantitative GC analysis. Samples taken were diluted with CH_2Cl_2 and treated with $MgSO_4$ and MnO_2 to remove water and destroy the excess of peroxide. The resulting slurry was filtered, and the filtrate was injected into a GC column (DB5). The conversion of *cis*-cyclooctene and the formation of cyclooctene oxide were calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course.

Single-Crystal Determination of Compound 5. Crystal data and details of the structure are presented in Figure 1 and Table 2 (Supporting Information). Suitable single crystals for the X-ray diffraction study were grown in CH_2Cl_2/Et_2O solutions at 5 °C. Data collection was carried out in a Bruker Kappa-Appex-II diffractometer at 100 K. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and refined using the SHELXTL 6.1 software package (Sheldrick, G. M. *SHELXTL, version 6.1*; Bruker AXS, Inc.: Madison, WI, 2000). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 4, Supporting Information. The diffraction frames were integrated using the SAINT package (*SAINT*, *version 5.0*; Bruker Analytical X-ray System: Madison, WI, 1998).

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Supporting Information Available: Crystallographic data of compound **5** in the form of CIF files. Experimental details on X-ray data collection and structure refinement of compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.