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Chiral *ansa*-bridged η^5-cyclopentadienyl molybdenum complexes: Synthesis, structure and application in asymmetric olefin epoxidation

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Abstract

Ansa-bridged η^5-cyclopentadienyl carbonyl molybdenum complexes were synthesized with stereogenic centers located in the side chain. An exemplary X-ray crystal structure and the catalytic activity for asymmetric olefin epoxidation are reported. In non-chiral epoxidation the compounds show a good catalytic activity, comparable to activities observed for the related non-chiral complexes of composition $CpMo(CO)_3X$ ($X = Cl$, CH_3). For the asymmetric epoxidation of *trans*-β-methylstyrene the chiral induction is up to ca. 20%. The high ring strain of the *ansa*-bridged system hampers, unfortunately, its stability under oxidative condition.

Keywords: Chirality; Cyclopentadienyl; Molybdenum; Olefin epoxidation

1. Introduction

Chiral epoxidations are of high interest for the synthesis of chiral intermediates in chemical and pharmaceutical processes to generate enantiomerically pure products [1,2]. Mimoun et al. [3] reported on the enantioselective epoxidation of prochiral alkyl-substituted olefins in 1979 utilizing a Mo(VI) complex bearing a chiral ligand, but the observed enantioface selectivity was not high. One year later, Katsuki and Sharpless [4] achieved the asymmetric epoxidation of allylic alcohols, mediated by a titanium (IV) complex using (+)-*R*,*R* or (−)-*S*,*S* tartrate as chiral ligand. In this case, the enantioselectivity was very high, but the titanium complex had to be applied in stoichiometric amounts. The reaction was improved later, enabeling a reduction of the catalyst:substrate ratio to ca. 1:10–1:20 and X-ray structures of the titanium tartrate catalysts could be determined [5]. More recently, also non-functionalized prochiral *cis*-olefins have been successfully applied as substrates, but high enantiometric excesses have only been achieved with a few catalytic systems, among them chiral salene manganese (III) catalysts where up to 98% enantiomeric excess (ee) could be obtained [6]. Yamamoto et al. developed new catalytic systems based on chiral vanadium complexes for the asymmetric epoxidation of allylic alcohols very recently. Enantiomeric excesses of up to 97% have been reached for a variety of substrates [7].

Several other attempts to achieve chiral epoxidation, e.g., with Mo, W and Re based catalysts have been made, but usually led only to moderate enantiomeric excesses [8]. The generally good catalytic activities of a variety of molybdenum (VI)-oxo complexes, however, in oxidation reactions make this type of complexes – in principle – promising candidates for asymmetric catalysis by replacing the achiral by chiral ligands [9].

Although the *ansa*-bridged η^5-cyclopentadienyl complexes of transition metals, in which a distal methyl group of the substituted cyclopentadienyl ligand can undergo a cyclometallation reaction to produce metallacyclic compounds, where the metal center is coordinated to both the η^5-cyclopentadienyl and the η^1-alkyl group, are relatively rare, some examples with group 6 and 9 metals have been reported [10]. Eilbracht et al. [11] have described

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several examples of this kind of reaction for a wide variety of spiro-dienes. The resulting ligand can be considered as chelate, where the cyclopentadienyl group and the alkyl group are both interacting with the metal center [12]. Recently, the formation of some molybdenum and tungsten complexes containing a linked cyclopentadienyl-ethyl ligand has been described and the stabilities of their metal-alkyl bond were investigated. The crystal structure of a tungsten tricarbonyl complex has been determined [13]. More recently, it was found that the *ansa*-bridged Mo tricarbonyl complex **1** (see Scheme 1) possesses a comparable catalytic activity to its alkyl- and chloro-analogues of composition $Cp'Mo(CO)_3X$ (X = alkyl or Cl) [9d,9e]. In fact, its epoxidation activity surpasses most other Mo-based epoxidation catalysts (e.g., of the composition $MoX_2O_2L_2$ (X = Cl, Br, Me; L = Lewis base)) significantly and rivals even the very active and well examined Re(VII) epoxidation catalyst methyltrioxorhenium (MTO) [14]. The synthetic pathway used for the preparation of *ansa*-bridged compounds might allow the easy introduction of a chiral ligand instead of a non-chiral alkyl group. The presence of a chiral group in the immediate surrounding of the metal center might assist in controlling the stereochemistry of reactions taking place at the metal center. Therefore, it could eventually increase the stereoselection in the catalytic reactions and might lead to much higher enantiomeric excesses as have been reached in the past with related complexes, where the chirality center was usually quite far away from the metal. Furthermore, the *ansa*-bridge would hold the chiral center in place, avoiding rotation of a chiral ligand placed on the cyclopentadienyl group not fixed in place by an *ansa*-bridge.

In this work, we report on the synthesis of some *ansa*-bridged η^5-cyclopentadienyl carbonyl molybdenum complexes (see Scheme 1), in which the stereogenic centers are located in the side chain. An exemplary X-ray crystal structure and catalytic activity tests for asymmetric olefin epoxidation are also described.

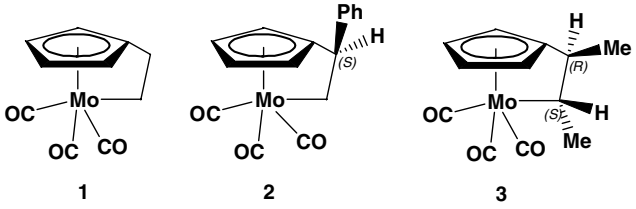
2. Results and discussion

2.1. Synthesis and spectroscopic examinations

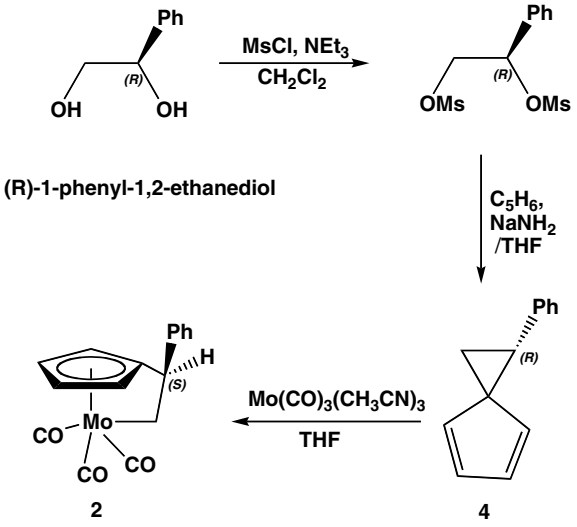
The synthesis of chiral derivatives of spiro cyclopentadienes **4** and **5** starts from optically active 1,2-diols according to published procedures [15]. Displacement of the methanesulfonate groups by cyclopentadiene in the presence of excess $NaNH_2$ affords the spiro annulated diene with inversion of the configuration at the chiral carbon atom [15b]. Reaction of a THF solution of the spiro cyclopentadienes with the tricarbonyl complex $Mo(CO)_3(CH_3CN)_3$ at room temperature takes place by a coordination followed by activation of one C_{diene}–C bond and transfer of the terminal R group to the metal center, as reported previously by Eilbracht et al. [11] (Schemes 2 and 3).

Complex **2** is isolated as yellow crystals in ca. 75% yield at room temperature and complex **3** is obtained as orange red needle shaped crystals at −30 °C and as an oily solid at room temperature in ca. 60% yield. Both compounds are stable at room temperature, can be handled in laboratory atmosphere and may be kept under air for some hours without significant change.

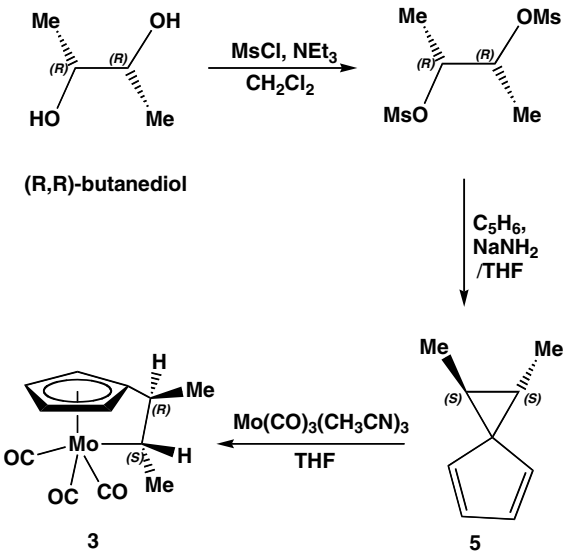
The composition and spectroscopic data of compounds **2** and **3** were determined by elemental analysis, IR- and NMR-spectroscopy (^1H, ^{13}C, ^{95}Mo) as well as mass spectroscopy (MS). In the related ligands **4** and **5**, the ^1H NMR spectra display two multiplets corresponding to an AA′BB′ spin system for the substituted cyclopentadienyl ring. The four protons of the Cp ring in complex **2** and **3**, however, appear as four multiplets. This feature is also confirmed by the $^{13}C\{^1H\}$ NMR spectra, which show five signals for the cyclopentadienyl carbon atoms. This result is different from the ^1H NMR spectra of the molybdenum complex containing a linked cyclopentadienyl-ethyl ligand (complex **1**, see Scheme 1), whose Cp ring represents an AA′BB′ spin system [13]. The substitution on the side chain with a phenyl or methyl group leads to the observed magnetic inequivalency of the nuclei. In the case of complex **3**, the protons of both bridging CH groups appear as two multiplets at −0.07 and 2.39 ppm, respectively, the one closer to the metal center being shifted to higher field. The two substituted methyls on



Scheme 1.



Scheme 2.



Scheme 3.

the side chain appear as two doublets (at 1.11 and 1.46 ppm, respectively), the one closer to the metal center being shifted to higher field. The coupling constant of $J_{CH_3-CH} = 6.8$ Hz is in accordance with the configuration of *trans*-protons [11g]. These finding confirm that after the ring-opening of the spiro ligand during the reaction with $Mo(CO)_3(CH_3CN)_3$, the product complex **3** displays a *trans*-configuration as the free ligand does.

Interestingly, the two protons of the CH_2 group on the side chain of complex **2** are diastereotopic because of the presence of a chiral center in the neighborhood, appearing as a quadruplet at −0.11 and at 0.50 ppm, owing to the strong shielding effect of the neighboring metal center. The ^1H NMR shift of the CH group on the side chain, being connected with the phenyl group, appears as pseudo-triplet at 4.03 ppm. This result also shows that the phenyl group is located on the bridging carbon atom in α-position to the Cp ring, and not in α-position to the metal center. It further indicates that the C–C bond, which is opposite to the phenyl group has been cleaved, which is also in accordance with the literature known ring-opening of 1,1-dimethylspiro[2,4]hepta-4,6-diene by a Mo carbonyl complex [11g]. This molecular disposition was confirmed by the X-ray structure of complex **3** (see below), which further proves that the Mo center coordinates to the less hindered side of the diene system.

The ^{95}Mo chemical shift is not an appropriate tool to distinguish between complexes in different oxidation states, however, it is highly sensitive to structural and electronic variations within a series of closely related mononuclear compounds [16], allowing insight into the electronic situation at the molybdenum center. The compounds examined in this work exhibit highly shielded chemical shifts, which can be in general associated with low formal oxidation states. Compounds **2** and **3** display their ^{95}Mo NMR signal in $CDCl_3$ at −1728 and −1696 ppm, respectively, which are in the same region as that of the complex **1** (−1628 ppm) [9e].

2.2. X-ray crystal structure of compound 2

The X-ray crystal structure of racemic compound **2** has been determined (see Fig. 1). The ligands are disposed in a distorted four-legged piano stool fashion similar to that established for analogous tricarbony cyclopentadienyl group VI metal complexes [9e,13,17]. The angles between contiguous legs range from 76.67(9)° to 81.06(8)°, being typical values for this type of structure. The cyclopentadieny ligand is bound in a pentahapto fashion, as inferred from the total value of the angels at the ring (540°) and the metal ring–carbon distances, which range from 2.287(2) to 2.338(2) Å. The carbonyl ligands have, as expected, a lineal arrangement, with Mo–C–O angles ranging from 175.3(2)° to 177.8(2)°. The C–O bond lengths between 1.144(3) and 1.153(3) Å and the averaged Mo–C_{CO} bond length of 1.997 Å (with bond lengths ranging from 1.986(2) to 2.016(2) Å) are usual for terminal CO groups. The slightly elongated Mo–C_{sp^3} bond distance of 2.347(2) is within the range for a methyl group bound to a molybdenum center, e.g., as reported for $Mo(\eta^5\text{-}C_5HMe_4)(CO)_3Me$ (2.311(2) Å) [9e], suggesting an electronically relatively saturated metal center due to the presence of the carbonyl groups. The bond angles at the lateral chain are rather different from the expected values for normal

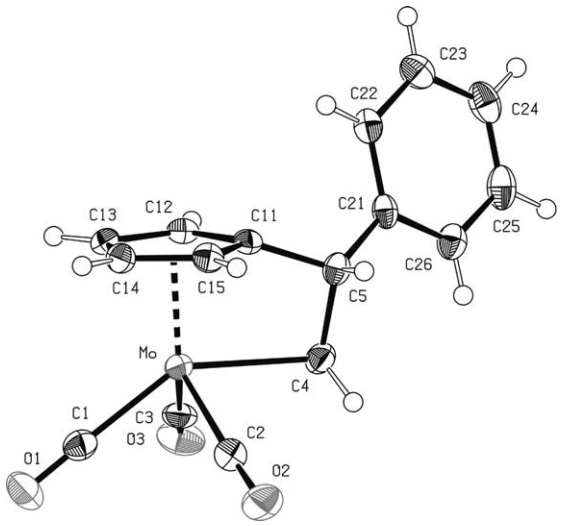


Fig. 1. ORTEP style plot [19e] of compound **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Mo–C1 2.016(2), Mo–C2 1.986(2), Mo–C3 1.988(2), Mo–C4 2.347(2), Mo–C11 2.287(2), Mo–C12 2.295(2), Mo–C13 2.324(2), Mo–C14 2.338(2), Mo–C15 2.323(2), Mo–Cg 1.974; C1–Mo–C2 81.06(9), C1–Mo–C3 80.05(9), C1–Mo–C4 143.63(9), C1–Mo–Cg 123.65, C2–Mo–C3 104.30(10), C2–Mo–C4 78.12(9), C2–Mo–Cg 126.07, C3–Mo–C4 76.67(9), C3–Mo–Cg 125.27, C4–Mo–Cg 92.68, Mo–C4–C5 97.1(1), C4–C5–C11 100.4(2), C4–C5–C21 116.2(2), C11–C5–C21 115.6(2). Cg denotes the center of gravity of the cyclopentadienyl ligand.

tetrahedral angles showing that the Mo–C(4)–C(5)–C(11) moiety is quite strained [13].

2.3. Application in epoxidation catalysis

Compounds **1**–**3** were tested as catalysts for the epoxidation of cyclooctene with TBHP. The details concerning the catalytic reaction are given in Section 3. Blank reactions show that no significant amount of epoxide was formed in the absence of catalyst. A catalyst:oxidant:substrate ratio of 1:200:100 was used in all experiments unless stated otherwise. The catalysts were first stirred with TBHP until a color change from orange to yellow occurred, indicative for the oxidation of the carbonyl complexes to the corresponding dioxo Mo(VI) compounds, as has been examined and described before [9d,9e]. For cyclooctene no significant formation of by-products (e.g., diol) was observed. Both catalytic reactions show similar time-dependent curves, in which the yield increases steadily in the first 2 h of the reaction and then slows down (first-order kinetics). The curves for complexes **1** and $CpMo(CO)_3Me$ were also measured for sake of comparison (Fig. 2).

Compounds **1**–**3** and $CpMo(CO)_3Me$ show a similar behavior indicating that introduction of substituents on the side chain between the metal center (as can be also concluded from the ^{95}Mo NMR of the carbonyl precursors) and the Cp ring does not influence much the electronic situation at the metal center and therefore also not significantly the catalytic performance. Comparison with $CpMo(CO)_3Me$ indicates that the replacement of a methyl group by a *ansa*-bridge does not strongly influence the overall catalytic performance, but leads to a somewhat slower reaction. This observation may be caused by the more pronounced steric hindrance of the *ansa*-bridged systems. Similar observations for more sterically crowded related system have been reported before [9f].

We examined the compounds **2** and **3** for their catalytic activity in the asymmetric epoxidation of unfunctionalized *trans*-olefins. This class of substrates is particularly interesting because the Jacobsen method [6] works highly efficient mainly for *cis*-olefins. For our catalytic experiments, we chose *trans*-β-methylstyrene as model substrate and TBHP as oxidant. Like several Mo(VI)-dioxo based complexes as well as η^5-cyclopentadienyl carbonyl molybdenum complexes, compounds **2** and **3** show a similar, relatively low catalytic activity at lower reaction temperature (i.e., at room temperature and below). For example, the yield of *trans*-β-methylstyrene epoxide at room temperature is less than 20% after 24 h. Thus, the chiral induction of compounds **2** and **3** for the asymmetric epoxidation was measured at 55 °C, although the lower temperature is usually regarded as being beneficial for the improvement of the chiral catalyst selectivity [8f,8j]. For the epoxidation of *trans*-β-methylstyrene, compounds **2** and **3** show good selectivity towards the epoxide. The conversion after 4 h reaches 66% and 50%, respectively. The obtained enantiomeric excess for *trans*-β-methylstyrene is up to ca. 20%. Compared to compound **2**, compound **3** displays a better chiral induction because of the chirality center being located in close proximity to the Mo center (see Fig. 3).

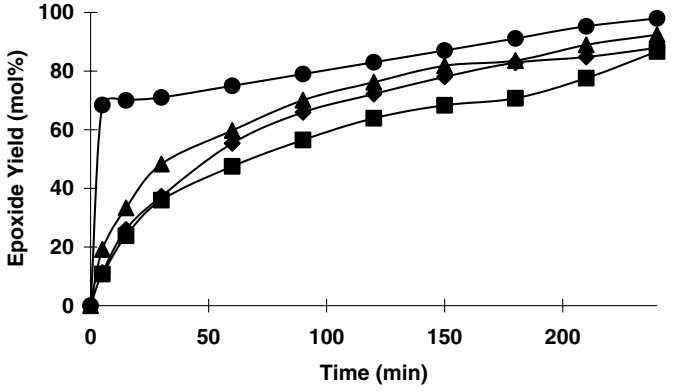


Fig. 2. Time-dependent yield of cyclooctene epoxide in the presence of compounds **1** (closed triangles), **2** (closed squares), **3** (closed diamonds) and $CpMo(CO)_3Me$ (closed circles) as catalysts at 55 °C with 1 mol% catalyst charge.

The enantiomeric excesses are in a similar order of magnitude as with dioxomolybdenum (VI) complexes bearing chiral ligands, such as 2′-pyridinyl alcoholate ligands, *cis*-diol, bis-oxazoline, etc. for the asymmetric epoxidation [8]. The moderate enantiomeric excesses reached with the latter dioxomolybedenum (VI) complexes has been assigned to rather weak metal–ligand-interactions [8]. However, in the case of complexes **2** and **3**, the not satisfying ee values obtained are likely due to the sensitivity of the compounds, originating form the quite strong tension of the cyclic system as already indicated by X-ray crystallography. Previously, it has been reported that the tungsten analogue of complex **1** can be oxidized by phosphorous pentachloride and $C_6H_5ICl_2$ involving a breaking of the bond between the metal and the attached carbon atom of the cyclic system [13]. In order to examine the stability of complexes **2** and **3** under catalytic epoxidation conditions with TBHP as oxidant, kinetic ^1H NMR examinations have been carried out. The catalyst precursor complexes are mixed with a 10-fold excess TBHP (5.5 M in decane) at room temperature in $CDCl_3$. To avoid the overlap of the methyl and methane group signals with those of TBHP, complex **1** and its tungsten analogue were used instead of the chiral complex **2**. It was found that the signals of the two CH_2 groups in the side chain (−0.46 and 2.92 ppm for complex **1** and −0.25 and 2.91 ppm for its tungsten analogue) and the Cp ring still remained detectable for ca. 4 h reaction time, however, the intensity declines gradually with the ongoing reaction. After 4 h they disappear completely and the original multiplets of the Cp ring turn into a single peak at approximately 5 ppm. Due to the presence of strong peaks of TBHP and decane, no more new peaks could be observed. A similar observation was obtained also in the case of complex **3**, the CH_2 and Ph groups attached to the bridged chain as well as the multiplets originating from the Cp ring remain for a few hours and then disappear, involving the appearance of new peak at ca.

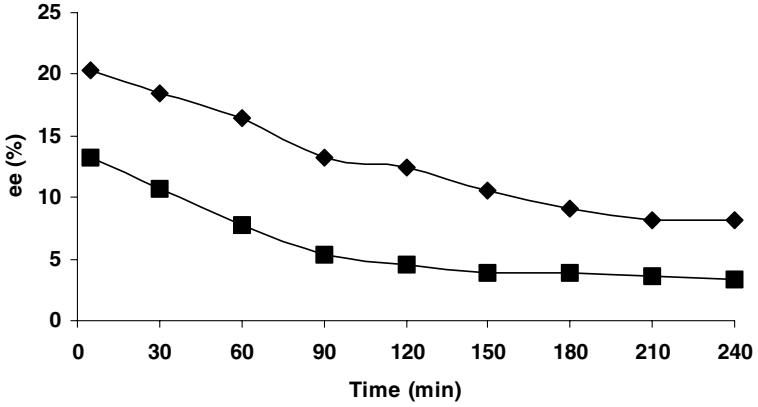


Fig. 3. Time-dependent enantiomeric excess (ee) during 4 h reaction time for the asymmetric epoxidation of *trans*-β-methylstyrene in the presence of compounds **2** (closed squares), **3** (closed diamonds) as catalysts at 55 °C with 1 mol% catalyst charge.

5 ppm. Furthermore, the appearance of a bluish compound can be observed, which has been identified as a mixture of molybdenum oxide decomposition products in related reactions [8,9,14]. The formation of dimeric compounds of formula $[Cp'MoO_2]_2O$ has been described as additional reaction pathway for related reactions [9f,18]. Given the ring strain in compounds **1**–**3**, it is likely that more side reactions appear at the same time, leading to the inconclusive appearance of the NMR spectra, the reduction of the catalytic activities during the course of the reaction and the decreasing ees. The comparatively low ee values are therefore most likely due to the breaking of the carbon–metal under the oxidative conditions leading to a significant decomposition of the catalyst and accordingly to the disappearance of the chiral centers during the course of the catalytic reaction. A promising way to obtain higher ee values might be the use of chiral *ansa*-bridged η^5-cyclopentadienyl complexes with lower ring tension (e.g., a five- or six-membered ring). The importance of the size of the *ansa*-bridge will become much clearer during the execution of these experiments. Work in this direction is currently under way in our laboratories.

3. Experimental

3.1. Synthesis and characterization

All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately (THF) or kept over 4 Å molecular sieves. TBHP was purchased from Aldrich as 5.0–6.0 mol% solution in decane and used after drying over molecular sieves to remove the water (<4% when received). Microanalyses were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra of isolated compounds were measured on a Bio-Rad FTS 525 spectrometer using KBr pellets. ^1H, ^{13}C, and ^{95}Mo NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Mass spectra were obtained with a Finnigan MAT 311 A and a MAT 90 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II. Compounds (*R*)-1-phenyl-1,2-ethanediol bis(methanesulfonate), (*R*)-1-phenyl-spiro[2,4]hepta-4,6-diene (**4**), (*R*,*R*)-2,3-butanediol bis (methanesulfonate) and (*S*,*S*)-1,2-dimethyl-spiro[2,4]hepta-4,6-diene (**5**) were synthesised according to the literature procedures [15].

3.1.1. (*S*)-[$Mo(\eta^5$-C_5H_4CHPh-η^1-$CH_2)(CO)_3$] (**2**)

The addition of a THF (ca. 20 mL) solution of the ligand (*R*)-1-phenyl-spiro[2,4]hepta-4,6-diene (0.60 g, 3.3 mmol) to $Mo(CO)_3(CH_3CN)_3$ (0.91 g, 3.0 mmol) at 0 °C produces an orange solution, which is stirred overnight at r.t. All volatiles are removed in vacuo, and the sticky residue is extracted with 15 mL hexane (three times) and filtered. The obtained orange red filtrates are concentrated and chromatographed on Florisil (60–100 mesh). The orange yellow fraction is eluted with *n*-hexane and collected. After cooling to −30 °C yellow crystals are obtained. Yield (1.68 g, 75%). Anal. Calc. for $C_{16}H_{12}O_3Mo$ (348): C, 55.17; H, 3.45. Found: C, 55.28; H, 3.37%. IR (KBr, ν cm^{-1}): 3110 (w, ν(CH) of Cp-ring), 2961, 2932, 2891 and 2859 (w, $\nu(CH_3)$ and $\nu(CH_2)$), 2003.6, 1903.9 (vs, ν(CO)); ^1H NMR ($CDCl_3$, 400 MHz, r.t.): δ (ppm) = −0.11 (q, 1H, Mo–C*H*), 0.50 (q, 1H, Mo–C*H*), 4.03 (t, 1H, Cp–C*H*–Ph), 5.29 (m, 1H, Cp), 5.28 (m, 1H, Cp), 5.21 (m, 1H, Cp) and 5.13 (m, 1H, Cp), 7.24, 7.37, 7.36 and 7,35 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.28 MHz, r.t.): δ (ppm) = 222.4 (CO) 151.1, 144.9, 128.5, 128.4, 126.7, 126.1 (C_6H_5), 90.3, 88.6, 88.59, 87.9, 75.1 (C_5H_4), 38.57 (Cp–*C*H), −36.41 (Mo–CH_2); ^{95}Mo NMR ($CDCl_3$, 26.07 MHz, r.t.): δ (ppm) = −1728; FAB-MS (70 eV) *m*/*z* (%); $M^+ = 348$.

3.1.2. (*R*,*S*)-[$Mo(\eta^5$-C_5H_4CHMe-η^1-$CHMe)(CO)_3$] (**3**)

The addition of a THF (ca. 20 mL) solution of the ligand (*S*,*S*)-1,2-dimethyl-spiro[2,4]hepta-4,6-diene (0.35 g, 2.9 mmol) to $Mo(CO)_3(CH_3CN)_3$ (0.80 g, 2.65 mmol) at

0 °C produces an orange solution, which is stirred overnight at r.t. All volatiles are removed in vacuo, and the sticky residue is extracted with 15 mL hexane (three times) and filtered. The obtained orange red filtrates are concentrated and chromatographed on Florisil (60–100 mesh). The orange yellow fraction is eluted with *n*-hexane and collected. After removal of all solvent, compound **3** is obtained as orange red oily solid. After cooling to −30 °C thermally unstable orange-red needles are formed. Yield (1.68 g, 60%). Anal. Calc. for $C_{12}H_{12}O_3Mo$ (300): C, 48.00; H, 4.00. Found: C, 48.17; H, 4.18%. IR (KBr, ν cm^{-1}): 3118 (w, ν(CH) of Cp-ring), 2969, 2938, 2897 and 2854 (w, $\nu(CH_3)$ and $\nu(CH_2)$), 1999.5, 1902.4 (vs, ν(CO)); ^{1}H NMR ($CDCl_3$, 400 MHz, r.t.): δ (ppm) = −0.07 (m, 1H, Mo–C*H*), 1.11 (d, J = 6.8 Hz, 3H, Mo–CH–CH_3), 1.46 (d, J = 6.8 Hz, 3H, Cp–CH–CH_3), 2.39 (m, 1H, Cp–C*H*), 5.21 (m, 1H, Cp), 5.18 (m, 1H, Cp), 5.16 (m, 1H, Cp) and 5.12 (m, 1H, Cp); ^{13}C NMR ($CDCl_3$, 100.28 MHz, r.t.): δ (ppm) = 224 (*C*O), 89.90, 88.65, 87.74, 86.73, 74.26 (C_5H_4), 38.18 (Cp–*C*H), 24.41 (Cp–CH–*C*H_3), 20.79 (Mo–CH–*C*H_3), −17.48 (Mo–*C*H); ^{95}Mo NMR ($CDCl_3$, 26.07 MHz, r.t.): δ (ppm) = −1696; FAB-MS (70 eV) m/z (%); M^+ = 300.

3.2. Single-crystal X-ray structure determination of racemic compound 2

Crystal data and details of the structure determination are presented in Table 1. Suitable single crystals for the X-ray diffraction study were grown from hexane. A clear yellow plate was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was performed at 173 K within the Θ range of $2.15° < \Theta < 25.30°$. A total of 68 512 reflections were integrated, corrected for Lorentz, polarization, and, arising from the scaling procedure, corrected for latent decay and absorption effects. After merging (R_{int} = 0.058), 2497 [2210: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 229 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with R_1 = 0.0230 [$I_o > 2\sigma(I_o)$], wR_2 = 0.0497 (all data), GOF = 1.106, and shift/error < 0.001. The final difference-Fourier map shows no striking features [19].

Table 1
Crystallographic data for [Mo(η^5-C_5H_4CHPh-η^1-CH_2)(CO)$_3$] (**2**)

Compound	**2**
Formula	$C_{16}H_{12}MoO_3$
Formula weight	348.20
Color/habit	Yellow/plate
Crystal dimensions (mm)	0.08 × 0.15 × 0.46
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
a (Å)	12.7778(1)
b (Å)	7.5948(1)
c (Å)	28.3288(3)
V (Å^3)	2749.16(5)
Z	8
T (K)	173
D_{calc} (g cm^{-3})	1.683
μ (mm^{-1})	0.957
F(000)	1392
Θ range (°)	2.15–25.30
Index ranges (h,k,l)	±15, ±9, ±34
Number of reflections collected	68 512
Number of independent reflections (R_{int})	2497 (0.058)
Number of observed reflections ($I > 2\sigma(I)$)	2210
Number of data/restraints/parameters	2497/0/229
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0230/0.0480
R_1/wR_2 (all data)[a]	0.0294/0.0497
Goodness-of-fit (GOF)[b] on F^2	1.106
Largest difference in peak and hole (e Å^{-3})	+0.34 and −0.35

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[b] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

3.3. Catalytic reactions

The catalytic reactions were performed under an air atmosphere, in a reaction vessel equipped with a magnetic stirrer, immersed into a 55 °C thermostated bath.

Achiral catalytic epoxidation: *cis*-cyclooctene (800 mg, 7.3 mmol), mesitylene (1 g, internal standard), 1 mol% (73 μmol) of compounds **2** or **3** as catalysts were added to the reaction vessel. With the addition of TBHP (2.65 mL, 5.5 M in *n*-decane) the reaction was started. The course of the reactions was monitored by quantitative GC analysis. Samples were taken and diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and destroy the excess of peroxide, respectively. The resulting slurry was filtered and the filtrate injected into a chiral 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.

Chiral catalytic epoxidation: *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene (100 mg, internal standard), and 1 mol% (17 μmol) of the compounds **2** or **3** as catalysts and 2 mL toluene as solvent were added to the reaction vessel. With the addition of TBHP (0.62 mL, 5.5 M in *n*-decane) the reaction started. The course of the reactions was monitored by quantitative GC analysis. The samples were processed as described above. The enantiomeric excess was calculated with the ratio of the peaks corresponding to both epoxides formed.

4. Conclusions

The *ansa*-bridged η^5-cyclopentadienyl carbonyl molybdenum complexes **1**–**3** were synthesized and in the case of complexes **2** and **3**, stereogenic centers are located on the side chain. The X-ray crystal structure of **2** shows a distorted four-legged piano stool conformation similar to that established for analogous tricarbonyl cyclopentadienyl molybdenum complexes. Compounds **1**–**3** show a similar catalytic behavior and similar ^{95}Mo NMR shifts indicating that the introduction of substitutes on the side chain between metal center and the Cp ring does not influence much the electronic situation at the metal center and therefore also not the catalytic performance. Comparison to $CpMo(CO)_3Me$, indicates that the replacement of a methyl group by an *ansa*-bridge does not very strongly influence the overall catalytic performance, but leads to a somewhat slower reaction due to the increased steric hindrance. For the asymmetric epoxidation of *trans*-β-methylstyrene, the chiral induction is up to 20% and compound **3** displays a better chiral induction, most likely because of the closer proximity of the chiral center to the metal atom. The ring strain leads to somewhat sensitive systems that break down slowly under the oxidative reaction conditions.

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Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-286972 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html). Supplementary data associated with this article can be found, in the online versions, at doi:10.1016/j.jorganchem.2005.10.044.

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