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Stable and Catalytically Highly Active *ansa* Compounds with Cycloalkyl Moieties as Bridging Units

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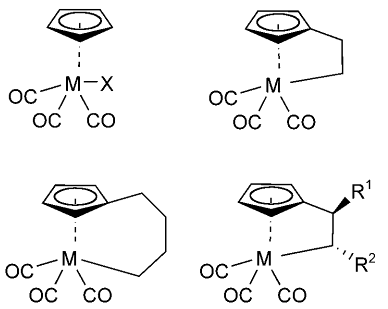
Abstract: The complexes $Mo\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}(CO)_3$ (**2a**) and $W\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}CO)_3$ (**2b**) were synthesized by reacting spiro-[4.2]bicyclo[4.1]deca-6,8-diene (**1**) with the tri(acetonitrile)tri(carbonyl)metal complexes $M(CO)_3(CH_3CN)_3$ (M = Mo, W). Thermogravimetric (TGA) measurements confirm that the complexes are stable up to 140 °C in air in the solid state. The complexes **2a** and **2b** are very active catalysts at room temperature for the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (TBHP) as oxidant, reaching TOFs of up to 3650 h^{-1}. Complex **2a** achieves a quantitative product yield without formation of any by-products within 1.5 h, outperforming previously published *ansa* compounds and performing on par with the cyclopentadienyltri(carbonyl)(halo)- or (alkyl)molybdenum compelxes $CpMo(CO)_3R$ (R = Hal, Me, Et).

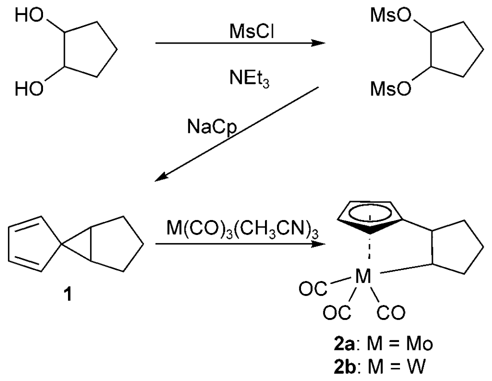
Keywords: *ansa* compounds; catalyst design; epoxidation; molybdenum; tungsten

Epoxidation reactions and especially asymmetric epoxidations of double bonds are of high interest for the synthesis of fine chemicals, pharmaceuticals and aroma and flavor molecules.[1] A broad range of compounds have been applied as catalysts for this type of reaction. Besides the well-known and highly active methyltrioxorhenium (MTO), several other Re(VII), Mo(VI), Ti(IV), Mn(III) and V(III) compounds have been found to catalyze olefin epoxidation, in some cases with high enantiomeric excesses.[2] Many other catalyst systems based on Mo and W have been extensively studied and applied in asymmetric epoxidation catalysis, but were found to give only moderate *ee* values at best.[3] These can be improved by performing the catalytic experiments at lower temperatures, leading in all cases to a significant loss of activity.[4] In the last years, $CpM(CO)_3R$ compounds (M = Mo, W, R = halogen, alkyl) (Scheme 1) have been thoroughly examined in epoxidation catalysis. Amongst these, *ansa*-type complexes, which had first been described by Eilbracht et al. in the late 1970s, have aroused attention due to their potential applications in the field of asymmetric catalysis.[5–8] Herein the first representatives of a series of new molybdenum and tungsten *ansa* complexes with cycloalkyl moieties as exceptionally stable bridging units are described as is also the use of these complexes as catalysts for olefin epoxidation reactions at room temperature.



Scheme 1. General catalysts of the type $CpM(CO)_3R$ and *ansa*-$CpM(CO)_3R$. M = Mo, W; R = Cl, CH_3, CH_2CH_3; R^1 = Ph, CH_3, R^2 = H, CH_3.

Reaction of cyclopentanediol bis(methanesulfonate) with sodium cyclopentadienide in THF was carried out following known reaction procedures[8], and resulted in the novel spiro-annulated diene **1**, which was then reacted with $M(CO)_3(CH_3CN)_3$ (M = Mo, W) in THF to afford the complexes $Mo\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}(CO)_3$ (**2a**) and $W\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}(CO)_3$ (**2b**) (Scheme 2). Complex **2a** was isolated with a 50% yield as orange, flat, rectangular crystals. Complex **2b** was isolated with a 40% yield as an orange powder. Both compounds are slightly sensitive towards light and moisture, but show an improved stability in comparison to previously synthesized *ansa* compounds. Thus, **2a** can be handled at room temperature under air for some hours without decomposition in the solid state, whereas **2b** can be



Scheme 2. Synthesis of *ansa*-complexes **2a** and **2b**.

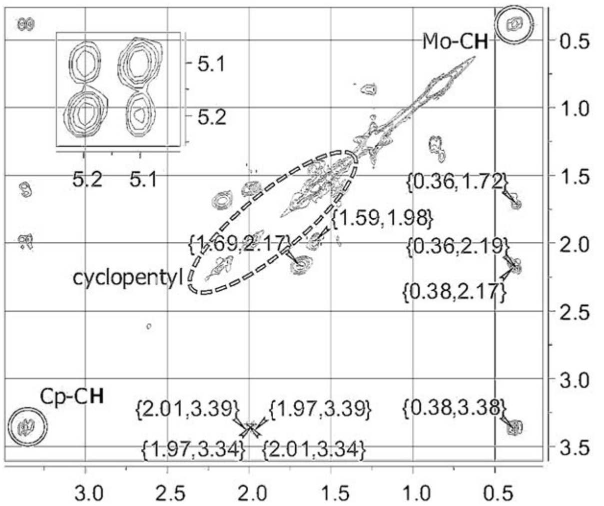


Figure 1. 2D-COSY of **2a**, showing both the cyclopentadienyl (upper left corner) and the ansa cyclopentyl spin systems.

Table 1. Catalytic activity of **2a** and **2b** for *cis*-cyclooctene epoxidation.

Compound[a]	Yield[b] [%] (after 1.5 h)	Yield[b] [%] (after 24 h)	TOF [h^{-1}]
2a	quant./30[c]	quant.	750/3650[c]
2b	15	67	160

[a] Catalyst:oxidant (TBHP):substrate ratio 1:200:100, solvent CH$_2$Cl$_2$, room temperature.

[b] GC yield.

[c] Catalyst:oxidant:substrate ratio 1:2000:1000.

stored indefinitely under air. TG-MS measurements for **2a** show a first decomposition step at 140 °C by loss of the carbonyl ligands according to a sharp MS signal of $m/z = 28$. For **2b**, the starting temperature of decomposition is 180 °C. ^{1}H NMR for **2a** shows two multiplets at $\delta = 5.21$ and 5.12 ppm which are attributed to the four protons of the cyclopentadienyl moiety, indicating a cleavage of the spirocycle and the insertion of the metal into one of the C$_{\text{diene}}$–C bonds, forming a η^5-coordinated cyclopentadienyl moiety and a η^1 metal-carbon bond. The Cp-CH proton signal appears at $\delta = 3.38$ ppm, whereas the proton bound to the η^1-coordinating carbon has a chemical shift of $\delta = 0.40$ ppm due to the deshielding effect of the metal center.

Both ^{13}C NMR and two-dimensional COSY experiments support these assignments. ^{13}C NMR shows four different signals in the range of $\delta = 90.0$–86.6 ppm, attributed to the four non-substituted cyclopentadienyl carbons, and a signal at $\delta = 76.6$ ppm, corresponding to the cyclopentadienyl carbon bearing the *ansa*-cyclopentadienyl unit. The η^1-bound carbon has a chemical shift of $\delta = -26.9$ ppm. 2D-COSY experiments (Figure 1) show two separate spin systems, one for the four protons of the Cp moiety and other for the *ansa* fragment. Similar values are observed for the tungsten complex **2b** (see Experimental Section). ^{95}Mo NMR of compound **2a** shows the molybdenum at $\delta = -1388$ ppm. This value is consistent with previously reported *ansa*-compounds.[5d,e]

Complexes **2a** and **2b** were tested in the epoxidation of *cis*-cyclooctene (Table 1), 1-octene, *cis*-stilbene and *trans*-stilbene, with *tert*-butyl hydroperoxide (TBHP) as the oxidant and under air at room temperature. A catalyst:oxidant:substrate ratio of 1:200:100 was used for all reactions. Upon addition of TBHP, the solution turned light yellow, owing to the oxidation of the carbonyl compound to yield the catalytically active species, as described previously.[3,9,10] The reaction mixture was analyzed *via* GC-MS. Although both compounds were found to be highly active catalysts for the epoxidation of cyclooctene, only **2a** shows moderate to good activities towards the other substrates. In the case of *cis*-cyclooctene, **2a** reaches quantitative conversion (90–100%) after 1.5 h, whereas **2b** reaches 15% conversion after 1.5 h and 67% after 24 h. A turnover frequency of 750 h^{-1} is obtained in the case of compound **2a**, which is within the range of other non-*ansa* cyclopentadienyl molybdenum alkyls such as CpMo(CO)$_3$Me. An additional experiment was carried out using a 1:2000:1000 ratio of **2a**. In this case, a TOF of 3650 h^{-1} is obtained. Experiments with 1-octene catalyzed by **2a** afford a yield of *ca.* 45% after 4 h (TOF *ca.* 40 h^{-1} with a 1:200:100 ratio, no diols were detected during the course of the experiment). Moreover, **2a** is found to be a highly stereoselective catalyst in the epoxidation of *cis*- and *trans*-stilbene, affording the respective epoxides with a *cis*/*trans*-ratio of 95:5 and 1:99, respectively, TOFs are up to 140 h^{-1}. The epoxide yield after 4 h is *ca.* 35% and *ca.* 75% after 24 h for *cis*-stilbene as the substrate. It has to be noted that catalytic runs with all previously reported CpMo(CO)$_3$R complexes[6] (see Scheme 1) were conducted at 55 °C (for Mo compounds) and 90 °C (for W compounds). Thus, compound **2a** (and **2b** in the case of cyclooctene) reach conversions similar to the non-*ansa* complexes of the type $CpM(CO)_3R$ ($R = Cl$, CH_3, CH_2CH_3), despite being reacted at room temperature.

In conclusion, the new molybdenum and tungsten *ansa* complexes **2a** and **2b** with a cyclopentyl unit as the *ansa* bridge have been synthesized by the reaction of spiro-annulated diene **1** with $M(CO)_3(CH_3CN)_3$ ($M = Mo$, W). The complexes have been characterized by ^1H, ^{13}C, ^{95}Mo and two-dimensional COSY NMR experiments. In comparison to previously reported *ansa* compounds of Mo and W, these complexes show an improved thermal stability and can be stored under air for long periods of time. Catalytic epoxidation with *cis*-cyclooctene, 1-octene, *cis*-stilbene and *trans*-stilbene as substrate and TBHP as oxidant show that **2a** is a highly active and stereoselective epoxidation catalyst, achieving TOFs up to $3650\,h^{-1}$ at room temperature. Complex **2b** shows only moderate activities with *cis*-cyclooctene as substrate at room temperature and requires higher reaction temperatures to afford high product yields. Further research in the field of *ansa* compounds, both synthetic and catalytic, is currently underway in our group.

Experimental Section

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 and pentane over CaH_2), distilled under an argon atmosphere and used immediately (THF) or kept over 4 Å molecular sieves. TBHP was purchased from Aldrich as 5.0–6.0 mol% solution in *n*-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. Thermogravimetric analyses were performed with a Netzsch TG 209 system at a heating rate of $5\,°C\,min^{-1}$ under air. ^1H, ^{13}C and ^{95}Mo NMR spectra were recorded using a Jeol-JMX-GX 400 MHz or a Bruker Avance DPX-400 spectrometer. Mass spectra were recorded with Finnigan MAT 311 A and MAT 90 spectrometers. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with an FID and a VF-5 ms column (*cis*-cyclooctene, 1-octene) or a Hewlett–Packard HP-6890 instrument with a mass selective detector and a DB-225 column (*cis*-stilbene, *trans*-stilbene). Cyclopentanediol bis(methanesulfonate) was synthesized from 1,2-cyclopentanediol using published procedures.[8]

Spiro[4.2]bicyclo[4.1]deca-6,8-diene (1)

Compound **1** was synthesized according to a modified literature procedure.[5a] Freshly distilled cyclopentadiene (5 mL, 0.06 mol) was added to a suspension of NaH (1.9 g, 0.08 mol) in 200 mL THF at 0 °C. The flask was then cooled again to 0 °C and cyclopentanediol bis(methanesulfonate) (10 g, 0.04 mol) in 100 mL THF was added dropwise. The mixture was stirred overnight at room temperature and 20 mL of methanol were added to quench any excess of NaH and NaCp. After addition of 100 mL of water, the THF layer was separated and the aqueous layer was washed with hexane (3×50 mL). The combined organic layers were washed with 100 mL of water, 100 mL of HCl (10%) and 100 mL of water to obtain an orange-yellow solution. All the organic solvents were distilled off and the residue was extracted with pentane. After drying under high vacuum, spiroligand **1** was obtained as a yellow oil ($d = 1.5\,g\,cm^{-3}$) that was used without further purification; yield: 5.3 g (50%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 6.56$ (m, 1H, Cp), 6.43 (m, 1H, Cp), 6.41 (m, 1H, Cp), 6.02 (m, 1H, Cp), 2.63 (m, 2H, Cp-CH), 2.2–1.9 (m, 5H, cyclopentyl), 1.75 (m, 1H, cyclopentyl); ^{13}C NMR (100.28 MHz, $CDCl_3$): $\delta =$ 140.17, 132.76, 131.57, 126.87 (Cp), 48.37 (C_{spiro}), 36.09 (Cp-CH), 28.81, 24.80 (cycloalkyl); CI-MS: parent peak at $m/z = 133$ corresponding to $[M]^+$.

$Mo\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}(CO)_3$ (2a)

The dropwise addition of a THF (*ca.* 20 mL) solution of **1** (0.1 g, 0.7 mmol) to 20 mL of a solution of $Mo(CO)_3(CH_3CN)_3$ (0.22 g, 0.7 mmol) at 0 °C produced a yellow suspension, which was stirred overnight at 25 °C. Volatiles were removed under vacuum, the sticky residue was extracted with *n*-hexane (3×15 mL), filtered, and the obtained orange filtrates were concentrated. After cooling to −30 °C orange crystals were obtained; yield: 0.11 g (50%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.21$ (m, 2H, Cp), 5.12 (m, 2H, Cp), 3.38 [td, $^3J(H,H_{cyclopentyl}) = 9.4$ Hz, $^3J(H,H_{Mo-C}) =$ 4.2 Hz, 1H, Cp-CH], 2.17 (m, 1H, cycloalkyl), 2.0 (m, 1H, cycloalkyl), 1.71 (m, 1H, cycloalkyl), 1.60 (m, 2H, cycloalkyl), 1.45 (m, 1H, cycloalkyl), 0.40 [dt, $^3J(H,H_{cyclopentyl}) =$ 9.8 Hz, $^3J(H,H_{Cp-CH}) = 5.8$ Hz, Mo-CH]; ^{13}C NMR (100.28 MHz, $CDCl_3$): $\delta = 90.0$, 89.0, 88.6, 86.6 (Cp), 76.6 (Cp-CH), 38.1, 35.9, 32.4, 26.1 (cycloalkyl), −25.9 (Mo-C); ^{95}Mo NMR (26 MHz, $CDCl_3$, 25 °C): <ιτ>δ</ιτ>= −1389; CI-MS: parent peak at $m/z = 314$ corresponding to $[M]^+$, $m/z = 286$ corresponding to $[M-CO]^+$; anal. calcd. for $C_{13}H_{12}O_3Mo$ (312): C 50.02, H 3.87; found: C 49.62, H 3.65%.

$W\{\eta^5\text{-}C_5H_4[CH(CH_2)_3]\text{-}\eta^1\text{-}CH\}(CO)_3$ (2b)

The dropwise addition of a THF (*ca.* 20 mL) solution of **1** (0.21 g, 1.6 mmol) to 20 mL of a solution of $W(CO)_3(CH_3CN)_3$ (0.63 g, 1.6 mmol) at 0 °C produced a yellow suspension, which was stirred overnight at 25 °C. Volatiles were removed under vacuum, the sticky residue was extracted with *n*-hexane (3×15 mL), filtered, and the obtained orange filtrates were concentrated. After cooling to −30 °C an orange powder was obtained; yield: 0.26 g (40%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.37$ (m, 1H, Cp), 5.25 (m, 2H, Cp), 5.12 (m, 1H, Cp), 3.40 [td, $^3J(H,H_{cyclopentyl}) =$ 9.4 Hz, $^3J(H,H_{W-C}) = 4.2$ Hz, 1H, Cp-CH], 2.17 (m, 1H, cycloalkyl), 2.03 (m, 1H, cycloalkyl), 1.95 (m, 1H, cycloalkyl), 1.71 (m, 1H, cycloalkyl), 1.55 (m, 2H, cycloalkyl), 0.46 [dt, $^3J(H,H_{cyclopentyl}) = 9.8$ Hz, $^3J(H,H_{Cp-CH}) = 5.8$ Hz, W-CH]; ^{13}C NMR (100.28 MHz, $CDCl_3$): $\delta = 88.0$, 87.8, 86.4, 84.6 (Cp), 80.2 (Cp-CH), 38.0, 36.1, 32.5, 26.3 (cycloalkyl), −38.2 (W-C); CI-MS: parent peak at $m/z = 401$ corresponding to

$[M]^+$ $m/z=373$ corresponding to $[M-CO]^+$; anal. calcd. for $C_{13}H_{12}O_3W$ (403): C 38.73, H 3.75; found: C 38.57, H 3.58%.

Application in Epoxidation Catalysis

The catalytic reactions were performed in air, within a reaction vessel equipped with a magnetic stirrer. For *cis*-cyclooctene: 800 mg (7.3 mmol) of the olefin, 500 mg of mesitylene (internal standard) and 1 mol% (73 μmol) of the catalysts (**2a**, **2b**) or 0.1 mol% (**2a**) were added to the reaction vessel and diluted in 20 mL CH_2Cl_2. For 1-octene: 410 mg (3.65 mmol) of the olefin, 250 mg of mesitylene (internal standard) and 1 mol% (36 μmol) of the catalysts (**2a**, **2b**) were added to the reaction vessel and diluted in 10 mL CH_2Cl_2. For *trans*-stilbene: 660 mg (3.65 mmol) of the olefin, 500 mg of 4-methylbenzophenone (internal standard) and 1 mol% (36 μmol) of the catalysts (**2a**, **2b**) were added to the reaction vessel and diluted in 10 mL CH_2Cl_2. For *cis*-stilbene: 200 mg (1.10 mmol) of the olefin, 100 mg of 4-methylbenzophenone (internal standard) and 1 mol% (11 μmol) of the catalysts (**2a**, **2b**) were added to the reaction vessel and diluted in 10 mL CH_2Cl_2. The reaction begins with the addition of TBHP (5.5 M in *n*-decane). 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 obtained was injected into a GC column. The conversions of *cis*-cyclooctene, 1-octene, *cis*- and *trans*-stilbene and the formation of their respective oxides were calculated from calibration curves ($r^2>0.999$) recorded prior to the commencement of the reaction.

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