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Reactions of complex ligands Part 84. Chiral diene–dienophile-functionalized aminocarbene complexes of molybdenum: synthesis and intramolecular Diels–Alder reaction☆,☆☆

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Abstract

Chiral at metal carbene complexes (η^5-C_5H_5)(CO)(NO)Mo=C[C(CH_3)=CH_2(NRCH_2(2-C_4H_3O)] **2**–**4** have been synthesized from (η^5-C_5H_5)Mo$(CO)_2$NO via a nucleophilic addition/alkylation/aminolysis sequence. In contrast to **2** (R = H), the *N*-alkylated analogs **3** and **4** undergo intramolecular Diels–Alder reaction upon warming to give the isoindole derivatives **6** and **7** with moderate diastereoselection. These molybdenum carbenes cyclize more readily than their isolobal analogous methacrylic amides, but they are less reactive than their analogs containing a [η^5-$C_5(CH_3)H_4$](CO)$_2$Mn or a $(CO)_5$W fragment. This sequence reflects the increasing electron-withdrawing ability of the metal coligand moiety in the order of the molybdenum < manganese < tungsten coligand fragments. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbene complexes; Cycloaddition reactions; Diels–Alder reactions; Intramolecular cycloaddition; Molybdenum complexes

1. Introduction

Over the past two decades, Fischer-type carbene complexes have been established as useful tools in organic chemistry [2]. Based on the strongly electrophilic carbene carbon atom attached to a low-valent metal center, manifold applications have been developed for selective carbon–carbon bond formation [3]. Both metal-centered and ligand-centered cycloaddition reactions, such as the chromium-mediated carbene benzannulation by alkynes [4], the Pauson–Khand reaction [5] and Diels–Alder reaction [6] have been shown to proceed with excellent regio- and stereoselectivity.

Recently, we reported on the intramolecular Diels–Alder reaction of diene–dienophile-functionalized aminocarbene complexes [7] which, according to the isolobal analogy of a $M(CO)_5$ fragment (M = Cr, Mo, W) and an oxygen atom [8], represent the organometallic counterparts of carboxylic amides. The pentacarbonyl metal fragment is a potent electron-withdrawing functionality, even superior to a Lewis acid coordinated oxygen atom that allows mild conditions for metal carbene based Diels–Alder reactions. After we found that intramolecular Diels–Alder reactions of 2-furfurylamino carbene ligands are promoted by half-sandwich carbene complexes of manganese [9], we focused our attention on a similar type of complexes $CpML^1L^2L^3$ in order to examine whether a chiral metal center [10] can be exploited in an asymmetric induction along the cycloaddition reaction. Based on the straightforward synthetic access to Cp(CO)(NO)Mo=C(OCH_3)Ph [11], which can be easily prepared from dicarbonylcyclopen-

☆ Dedicated to Professor A. Ceccon on the occasion of his 65th birthday.

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tadienyl(nitrosyl)molybdenum(0) [12], we chose the Cp(CO)(NO)Mo moiety to control the diastereoselectivity of the intramolecular Diels–Alder reaction.

2. 'Chiral at metal' molybdenum carbene complexes

The diene–dienophile-functionalized carbene complex **2** was synthesized from $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ by addition of 2-lithiopropene, alkylation of the resulting acylmolybdate with $[(CH_3)_3O][BF_4]$ to give methoxycarbene complex **1** followed by aminolysis with 2-furfuryl amine (Scheme 1). High yield-aminolysis of **1** requires four equivalents of furfuryl amine which have to be added to a concentrated solution (3.5 M) of **1** in dichloromethane at -30°C; following this protocol the furfurylaminocarbene complex **2** is obtained as a 1/4 mixture of *E*/*Z* isomers in 94% yield. Since the propensity of carbene complexes for intramolecular Diels–Alder reactions is enhanced by *N*-substitution [9,13] carbene complex **2** was alkylated with lithium diisopropylamide/methyl iodide or benzyl bromide to give aminocarbene complexes **3** and **4** as a mixture of diastereomers **3a**:**3b**:**3c**:**3d** = 1.9:1.4:1.4:1 and **4a**:**4b**:**4c**:**4d** = 2.0:1.3:1.3:1 in 80 and 68% overall yield, respectively (Scheme 1).

To elucidate the stereochemistry within the amino substituent NMR spectra of **3** and **4** were recorded both in an isotropic ($CDCl_3$) and in an anisotropic solvent (C_6D_6). Based on the well-documented fact that the upfield shift of *E*-CH_2 protons is more pronounced than that of *Z*-CH_2 protons if $CDCl_3$ is replaced as a solvent by C_6D_6 [14] an *E*-configuration is assigned to **3a** and **3b**, whereas **3c** and **3d** are identified as *Z*-aminocarbene complexes. The *E*/*Z* ratios **3a**, **3b**/**3c**, **3d** and **4a**, **4b**/**4c**, **4d** are reversed in comparison with the precursor **2** indicating that the aminocarbene complex anion formed upon deprotonation is configurationally labile under the reaction conditions shifting the equilibrium towards the less congested *E*-configuration. The isomers having the same configuration at the $C_{carbene}$–N bond differ partly in the ^{13}C-NMR spectra reflecting the complementary configuration at the metal. This is most evident for the chemical shifts of the terminal alkene carbon atoms in **3a**/**b** or **3c**/**d** which, assigned by DEPT 135 experiments, differ by ca. 7 ppm. This fact is underlined by the splitting of the IR absorption of the NO ligand as a strong π-acceptor ligand. For both compounds **3** and **4** a strong absorption at 1620 cm^{-1} with a shoulder at about 1609 cm^{-1} is observed in the spectra recorded in petroleum ether (Fig. 1). Increasing *N*-substitution hinders the rotation of the metal fragment around the molybdenum–carbene bond. As a consequence the NO ligand adopts two different orientations relative to the conjugated double bond of the carbene ligand as indicated in Fig. 1, which explains both the splitting of the NO absorption and the ^{13}C-NMR shifts of the sp^2-methylene carbon atoms. Similar results were obtained for methyloxycarbene complexes of molybdenum bearing hydridotris(3,5-dimethylpyrazolyl)borate as η^5-ligand attached to the metal center [15]. This bulky σ-donor ligand hampers the rotation around the molybdenum–carbene bond and two isomers that are conformationally stable on the NMR time scale were observed representing the two different orientations of the NO ligand with respect to the car-

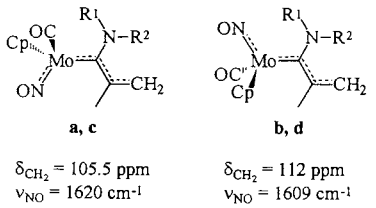
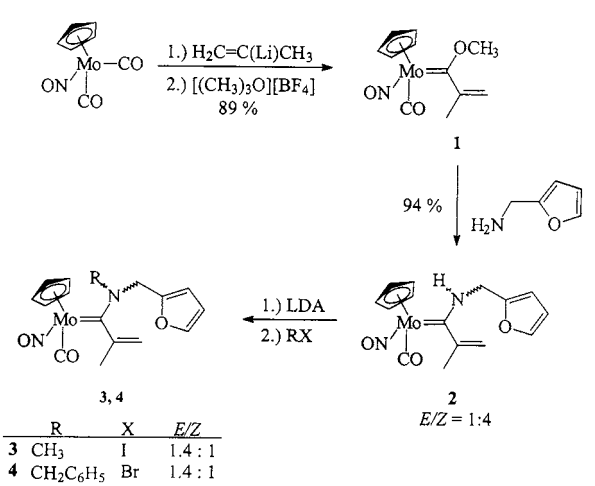
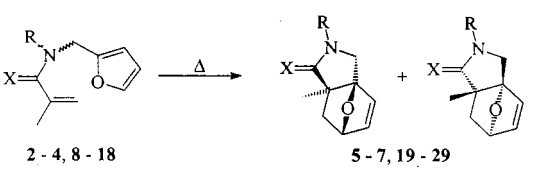


Fig. 1. Conformations of the Mo–carbene bond.



Scheme 1. Synthesis of chiral carbene complexes **2**–**4**.



X	R: H	R: CH_3	R: CH_2Ph	R: (*S*)-$CH(CH_3)Ph$
Cp(CO)(NO)Mo	**2, 5**	**3, 6**	**4, 7**	
O	**8, 19**	**9, 20**	**10, 21**	**11, 22**
$(CO)_5W$	**12, 23**	**13, 24**	**14, 25**	**15, 26**
$MeCp(CO)_2Mn$	**16, 27**	**17, 28**	**18, 29**	

Scheme 2. Intramolecular Diels–Alder reactions.

Table 1
Intramolecular Diels–Alder reaction of methacrylic acid derivatives **2**–**4** and **8**–**18**

Entry	Educt	X	R	Conditions	Product	Yield [a] (%)	d.e. (%)
1	**2**	Cp(CO)(NO)Mo	H	3 h; 90°C	**5**	0	–
2	**2**		H	120 h; 90°C	**5**	0	–
3	**3**		CH_3	3 h; 90°C	**6**	22	62
4	**3**		CH_3	4 h; 70°C	**6**	19	59
5	**3**		CH_3	24 h; 50°C	**6**	7.5	67
6	**4**		CH_2Ph	3 h; 90°C	**7**	50	71
7	**8**	O	H	"	**19**	0	–
8	**9**		CH_3	"	**20**	27	–
9	**10**		CH_2Ph	"	**21**	36	–
10	**11**		(*S*)-CH(CH_3)Ph	"	**22**	97	
11	**12**	$(CO)_5W$	H	"	**23**	79	–
12	**13**		CH_3	"	**24**	100	–
13	**14**		CH_2Ph	"	**25**	100	–
14	**15**		(*S*)-CH(CH_3)Ph	"	**26**	100	0
15	**15**		(*S*)-CH(CH_3)Ph	6 h; rt	**26**	73	15
16	**16**	$MeCp(CO)_2Mn$	H	24 h; 80°C	**27**	48	–
17	**17**		CH_3	6 h; 80°C	**28**	72	–
18	**18**		CH_2Ph	4 h; 80°C	**29**	75	–

[a] Isolated yields of **6**, **7** and **27**–**29**; yields of **19**–**26** were determined by NMR spectroscopy [9].

bene ligand. Both electronic and steric effects may be responsible to explain the existence of rotamers at room temperature.

3. Intramolecular Diels–Alder reactions

While the *N*-protonated amino carbene complex **2** gave no epoxy-3aH-isoindolylidene complex **5** upon warming in di-*n*-butyl ether to 120°C, its *N*-alkylated analogs **3** and **4** underwent cyclization within 3 h at 90°C to give **6** and **7** in 22 and 50% yield with moderate diastereomeric excess of 62 and 71%, respectively (Scheme 2, Table 1, entries 1–6). As demonstrated for the *N*-methyl complex **3** lowering the reaction temperature does not result in a significant increase of the d.e. but, instead, in a dramatical decrease of the yield; for instance, only a 7.5% yield of **6** is obtained at 50°C. As previously observed both in the pentacarbonyl tungsten series and in the dicarbonyl(methylcyclopentadienyl)manganese series the propensity for ring closure increases with increasing bulk of the *N*-substitution pattern [9]. A similar tendency was also found for their isolobal-analogous acrylic furfuryl amides [13]. These results can be rationalized in terms that bulky *N*-substitution favors the conformation within the furfuryl group required for cyclization. Unreacted **3** recovered from the reaction mixture revealed an unchanged ratio of isomers indicating that *N*-alkylation was performed under thermodynamic control (in spite of low temperature). Single diastereomers were obtained from the cyclization of **3** and **4**. ^{1}H- and ^{13}C-NMR spectra of the cycloaddition products **6** and **7** resemble those recorded for the pentacarbonyl tungsten analog **23** [9] suggesting a similar *trans*-fusion of the newly formed five-membered rings as has been established for **23** by X-ray analysis [7].

In order to compare the diastereoselection arising from the chiral metal center with that due to a chiral *N*-substituent we incorporated the (*S*)-1-phenylethyl group into the heteroatom carbene side chain of the pentacarbonyl tungsten complex [16]. When a solution of chiral **15** was warmed in toluene at 90°C for 3 h quantitative conversion to the cycloaddition product occurred but no diastereomeric excess could be detected (entry 14). Under milder conditions, in diethyl ether at room temperature for 6 h, tungsten carbene **15** underwent cyclization to give **26** in low diastereomeric excess (15% d.e., entry 15). These results demonstrate that the stereodifferentiating potential of the chiral metal fragment is superior to chiral *N*-substitution.

On the other hand, in comparison with the $(CO)_5W$ fragment, the more electron-rich Cp(CO)(NO)Mo moiety is a less efficient acceptor group, which results in a reduced reactivity towards intramolecular Diels–Alder reaction. Within the *N*-protonated (entries 1, 11 and 16), the *N*-methyl (entries 3, 12 and 17) and the *N*-benzyl (entries 6, 13 and 18) series the pentacarbonyl tungsten complexes gave the highest (entries 11–13) and the carbonyl(cyclopentadienyl)(nitrosyl)molybdenum (entries 1, 3 and 6) the lowest yields, while the dicarbonyl(methylcyclopentadienyl)manganese complexes range in between (entries 16–18). Although the molybdenum compounds bear the strongly electron-withdrawing the NO ligand, its striking π-acceptor capability is overruled by the efficient π-donating cyclopentadienyl ligand. The different overall acceptor properties of the metal coligand fragments are reflected

in the *N*-H acidities as evident from the ^{1}H-NMR spectra: An increased deshielding for the *N*-H proton is observed in the order of molybdenum complex *E*/*Z*-**12** ($\delta = 7.51$ and 8.25 ppm), the manganese complex *E*/*Z*-**16** ($\delta = 9.35$ and 9.54 ppm) and the tungsten complex **12** ($\delta = 10.77$ ppm).

4. Experimental

All operations were carried out under inert gas. Solvents were dried using standard methods, distilled, saturated and stored under argon. Merck silica gel 60 (0.063–0.200 mm) was used for column chromatography. ^{1}H- and ^{13}C-NMR: Bruker AC-200, AC-300, WM-250 and AM-400. MS: Kratos MS 50, Varian MAT CH 7A and MAT 711. FT-IR: Nicolet 510 and Magna 550. Elemental analyses: Heraeus-CH-*O*-Rapid.

The synthesis and analytical characterization of compounds **19**–**21**, **23**–**25** and **27**–**29** were previously described in Ref. [9].

4.1. *rac*-Carbonyl(cyclopentadienyl)[methoxy(2-propenyl)carbene](nitrosyl)molybdenum **1**

Dicarbonyl(cyclopentadienyl)(nitrosyl)molybdenum (2.47 g, 10 mmol) was added at −78°C to a solution of 2-lithiopropene prepared from 0.89 ml (10 mmol) 2-bromopropene and 11.8 ml (20 mmol) of a 1.7 M solution of *tert*-butyllithium in 50 ml of diethyl ether. After 45 min the solvent was removed at reduced pressure. The residue was dissolved in 50 ml of dichloromethane and 2.96 g (20 mmol) of trimethyloxonium tetrafluoroborate were added at −30°C. The reaction mixture was allowed to reach room temperature overnight, filtered over silica gel, and the residue was washed with dichloromethane until the filtrate remained colourless. The solvent was removed at reduced pressure, and the crude product was purified by column chromatography on silica gel (5 × 4 cm, eluent: petroleum ether). After elution of the starting material the eluent was changed to petroleum ether:diethyl ether (8:1) and 2.69 g (89%) of **1** were obtained as a yellow solid. $R_f = 0.06$ (petroleum ether); $R_f = 0.67$ (petroleum ether:diethyl ether 8:1). IR (petroleum ether): $\nu = 1975$ s (CO), 1638 s (NO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 5.60$ (s, 5H, C_5H_5), 4.99 (dq, 1H, $J = 1.54$, 1.37 Hz, CH_3–C=C*H*H), 4.62 (dq, 1H, $J = 0.78$, 1.56 Hz, CH_3–C=CH*H*), 4.38 (s, 3H, OCH_3), 1.77 (dd, 3H, $J = 0.78$, 1.37 Hz, C*H*$_3$–C=CHH). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 328.8$ (Mo=C), 225.4 (CO), 156.4 (H_3C–*C*=CH_2), 116.7 (H_3C–C=*C*H_2), 96.9 (C_5H_5), 66.2 (OCH_3), 19.7 (H_3C–C=CH_2). MS (EI): *m*/*z* (%): 305 (7) [M$^+$], 277 (100) [M$^+$ − CO], 231 (71), 202 (68), 177 (44), 163 (24), 137 (15), 41 (17).

Anal. Found: C, 43.94; H, 4.40; N, 4.62; $C_{11}H_{13}MoNO_3$ (303.2). Calc.: C, 43.58; H, 4.32; N, 4.62%.

4.2. *rac*-(*E*/*Z*)-Carbonyl(cyclopentadienyl)[*N*-2-furfuryl-amino(2-propenyl)carbene](nitrosyl)molybdenum **2**

2-Furfurylamine (2.44 ml, 27.6 mmol) was added at −30°C to a solution of 2.10 g (6.9 mmol) of **1** in 2 ml of dichloromethane. After stirring overnight the reaction mixture was allowed to reach room temperature. The solvent and excess of amine were removed at reduced pressure, and the residue was purified by column chromatography on silica gel at −10°C (eluent petroleum ether:diethyl ether 8:1) to give 2.38 g (94%) of **2** as a red solid (*E*/*Z* = 1:4). $R_f = 0.45$ (petroleum ether:diethyl ether 8:1). IR (petroleum ether): $\nu = 1942$ s (CO), 1620 s (NO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): *E*-isomer: $\delta = 8.25$ (s_{br}, 1H, NH), 7.40 (dd, 1H, $J =$ 0.78, 1.78 Hz, 5-H_{furyl}), 6.35 (dd, 1H, $J = 1.76$, 3.13 Hz, 4-H_{furyl}), 6.27 (dd, 1H, $J = 0.78$, 3.13 Hz, 3-H_{furyl}), 5.46 (s, 5H, C_5H_5), 4.80 (m, 1H, H_3C–C=C*H*H), 4.52 (dd, 1H, $J = 6.06$, 15.26 Hz, NC*H*H), 4.49 (m, 1H, H_3C–C=CH*H*), 4.46 (dd, 1H, $J = 6.06$, 15.26 Hz, NCH*H*), 1.89 (m, 3H, $J = 1.37$ Hz, H_3C–C=CH_2). *Z*-isomer: $\delta = 7.51$ (s_{br}, 1H, NH), 7.41 (dd, 1H, $J = 0.78$, 1.76 Hz, 5-H_{furyl}), 6.43 (dd, 1H, $J = 0.78$, 3.32 Hz, 3-H_{furyl}), 6.37 (dd, 1H, $J = 1.76$, 3.32 Hz, 4-H_{furyl}), 5.48 (s, 5H, C_5H_5), 4.94 (dd, 1H, $J = 6.06$, 15.65 Hz, NC*H*H), 4.86 (dd, 1H, $J = 6.06$, 15.65 Hz, NCH*H*), 4.61 (dq, 1H, $J = 1.37$, 1.56 Hz, H_3C–C=C*H*H), 4.48 (dq, 1H, $J = 0.78$, 1.37 Hz, H_3C–C=CH*H*), 1.84 (m, 3H, $J = 1.37$ Hz, H_3C–C=CH_2). ^{1}H-NMR (400 MHz, C_6D_6): *E*-isomer; $\delta = 8.19$ (s_{br}, 1H, NH), 7.04 (m, 1 H, 5-H_{furyl}), 6.05 (m, 1H, 4-H_{furyl}), 5.91 (m, 1H, 3-H_{furyl}), 5.15 (s, 5H, C_5H_5), 4.43 (m, 1H, H_3C–C=C*H*H), 4.33 (m, 1H, H_3C–C=CH*H*), 3.86 (dd, 1H, $J = 6.06$, 15.3 Hz, NC*H*H), 3.81 (dd, 1H, $J = 6.06$, 15.3 Hz, NCH*H*), 1.59 (m, 3H, H_3C–C=CH_2). *Z*-isomer: $\delta = 7.06$ (dd, 1H, $J = 0.8$, 1.8 Hz, 5-H_{furyl}), 7.04 (s_{br}, 1H, NH), 6.23 (dd, 1H, $J = 0.8$, 3.3 Hz, 3-H_{furyl}), 6.05 (m, 1H, 4-H_{furyl}), 5.19 (s, 5H, C_5H_5), 4.93 (m, 1H, H_3C–C=C*H*H) 4.93 (dd, 1H, $J = 5.36$, 15.65 Hz, NC*H*H), 4.89 (dd, 1H, $J = 5.36$, 15.65 Hz, NC*H*H), 4.20 (m, 1H, H_3C–C=CH*H*), 1.50 (m, 3H, H_3C–C=CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): *E*-isomer: $\delta = 284.7$ (Mo=C), 237.5 (CO), 150.3 (2-C_{furyl}), 149.4 (H_3C–*C*=CH_2), 142.9 (5-C_{furyl}), 110.6 (3-C_{furyl}), 108.8 (4-C_{furyl}), 108.3 (CH_3–C=*C*H_2), 95.9 (C_5H_5), 44.8 ($NHCH_2$), 26.8 (*C*H_3–C=CH_2). *Z*-isomer: $\delta_r = 280.1$ (Mo=C), 235.9 (CO), 156.5 (2-C_{furyl}), 149.9 (H_3C–*C*=CH_2), 142.7 (5-C_{furyl}), 110.6 (3-C_{furyl}), 108.8 (4-C_{furyl}), 107.7 (CH_3–C=*C*H_2), 96.0 (C_5H_5), 48.9 ($NHCH_2$), 23.4 (*C*H_3–C=CH_2). ^{13}C-NMR (100 MHz, C_6D_6): *E*-isomer: $\delta = 285.8$ (Mo=C), 239.3 (CO), 157.4 (2-C_{furyl}), 150.9 (H_3C–*C*=CH_2), 143.3 (5-C_{furyl}), 111.4 (3-C_{furyl}), 109.6

(4-C_{furyl}), 108.6 (CH_3–C=CH_2), 96.7 (C_5H_5), 45.3 ($NHCH_2$), 24.0 (CH_3–C=CH_2). *Z*-isomer: $\delta = 281.3$ (Mo=C), 237.4 (CO), 157.4 (2-C_{furyl}), 151.2 (H_3C–C=CH_2), 143.4 (5-C_{furyl}), 111.5 (3-C_{furyl}), 109.6 (4-C_{furyl}), 107.9 (CH_3–C=CH_2), 96.7 (C_5H_5), 49.6 ($NHCH_2$), 24.0 (CH_3–C=CH_2). MS (EI): *m*/*z* (%): 370 (6) [M^+], 342 (100) [$M^+ - CO$], 312 (4) [$M^+ - CO - NO$], 280 (10), 259 (14), 232 (21), 231 (20), 202 (31), 194 (40), 163 (15), 148 (6), 132 (17), 81 (56), 53 (16). HR-MS: Found 338.0267. $C_{14}H_{16}MoN_2O_2$ [$M^+ - CO$]. Calc.: 338.0280.

Anal. Found: C, 46.66; H, 4.51; N, 7.22; $C_{15}H_{16}MoN_2O_3$ (368.2). Calc.: C, 48.93; H, 4.38; N, 7.61%.

4.3. Carbonyl(cyclopentadienyl)[N-2-furfuryl-N-methylamino(2-propenyl)carbene](nitrosyl)molybdenum **3**

A solution of 1.30 g (3.5 mmol) of **2** in 2 ml of THF was added dropwise at −78°C to a solution of lithium diisopropyl amide prepared from 0.59 ml (4.2 mmol) diisopropylamine and 2.75 ml (4.2 mmol) of a 1.53 M *n*-butyllithium solution in 20 ml of THF. After 1.5 h 0.26 ml (4.2 mmol) of methyl iodide were added and the reaction mixture was allowed to warm to room temperature overnight. After removal of the solvent and purification of the residue by chromatography on silica gel at −10°C (eluent petroleum ether:diethyl ether 8:1) 1.06 g (80%) of **3** were obtained as a red oil (ratio of isomers: **3a**:**3b**:**3c**:**3d** = 1.9:1.4:1.4:1). $R_f = 0.18$ (petroleum ether:diethyl ether 8:1). IR (petroleum ether): $\nu = 1933$ s (CO), 1620 s (NO), 1609 sh (NO) cm^{-1}. IR (di-*n*-butyl ether): $\nu = 1927$ s (CO), 1612 s (NO) cm^{-1}. **3a**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.40$ (dd, 1H, $J = 0.79$, 1.76 Hz, 5-H_{furyl}), 6.5–6.2 (m, 2H, 3-H_{furyl}, 4-H_{furyl}), 5.48 (s, 5H, C_5H_5), 4.77 (dd, 1H, $J = 1.37$, 1.57 Hz, H_3C–C=C*H*H), 4.67 (d, 1H, $J =$ 15.26 Hz, NC*H*H), 4.59 (d, 1H, $J = 15.26$ Hz, NCH*H*), 4.46 (dd, 1H, $J = 0.98$, 1.57 Hz, H_3C–C=CH*H*), 3.46 (s, 3H, NCH_3), 1.90 (dd, 3H, $J = 0.78$, 1.37 Hz, H_3C–C=CH_2). **3b**: $\delta = 7.39$–7.38 (m, 1H, 5-H_{furyl}), 6.5–6.2 (m, 2H, 3-H_{furyl}, 4-H_{furyl}), 5.48 (s, 5H, C_5H_5), 4.81 (d, 1H, $J = 15.06$ Hz, NC*H*H), 4.73 (dq, 1H, $J = 1.37$, 1.57 Hz, H_3C–C=C*H*H), 4.66 (d, 1H, $J = 15.06$ Hz, NCH*H*), 4.34 (dq, $J = 0.8$, 1.59 Hz, H_3C–C=CH*H*), 3.50 (s, 3H, NCH_3), 1.79 (dd, 3H, $J = 0.98$, 1.57 Hz, H_3C–C=CH_2). **3c**: $\delta = 7.39$–7.38 (m, 1H, 5-H_{furyl}), 6.5–6.2 (m, 2H, 3-H_{furyl}, 4-H_{furyl}), 5.40 (s, 5H, C_5H_5), 5.20 (d, 1H, $J = 15.06$ Hz, NC*H*H), 5.00 (d, 1H, $J = 15.06$ Hz, NCH*H*), 4.74 (dq, 1H, $J = 1.37$, 1.57 Hz, H_3C–C=C*H*H), 4.38 (dq, 1H, $J = 0.98$, 1.56 Hz, H_3C–C=CH*H*), 3.19 (s, 3H, NCH_3), 1.89 (m, 3H, H_3C–C=CH_2). **3d**: $\delta = 7.36$ (dd, 1H, $J = 0.7$, 1.7 Hz, 5-H_{furyl}), 6.44–6.39 (m, 1H, 3-H_{furyl}), 6.34–6.31 (m, 1H, 4-H_{furyl}) 5.40 (s, 5H, C_5H_5), 5.26 (d, 1H, $J = 15.06$ Hz, NC*H*H), 4.99 (d, 1H, $J = 15.06$ Hz, NCH*H*), 4.66 (m, 1H, $J = 1.57$ Hz, H_3C–C=C*H*H), 4.20 (m, 1H, H_3C–C=CH*H*), 3.23 (s, 3H, NCH_3), 1.79 (m, 3H, H_3C–C=CH_2). ^{1}H-NMR (400 MHz, C_6D_6). **3a**: $\delta = 7.08$ (dd, 1H, $J = 0.78$, 1.76 Hz, 5-H_{furyl}), 6.53 (m, 1H, 3-H_{furyl}), 6.08 (dd, 1H, $J = 1.76$, 3.2 Hz, 4-H_{furyl}), 5.22 (s, 5H, C_5H_5), 4.44 (2 dd, 2H, $J = 0.78$, 1.37, 1.57 Hz, H_3C–C=CH_2), 4.05 (d, 1H, $J = 15.26$ Hz, NC*H*H), 3.99 (d, 1H, $J = 15.26$ Hz, NCH*H*), 3.31 (s, 3H, NCH_3), 1.56 (m, 3H, H_3C–C=CH_2). **3b**: $\delta = 6.98$ (dd, 1 H, $J = 0.78$, 1.76 Hz, 5-H_{furyl}), 5.98 (dd, 1H, $J = 1.76$, 3.2 Hz, 4-H_{furyl}), 5.87 (dd, 1H, $J = 0.78$, 3.13 Hz, 3-H_{furyl}), 5.21 (s, 5H, C_5H_5), 4.39 (m, 1H, $J = 1.57$ Hz, H_3C–C=C*H*H), 4.31 (m, 1H, $J = 1.56$ Hz, H_3C–C=CH*H*), 4.15 (d, 1H, $J = 15.06$ Hz, NC*H*H), 4.11 (d, 1H, $J = 15.06$ Hz, NCH*H*), 3.31 (s, 3H, NCH_3), 1.69 (m, 3H, H_3C–C=CH_2). **3c**: $\delta = 6.96$ (dd, 1H, $J = 0.78$, 1.76 Hz, 5-H_{furyl}), 5.98 (dd, 1H, $J = 1.76$, 3.2 Hz, 4-H_{furyl}), 5.83 (dd, 1H, $J = 0.78$, 3.13 Hz, 3-H_{furyl}), 5.14 (s, 5H, C_5H_5), 5.11 (d, 1H, $J = 14.48$ Hz, NC*H*H), 4.81 (d, 1H, $J = 14.48$ Hz, NCH*H*), 4.37 (m, 1H, $J = 1.57$ Hz, H_3C–C=C*H*H), 4.13 (m, 1H, H_3C–C=CH*H*), 2.65 (s, 3H, NCH_3), 1.35 (m, 3H, H_3C–C=CH_2). **3d**: $\delta = 7.04$ (dd, 1H, $J = 0.78$, 1.76 Hz, 5-H_{furyl}), 6.19 (dd, 1H, $J = 0.78$, 3.13 Hz, 3-H_{furyl}), 6.03 (dd, 1H, $J = 1.76$, 3.2 Hz, 4-H_{furyl}), 5.14 (s, 5H, C_5H_5), 5.12 (d, 1H, $J = 14.86$ Hz, NC*H*H), 4.85 (d, 1H, $J =$ 14.86 Hz, NCH*H*), 4.26 (dd, 1H, $J = 1.37$, 1.57 Hz, H_3C–C=C*H*H), 3.87 (m, 1H, H_3C–C=CH*H*), 2.70 (s, 3H, NCH_3), 1.53 (m, 3H, H_3C–C=CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): **3a**: $\delta = 280.0$ (Mo=C), 238.1 (CO), 150.9 (2-C_{furyl}), 149.0 (H_3C–C=CH_2), 142.7 (5-C_{furyl}), 110.5 (3-C_{furyl}), 109.0 (4-C_{furyl}), 105.6 (H_3C–C=CH_2), 96.0 (C_5H_5), 52.1 (NCH_2), 46.7 (NCH_3), 21.7 (H_3C–C=CH_2). **3b**: $\delta = 279.0$ (Mo=C), 238.4 (CO), 151.1 (2-C_{furyl}), 149.1 (H_3C–C=CH_2), 142.7 (5-C_{furyl}), 111.5 (H_3C–C=CH_2), 110.5 (3-C_{furyl}), 109.0 (4-C_{furyl}), 95.8 (C_5H_5), 52.2 (NCH_2), 46.9 (NCH_3), 20.5 (H_3C–C=CH_2). **3c**: $\delta = 279.2$ (Mo=C), 238.9 (CO), 151.6 (2-C_{furyl}), 149.9 (H_3C–C=CH_2), 142.4 (5-C_{furyl}), 110.6 (3-C_{furyl}), 109.1 (4-C_{furyl}), 105.0 (H_3C–C=CH_2), 96.5 (C_5H_5), 57.7 (NCH_2), 40.4 (NCH_3), 24.2 (H_3C–C=CH_2). **3d**: $\delta = 278.4$ (Mo=C), 239.3 (CO), 151.8 (2-C_{furyl}), 149.7 (H_3C–C=CH_2), 142.4 (5-C_{furyl}), 111.8 (H_3C–C=CH_2), 110.5 (3-C_{furyl}), 109.1 (4-C_{furyl}), 96.4 (C_5H_5), 57.8 (NCH_2), 40.6 (NCH_3), 23.3 (H_3C–C=CH_2). ^{13}C-NMR (100 MHz, C_6D_6): **3a**: $\delta =$ 281.3 (Mo=C), 239.7 (CO), 152.8 (2-C_{furyl}), 150.3 (H_3C–C=CH_2), 143.5 (5-C_{furyl}), 111.4 (3-C_{furyl}), 109.8 (4-C_{furyl}), 106.0 (H_3C–C=CH_2), 97.3 (C_5H_5), 52.7 (NCH_2), 47.3 (NCH_3), 22.3 (H_3C–C=CH_2). **3b**: $\delta =$ 280.4 (Mo=C), 240.0 (CO), 152.9 (2-C_{furyl}), 150.4 (H_3C–C=CH_2), 143.3 (5-C_{furyl}), 111.9 (H_3C–C=CH_2), 111.7 (3-C_{furyl}), 109.8 (4-C_{furyl}), 96.6 (C_5H_5), 52.5 (NCH_2), 47.6 (NCH_3), 21.0 (H_3C–C=CH_2). **3c**: $\delta =$ 280.7 (Mo=C), 240.4 (CO), 152.2 (2-C_{furyl}), 151.3

(H_3C–C=CH_2), 143.3 (5-C_{furyl}), 111.6 (3-C_{furyl}), 110.2 (4-C_{furyl}), 105.3 (H_3C–C=CH_2), 96.8 (C_5H_5), 58.5 (NCH_2), 40.8 (NCH_3), 24.9 (H_3C–C=CH_2). **3d**: δ = 279.9 (Mo=C), 240.8 (CO), 152.3 (2-C_{furyl}), 151.1 (H_3C–C=CH_2), 143.4 (5-C_{furyl}), 111.9 (H_3C–C=CH_2), 111.7 (3-C_{furyl}), 110.2 (4-C_{furyl}), 97.3 (C_5H_5), 58.6 (NCH_2), 41.0 (NCH_3), 24.0 (H_3C–C=CH_2). MS (EI): m/z (%): 356 (7) [$M^+ - CO$], 234 (4), 179 (100), 164 (9), 81.0 (88), 41 (25). HR-MS: Found 350.0441. $C_{15}H_{18}MoN_2O_2$ [$M^+ - CO$]. Calc.: 350.0436.

4.4. [N-Benzyl-N-2-furfurylamino(2-propenyl)carbene](carbonyl)(cyclopentadienyl)(nitrosyl)molybdenum **4**

As described for the preparation of **3**, the reaction of 4.87 ml (7.4 mmol) of 1.6 M *n*-butyllithium, 1.04 ml (7.4 mmol) of diisopropylamine, 2.28 g (6.2 mmol) of **2** and 0.88 ml (7.4 mmol) of benzyl bromide gave 1.94 g (68%) of **4** as a red oil (ratio of isomers **4a**:**4b**:**4c**:**4d** = 2:1.3:1.3:1). R_f = 0.23 (petroleum ether:diethyl ether 8:1). IR (petroleum ether): ν = 1933 s (CO), 1620 s (NO), 1609 sh (NO) cm^{-1}. IR (di-*n*-butyl ether): ν = 1927 s (CO), 1612 s (NO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43–7.26 (m, 5H, C_6H_5), 7.20–7.13 (m, 1H, 5-H_{furyl}), 6.45–6.15 (m, 2H, 3-H_{furyl}, 4-H_{furyl}), 5.51, 5.49, 5.44, 5.40 (s, 5H, C_5H_5), 5.25–4.30 (m, 6H, H_3C–C=CH_2, NC$H_{2,benzyl}$, NC$H_{2,furfuryl}$), 1.99, 1.94, 1.83, 1.79 (dd, 3H, J = 0.78, 1.37 Hz, H_3C–C=CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): **4a**: δ = 281.4 (Mo=C), 237.7 (CO), 150.8 (2-C_{furyl}), 150.0 (CH_3–C=CH_2), 142.3 (5-C_{furyl}), 135.8 (1-C_{phenyl}), 128.9 (3, 5-C_{phenyl}), 127.5 (2, 6-C_{phenyl}), 127.0 (4-C_{phenyl}), 110.5 (3-C_{furyl}), 109.1 (4-C_{furyl}), 105.3 (CH_3–C=CH_2), 96.3 (C_5H_5), 56.4 (N$CH_{2,furfuryl}$), 53.7 (N$CH_{2,benzyl}$), 21.5 (CH_3–C=CH_2). **4b**: δ = 280.6 (Mo=C), 238.1 (CO), 150.9 (2-C_{furyl}), 150.0 (CH_3–C=CH_2), 142.4 (5-C_{furyl}), 135.7 (1-C_{phenyl}), 128.9 (3, 5-C_{phenyl}), 127.7 (2, 6-C_{phenyl}), 127.0 (4-C_{phenyl}), 112.4 (CH_3–C=CH_2), 110.4 (3-C_{furyl}), 109.1 (4-C_{furyl}), 96.7 (C_5H_5), 56.2 (N$CH_{2,furfuryl}$), 53.7 (N$CH_{2,benzyl}$), 21.8 (CH_3–C=CH_2). **4c**: δ = 282.2 (Mo=C), 239.0 (CO), 151.4 (2-C_{furyl}), 148.9 (CH_3–C=CH_2), 142.8 (5-C_{furyl}), 136.0 (1-C_{phenyl}), 128.7 (3, 5-C_{phenyl}), 127.7 (2, 6-C_{phenyl}), 127.0 (4-C_{phenyl}), 110.5 (3-C_{furyl}), 109.4 (4-C_{furyl}), 105.4 (CH_3–C=CH_2), 96.1 (C_5H_5), 60.7 (N$CH_{2,furfuryl}$), 48.0 (N$CH_{2,benzyl}$), 24.2 (CH_3–C=CH_2). **4d**: δ = 281.3 (Mo=C), 238.1 (CO), 151.3 (2-C_{furyl}), 149.0 (CH_3–C=CH_2), 142.8 (5-C_{furyl}), 135.8 (1-C_{phenyl}), 128.7 (3, 5-C_{phenyl}), 127.5 (2, 6-C_{phenyl}), 127.0 (4-C_{phenyl}), 111.9 (CH_3–C=CH_2), 110.6 (3-C_{furyl}), 109.5 (4-C_{furyl}), 95.8 (C_5H_5), 60.8 (N$CH_{2,furfuryl}$), 48.1 (N$CH_{2,benzyl}$), 24.4 (CH_3–C=CH_2). MS (EI): m/z (%): 432 (7) [$M^+ - CO$], 255 (50), 164 (31), 149 (29), 91 (100), 81 (38). HR-MS: Found: 426.0746. $C_{21}H_{22}MoN_2O_2$ [$M^+ - CO$]. Calc.: 426.0749.

4.5. Pentacarbonyl [E/Z-2-(S)-phenylethylamino(2-propenyl)carbene]tungsten

2-(*S*)-Phenylethylamine (0.46 ml, 4.00 mmol) was added slowly at −30°C to a solution of 0.82 g (2.00 mmol) pentacarbonyl[methoxy-(2-propenyl)carbene]-tungsten in 15 ml dichloromethane. After 30 min the solution was allowed to reach ambient temperature and was stirred for another hour. The solvent was removed and the residue was purified by chromatography on silica gel using petroleum ether:dichloromethane 3:1 as eluent. The first yellow band gave yellow needles of the *E*-isomer, while the second band afforded the *Z*-isomer as a bright-yellow oil. Aminolysis at −78°C afforded exclusively the *E*-isomer.

E-isomer: Yield 0,66 g (66%). ^{1}H-NMR (300 MHz, CD_3COCD_3): δ = 10.89 (s, 1H, NH), 7.42 (m, 5H, H_{aryl}), 5.26 (dq, 1H, J = 2.27 Hz, 6.85 Hz, CH), 4.76 (s, 1H, =CHH), 4.45 (s, 1H, =CHH), 1.95 (s, 3H, =C(CH_3), 1.76 (d, 3H, J = 6.90 Hz, CH_3); ^{1}H-NMR (300 MHz, C_6D_6): δ = 8.68 (s, 1H, NH), 7.00 (m, 5H, H_{aryl}), 4.48 (dq, 1H, J = 2.34 Hz, 6.77 Hz, CH), 4.28 (s, 1H, =CHH), 4.18 (s, 1H, =CHH), 1.51 (s, 3H, =C(CH_3), 0.86 (d, 3H, J = 6.86 Hz, CH_3). ^{13}C-NMR (75 MHz, CD_3COCD_3): δ = 255.1 (W=C), 204.2 (CO_{trans}), 199.6 (CO_{cis}), 154.0 (H_3C–C=CH_2), 142.0, 129.7, 128.6, 127.0 (C_{aryl}), 104.6 (H_3C–C=CH_2), 60.2 (CH), 21.9 (H_3C–C=CH_2), 20.1 (H_3C–CH).

Z-isomer: Yield 0.18 g (18%). ^{1}H-NMR (300 MHz, CD_3COCD_3): δ = 10.55 (s, 1H, NH), 7.55 (m, 5H, H_{aryl}), 5.57 (q, 1H, J = 6.77 Hz, CH), 4.66 (s, 1H, =CHH), 4.57 (s, 1H, =CHH), 2.04 (s, 3H, =C(CH_3)), 1.84 (d, 3H, J = 6.75 Hz, CH_3); ^{1}H-NMR (300 MHz, C_6D_6): δ = 8.11 (s, 1H, NH), 7.04 (m, 5H, H_{aryl}), 5.36 (q, 1H, J = 6.78 Hz, CH), 4.19 (s, 1H, =CHH), 4.16 (s, 1H, =CHH), 1.72 (d, 3H, J = 6.90 H, CH_3), 1.20 (d, 3H, J = 6.87 Hz, CH_3). ^{13}C-NMR (75 MHz, CD_3COCD_3): δ = 253.8 (W=C), 203.8 (CO_{trans}), 199.1 (CO_{cis}), 159.4 (H_3C–C=CH_2), 141.1, 129.7, 128.8, 127.3 (C_{aryl}), 105.8 (H_3C–C=CH_2), 65.5 (CH), 21.4 (H_3C–C=CH_2), 16.3 (H_3C–CH).

Anal. Found: C, 41.00; H, 3.02; N, 2.61; $C_{17}H_{15}NO_5W$ (497.2). Calc.: C, 41.07; H, 3.04; N, 2.82%.

4.6. Pentacarbonyl [E/Z-N-furfuryl-2-(S)-phenylethylamino-(2-propenyl)carbene]tungsten **15**

NaH (0.10 g, 4.00 mmol) was added to a solution of 2.6 ml (3.00 mmol) furfuryl alcohol in 10 ml THF at 0°C. After 30 min the solution was cooled to –45°C, combined with a solution of 0.46 g (2.4 mmol) tosyl chloride in 5 ml THF and kept below −35°C for 8 h. A solution of 1.00 g (2.00 mmol) pentacarbonyl [*E*/*Z*-2-(*S*)-phenylethylamino(2-propenyl)carbene]tungsten,

deprotonated with 0.05 g (2.20 mmol) NaH, in 10 ml THF was added, and the solution was allowed to reach room temperature over 4 h. Removal of the solvent and chromatographic work-up on silicia gel using petroleum ether:dichloromethane 3:1 afforded a mixture (40:60) of *E*/*Z*-**15** as a yellow oil.

Yield: 0.61 g (53%). ^{1}H-NMR (300 MHz, CD_3COCD_3): $\delta = 7.43$ (m, 12H, H_{aryl}, 5-H_{furyl}), 6.38 (m, 2H, 4-H_{furyl}), 6.21 (dd, 1H, $J = 0.95$ Hz, 2.16 Hz, 3-H_{furyl}), 6.09 (d, 1H, $J = 3.29$ Hz, 3-H_{furyl}), 6.09 (q, 1H, $J = 7.11$ Hz, CH), 5.83 (q, 1H, $J = 6.89$ Hz, CH), 5.44, 5.01 (d, 2H, $J = 16.2$ Hz, CH_2), 5.43, 4.93 (d, 2H, $J = 15.9$ Hz, CH_2), 4.84 (s, 1H, =C*H*H), 4.78 (s, 1H, =C*H*H), 4.72 (s, 1H, =CH*H*), 4.65 (s, 1H, =CH*H*), 2.23 (s, 3H, =C(CH_3), 2.14 (s, 3H, =C(CH_3), 1.69 (d, 3H, $J = 7.09$ Hz, CH_3), 1.58 (d, 3H, $J = 6.98$ Hz, CH_3). ^{13}C-NMR (75 MHz, CD_3COCD_3): $\delta = 199.8$, 199.6 (CO_{cis}), 157.5 (2-C_{furyl}), 149.0 (H_3C–*C*=CH_2) 143.3, 143.7 (5-C_{furyl}), 139.0, 127.9–130.9 (C_{aryl}), 111.7 (5-C_{furyl}) 109.5, 109.4 (4-C_{furyl}), 105.4, 104.5 (H_3C–C=*C*H_2), 69.3 (CH), 56.3, 54.8 (CH_2), 21.4 (H_3C–C=CH_2), 19.0, 18.4 (H_3C–CH). MS (EI): *m*/*z*: 577. $C_{22}H_{19}NO_6W$. Calc.: 577.25.

4.7. Carbonyl(cyclopentadienyl)[(2,7a-dimethyl-1,2,3,6,-7,7a-hexahydro-3a,6-epoxy-3aH-isoindol)-1-ylidene]-(nitrosyl)molybdenum **6**

Compound **3** (0.23 g, 0.7 mmol) was dissolved in 10 ml of di-*n*-butylether and stirred for 3 h at 90°C. After removal of the solvent the residue was purified by chromatography on silica gel at −10°C (eluent petroleum ether:diethyl ether 1:1). After elution of unreacted **3** the eluent was changed to petroleum ether:diethyl ether (1:4) and 0.05 g (22%) of **6** were obtained as a red oil (ratio of diastereomers **6a**:**6b** = 4.3:1, d.e. = 62%). $R_f = 0.15$ (petroleum ether:diethyl ether 1:1). IR (petroleum ether): $\nu = 1925$ s (CO), 1620 s (NO) cm^{-1}. IR (di-*n*-butyl ether): $\nu = 1923$ s (CO), 1611 s (NO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): **6a**: $\delta = 6.49$ (dd, 1H, $J = 1.58$, 5.50 Hz, 5-H), 6.40 (d, 1H, $J = 5.48$ Hz, 4-H), 5.45 (s, 5H, C_5H_5), 4.92 (dd, 1H, $J = 1.56$, 4.69 Hz, 6-H), 4.10 (d, 1H, $J = 13.30$ Hz, NC*H*H), 3.89 (d, 1H, $J = 13.30$ Hz, NCH*H*), 3.17 (s, 3H, NCH_3), 2.78 (dd, 1H, $J = 4.70$, 12.52 Hz, 7-$H_{anti\text{-}6\text{-}H}$), 1.72 (d, 1H, $J = 12.52$ Hz, 7-$H_{syn\text{-}H\text{-}6}$), 1.14 (s, 3H, CH_3). **6b**: $\delta = 6.47$ (dd, 1H, $J = 1.58$, 5.48 Hz, 5-H), 6.36 (d, 1H, $J = 5.48$ Hz, 4-H), 5.46 (s, 5H, C_5H_5), 4.94 (dd, 1H, $J = 1.62$ 5.48 Hz, 6-H), 4.11 (d, 1H, $J = 12.52$ Hz, NC*H*H), 3.79 (d, 1H, $J = 12.52$ Hz, NCH*H*), 3.16 (s, 3H, NCH_3), 2.82 (dd, 1H, $J = 5.48$, 12.52 Hz, 7-$H_{anti\text{-}6\text{-}H}$), 1.66 (d, 1H, $J = 11.73$ Hz, 7-$H_{syn\text{-}H\text{-}6}$), 1.06 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): **6a**: $\delta = 279.7$ (Mo=C), 241.1 (CO), 138.2 (4-C), 132.0 (5-C), 93.9 (3a-C), 93.8 (C_5H_5), 79.4 (6-C), 73.2 (7a-C), 60.0 (3-C), 42.3 (NCH_3), 40.1 (7-C), 23.0 (CH_3). **6b**: $\delta = 278.8$ (Mo=C), 241.1 (CO), 138.1 (4-C), 131.8 (5-C), 94.0 (3a-C), 93.9 (C_5H_5), 79.1 (6-C), 74.2 (7a-C), 60.5 (3-C), 42.9 (NCH_3), 39.3 (7-C), 25.5 (CH_3).-MS (EI): *m*/*z* (%): 384 (13) [M^+], 356 (28) [$M^+ - CO$], 275 (4), 234 (8), 179 (100), 81 (60), 57 (37). HR-MS: Found: 378.0388. $C_{16}H_{18}MoN_2O_3$. Calcd.: 378.0386.

4.8. Carbonylcyclopentadienyl[(2-benzyl-7a-methyl-1,2,-3,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol)-1-ylidene]nitrosylmolybdenum **7**

As described for **6** the reaction of 0.46 g (1.0 mmol) of **4** gave 0.23 g (50%) of **7** as a red solid (ratio of diastereomers **7a**:**7b** = 6:1, d.e. = 71%). $R_f = 0.15$ (petroleum ether:diethyl ether 1:1). IR (petroleum ether): $\nu = 1923$ s (CO), 1620 s (NO) cm^{-1} IR (di-*n*-butyl ether): $\nu = 1919$ s (CO), 1612 s (NO) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): **7a**: $\delta = 7.40$–7.21 (m, 5 H, C_6H_5), 6.48 (dd, 1H, $J = 1.69$, 5.76 Hz, 5-H), 6.33 (d, 1H, $J = 5.76$ Hz, 4-H), 5.41 (s, 5H, C_5H_5), 4.97 (dd, 1H, $J = 1.76$, 4.89 Hz, 6-H), 4.85 (d, 1H, $J = 14.67$ Hz, NCH*H*C_6H_5), 4.46 (d, 1H, $J = 14.67$ Hz, NC*H*HC_6H_5), 3.89 (d, 1H, $J = 13.2$ Hz, NC*H*H), 3.67 (d, 1H, $J = 13.2$ Hz, NCH*H*), 2.90 (dd, 1H, $J = 5.08$, 12.13 Hz, 7-$H_{anti\text{-}6\text{-}H}$), 1.79 (d, 1H, $J = 12.13$ Hz, 7-$H_{syn\text{-}6\text{-}H}$), 1.20 (s, 3 H, CH_3). **7b**: $\delta = 7.40$–7.21 (m, 5H, C_6H_5), 6.47 (dd, 1H, $J = 1.78$, 5.86 Hz, 5-H), 6.32 (d, 1H, $J = 5.87$ Hz, 4-H), 5.43 (s, 5H, C_5H_5), 4.82 (dd, 1H, $J = 1.76$ 4.89 Hz, 6-H), 4.77 (d, 1H, $J = 14.87$ Hz, NC*H*HC_6H_5), 4.45 (d, 1H, $J = 14.87$ Hz, NCH*H*C_6H_5), 3.82 (d, 1H, $J = 11.54$ Hz, NC*H*H), 3.72 (d, 1H, $J = 11.54$ Hz, NCH*H*), 2.94 (dd, 1H, $J = 4.89$, 12.13 Hz, 7-$H_{anti\text{-}6\text{-}H}$), 1.70 (d, 1H, $J = 12.13$ Hz, 7-$H_{syn\text{-}6\text{-}H}$), 1.18 (s, 3H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): **7a**: $\delta = 281.6$ (Mo=C), 240.8 (CO), 138.3 (4-C), 134.4 (1-C_{phenyl}), 132.0 (5-C), 129.2 (3, 5-C_{phenyl}), 128.2 (4-C_{phenyl}), 127.4 (2, 6-C_{phenyl}), 93.7 (C_5H_5), 93.6 (3a-C), 79.5 (6-C), 72.9 (7a-C), 58.9 (3-C), 56.7 (N*C*$H_2C_6H_5$), 40.3 (7-C), 22.9 (CH_3). **7b**: $\delta = 280.8$ (Mo=C), 239.9 (CO), 138.1 (4-C), 134.4 (1-C_{phenyl}), 131.8 (5-C), 129.1 (3, 5-C_{phenyl}), 128.1 (4-C_{phenyl}), 127.2 (2, 6-C_{phenyl}), 93.9 (C_5H_5), 93.1 (3a-C), 79.1 (6-C), 74.0 (7a-C), 58.8 (3-C), 56.4 (N*C*$H_2C_6H_5$), 39.5 (7-C), 20.7 (CH_3). MS (EI): *m*/*z* (%): 460 (14) [M^+], 432 (64) [$M^+ - CO$], 402 (6) [$M^+ - CO - NO$], 91 (100), 81 (32). HR-MS: Found: 454.0700. $C_{22}H_{22}MoN_2O_3$. Calcd.: 454.0699.

4.9. Pentacarbonyl[3a-(S*),6-(R*),7a-(R*)-2-(S)-phenylethyl-7a-methyl-1,2,3,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol)-1-ylidene]tungsten **26**

A solution of 1.36 g (2.35 mmol) **15** in 20 ml toluene was warmed to 90°C for 3 h. Removal of the solvent and chromatographic work-up gave a nearly quantitative yield of two diastereomeric yellow crystalline or

oily products **26**, respectively. When the reaction was carried out in diethyl ether at room temperature for 6 h a 73% overall yield of **26** was obtained.

Anal. Found: C, 47.20; H, 3.80; N, 2.31; $C_{22}H_{19}NO_6W$ (578.1). Calcd.: C, 45.78; H, 3.32; N, 2.43%. MS (EI): m/z: 577.

Major diastereomer: Yield 0.57 g (42%). IR (petroleum ether): $\nu = 2065$, 1965, 1930, 1915 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, CD_3COCD_3): $\delta = 7.46$ (m, 5H, H_{aryl}), 6.62 (dd, 1H, $J = 1.77$ Hz, 5.82 Hz, 5-H), 6.54 (d, 1H, $J = 5.72$ Hz, 4-H), 6.23 (q, 1H, $J = 6.92$ Hz, CH), 5.08 (dd, 1H, $J = 1.64$ Hz, 4.89 Hz, 6-H), 4.47, 3.74 (d, 2H, $J = 14.15$ Hz, 3-CH_2), 2.88 (dd, 1H, $J = 4.87$ Hz, 11.17 Hz, 7-H_{trans}), 1.96 (d, 3H, $J = 7.01$ Hz, CH_3), 1.64 (d, 1H, $J = 11.79$ Hz, 7-H_{cis}), 1.20 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, CD_3COCD_3): $\delta = 260.5$ (W=C), 203.3 (CO_{trans}), 199.8 (CO_{cis}), 139.6 (4-C), 132.8 (5-C), 138.6, 129.7, 128.9, 127.3 (C_{aryl}), 93.6 (3a-C), 80.0 (6-C), 75.6 (7a-C), 65.7 (CH), 54.2 (3-C), 40.8 (7-C), 23.0 (CH_3), 17.7. (H_3C–CH).

Minor diastereomer: Yield 0.42 g (31%). IR (petroleum ether): $\nu = 2065$, 1965, 1930, 1915 (CO) cm^{-1}. ^{1}H-NMR (200 MHz, CD_3COCD_3): $\delta = 7.41$ (m, 5H, H_{aryl}), 6.53 (dd, 1H, $J = 1.78$ Hz, 5.81 Hz, 5-H), 6.43 (d, 1H, $J = 5.78$ Hz, 4-H), 6.10 (q, 1H, $J = 6.09$ Hz, CH), 4.79 (dd, 1H, $J = 1.72$ Hz, 4.95 Hz, 6-H), 3.94, 3.58 (d, 2H, $J = 14.31$ Hz, 3-CH_2), 2.83 (dd, 1H, $J = 4.98$ Hz, 11.79 Hz, 7-H_{trans}), 1.81 (d, 3H, $J = 7.06$ Hz, CH_3), 1.55 (d, 1H, $J = 11.77$ Hz, 7-H_{cis}), 1.06 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, CD_3COCD_3): $\delta = 258.0$ (W=C), 203.3 (CO_{trans}), 199.8 (CO_{cis}), 139.5 (4-C), 132.8 (5-C), 137.8, 130.1, 129.6, 128.3 (C_{aryl}), 93.3 (3a-C), 79.8 (6-C), 75.4 (7a-C), 66.1 (CH), 54.5 (3-H), 40.9 (7-C), 22.7 (CH_3), 16.3 (H_3C-CH).

4.10. 3a-(S),6-(R*),7a-(R*)-2-(S)-Phenylethyl-7a-methyl-1,2,3,6,7,7a-hexahydro-3a,6-epoxy-3aH-isoindol-1-one* ***22***

A solution of 1.00 g (3.71 mmol) *N*-furfuryl-*N*-2-(*S*)-phenylethylmethacrylic amide in 50 ml toluene was warmed to 90°C for 3 h. After removal of the solvent and chromatographic work-up on silica gel using ether as eluent the product was obtained as a colourless liquid.

Yield 0.97 g (97%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.21$ (m, 10H, H_{aryl}), 6.38 (m, 2H, 5-H), 6.28 (d, 1H, $J = 5.83$ Hz, 4-H), 6.01 (d, 1H, $J = 5.81$ Hz, 4-H), 5.46 (q, 2H, $J = 7.06$ Hz, CH), 4.89 (m, 2H, 6-H), 3.68, 3.30 (d, 2H, $J = 11.60$ Hz, 3-CH_2), 3.46, 3.25 (d, 2H, $J = 11.79$ Hz, 3-CH_2), 2.43 (dd, 1H, $J = 11.74$ Hz, 7-H_{trans}), 2.42 (dd, 1H, $J = 4.83$ Hz, 11.74 Hz, 7-H_{trans}), 1.50 (d, 3H, $J = 7.14$ Hz, CH_3), 1.46 (d, 3H, $J = 7.12$ Hz, CH_3), 1.06 (d, 1H, $J = 11.80$ Hz, 7-H_{cis}), 1.04 (d, 3H, $J = 11.91$ Hz, 7-H_{cis}), 1.01 (s, 3H, CH_3), 0.93 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 178.0$ (1-C), 137.5 (4-C), 131.6 (5-C), 139.9, 126.8–128.6 (C_{aryl}), 91.0 (3a-C), 78.8 (6-C), 52.5, 52.4 (7a-C), 48.7, 48.5 (3-C), 43.3 (CH), 35.9 (7-C), 20.5, 20.2 (CH_3), 15.5, 15.2 (H_3C–CH).

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References

[1] B. Weyershausen, K.H. Dötz, Eur. J. Org. Chem. (1998) 1739.
[2] (a) K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim 1983. (b) U. Schubert (Ed.), Advances in Metal Carbene Chemistry, Kluwer Academic Publishers, Dordrecht 1989.
[3] (a) K.H. Dötz, Angew. Chem. 96 (1984) 573; Angew. Chem. Int. Ed. Engl. 23 (1984) 587. (b) W.D. Wulff, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, Vol. 5, Pergamon Press, New York 1991, p. 1065. (c) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. 12, Pergamon Press, Oxford 1995, p. 469. (d) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Vol. 12, Pergamon Press, Oxford 1995, p. 549.
[4] (a) R.P. Hsung, C.A. Challener, W.D. Wulff, Synthesis (1996) 773. (b) K.H. Dötz, C. Stinner, Tetrahedron Asymmetry 8 (1997) 1751.
[5] (a) F. Camps, J.M. Moreto, S. Ricart, J.M. Vinas, Angew. Chem. 103 (1991) 1540; Angew. Chem. Int. Ed. Engl. 30 (1991) 1470. (b) K.H. Dötz, J. Christoffers, J. Organomet. Chem. 426 (1992) C58. (c) R. Sabaté, U. Schick, J.M. Moreto, S. Ricart, Organometallics 15 (1996) 3611.
[6] (a) W.D. Wulff, D.C. Yang, J. Am. Chem. Soc. 105 (1983) 6726. (b) K.H. Dötz, W. Kuhn, J. Organomet. Chem. 286 (1985) C23. c) W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray, D.C. Yang, J. Am. Chem. Soc. 112 (1990) 3642. (d) W.D. Wulff, T.S. Powers, J. Org. Chem. 58 (1993) 2381.
[7] K.H. Dötz, R. Noack, K. Harms, G. Müller, Tetrahedron 46 (1990) 1235.
[8] (a) R. Hoffmann, Angew. Chem. 94 (1982) 725; Angew. Chem. Int. Ed. Engl. 21 (1982) 711. (b) F.G.A. Stone, Angew. Chem. 96 (1984) 85; Angew. Chem. Int. Ed. Engl. 23 (1984) 89.
[9] K.H. Dötz, D. Böttcher, M. Jendro, Inorg. Chim. Acta 222 (1994) 291.
[10] (a) M. Brookhart, R.C. Buck, J. Am. Chem. Soc. 111 (1989) 559. (b) N. Lugan, C. Kelly, M.R. Ferry, G.L. Geoffroy, A.L. Rheingold, J. Am. Chem. Soc. 112 (1990) 3220. (c) H. Fischer, J. Schleu, Chem. Ber. 129 (1996) 385.
[11] E.O. Fischer, H.-J. Beck, Chem. Ber. 104 (1971) 3101.
[12] T.T. Chin, J.K. Hoyano, P. Legdzins, J.T. Malito, Inorg. Synth. 28 (1990) 196.
[13] K.A. Parker, M.R. Adamchuk, Tetrahedron Lett. (1978) 1689.
[14] E.O. Fischer, M. Leupold, Chem. Ber. 105 (1972) 599.
[15] T. Brent Gunnoe, P.S. White, J.L. Templeton, Organometallics 16 (1997) 370.
[16] M. Jendro, Dissertation, Universität Marburg, 1991.