Probing the Dynamic Features of Bis(aminocyclopentadienyl) and Bis(aminoindenyl) Zirconium Complexes

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Treatment of 3-phenylcyclopent-2-enone (**1**) with either morpholine or pyrrolidine in the presence of 3 Å molecular sieves yielded the corresponding cyclopentadienamines **2a** and **2b**. Subsequent deprotonation with *n*-butyllithium followed by the reaction with zirconium tetrachloride led to the formation of the amino-substituted bent metallocenes **4a** and **4b**. Crystallization furnished the isomerically pure complex *meso*-bis(phenyl-3-pyrrolidinylcyclopentadienyl)zirconium dichloride (*meso*-**4b**), which was characterized by X-ray diffraction. Complex *meso*-**4b** exhibits a C(Cp)−N bond length of 1.349(3) Å. A rotational barrier of $\Delta G^{\ddagger}_{(\mathrm{CN-rot})}(248\ \mathrm{K}) = 12.1 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$ was measured for *meso*-**4b** in solution by dynamic 600 MHz ^{1}H NMR spectroscopy. Similar treatment of 2-indanone with morpholine, followed by deprotonation and reaction with $ZrCl_4$, gave bis(2-morpholinoindenyl)$ZrCl_2$ (**7a**), which was also characterized by an X-ray crystal structure analysis (the indenyl-C2/12−N bond lengths are 1.349(5)/1.381(5) Å). Two rotational processes were subsequently frozen out on the 600 MHz ^{1}H NMR time scale upon decreasing the temperature from ambient to give a C−N rotational barrier of $\Delta G^{\ddagger}_{(\mathrm{CN-rot})}(268\ \mathrm{K}) = 12.9 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$ and an activation energy of the rotation about the zirconium−Cp(indenyl) vector of $\Delta G^{\ddagger}_{(\mathrm{Ind-rot})}(178\ \mathrm{K}) = 7.6 \pm 0.5\ \mathrm{kcal\ mol^{-1}}$. In solution and in the solid state only a single C_2-symmetric metallocene rotamer of **7a** was detected. The same is found for bis(2-pyrrolidinoindenyl)$ZrCl_2$ (**7b**). By dynamic ^{1}H NMR spectroscopy the two rotational activation barriers of complex **7b** were determined as $\Delta G^{\ddagger}_{(\mathrm{CN-rot})}(338\ \mathrm{K}) = 16.4 \pm 0.2\ \mathrm{kcal\ mol^{-1}}$ and $\Delta G^{\ddagger}_{(\mathrm{Ind-rot})}(198\ \mathrm{K}) = 9.1 \pm 0.5\ \mathrm{kcal\ mol^{-1}}$.

Introduction

The catalytic features of nonbridged group 4 metallocenes that bear substituents at their cyclopentadienyl or indenyl ligands are often strongly influenced by their specific conformational properties. The equilibrium mixture of metallocene conformers, and to some extent also the rate of their mutual interconversion, can play a decisive role for the outcome of 1-alkene carbon−carbon coupling processes at, for example, the homogeneous Ziegler catalysts derived from such metallocene systems. Early examples include our observation of the conformational dependence of the stereospecific propene polymerization for a series of bis(1-terpenylindenyl)zirconium frameworks[1] and related systems.[2] Waymouth's proposed "conformational switch" that controls the formation of elastomeric polypropylene at bis(2-phenylindenyl)zirconium Ziegler catalysts probably represents an important application.[3]

Unfortunately, bent metallocene conformational equilibration processes are very fast in many such systems that bear alkyl or aryl substituents at their frameworks. They are frequently too fast to allow for the structural characterization of the respective rotamers by temperature-dependent dynamic NMR spectroscopy,[4] and hence, their rotational activation barriers could often not be determined experimentally as yet. We were curious to learn whether this situation was changed when het-

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[†] NMR spectroscopy.

[‡] X-ray crystal structure analyses.

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eroatom-containing substituents (or even organic functional groups) were attached at the Cp rings of the bent metallocenes.

The structural properties and the catalytic potential of amino-substituted bis(cyclopentadienyl) and bis(indenyl) group 4 metal complexes have found some interest recently. After the pioneering work by Boche et al.[5] a more convenient synthetic route to such systems was described by Plenio,[6] based on a *tert*-enamine synthesis starting from a substituted cyclopentenone or 2-indanone derivative, respectively. Several other groups, including those of H. H. Brintzinger,[7] J. H. Näsman, and others,[8] have used this synthetic pathway to generate active amino-substituted Ziegler catalysts. These readily available $R_2N{-}Cp$ and R_2N−indenyl ligands were also attached to other metals.[9]

We have prepared two new amino-substituted zirconocenes by a variant of the Plenio route, determined their structures in the solid state by X-ray crystal structure analysis, and characterized their dynamic features in solution by NMR spectroscopy, which included a successful conformational analysis in one case. For the purpose of comparison, an additional system, which was previously prepared by Plenio and characterized by X-ray diffraction,[6b] was included in this study.

Results and Discussion

3-Phenylcyclopent-2-enone (**1**) was converted to the enamine **2a** by treatment with morpholine in toluene solution in the presence of activated 3 Å molecular sieves. The product, 3-*N*-morpholino-1-phenylcyclopentadiene (**2a**), was isolated in 67% yield as a single isomer after recrystallization from ether. 1-Phenyl-3-*N*-pyrrolidinocyclopentadiene (**2b**) was prepared analogously by a condensation reaction of **1** with pyrrolidine. Deprotonation of these starting materials was readily achieved by treatment with *n*-butyllithium in toluene. The corresponding lithium 1-*N*-morpholino- and 1-*N*-pyrrolidino-3-phenylcyclopentadienides **3a** and **3b**, respectively, precipitated from the solution and were obtained as colorless air- and moisture-sensitive solids in close to quantitative yields. The lithium compounds were characterized spectroscopically (for details see the Experimental Section) and then directly used for the transmetalation reaction with zirconium tetrachloride. The reaction of **3a** (generated in situ) with $ZrCl_4$ gave a ca. 1:1 mixture of *rac*- and *meso*-**4a**, which was isolated in a ca. 50% yield as a red solid. Several attempts to separate the **4a** diastereoisomers were unsuccessful. The two components were therefore spectroscopically characterized from the mixture.

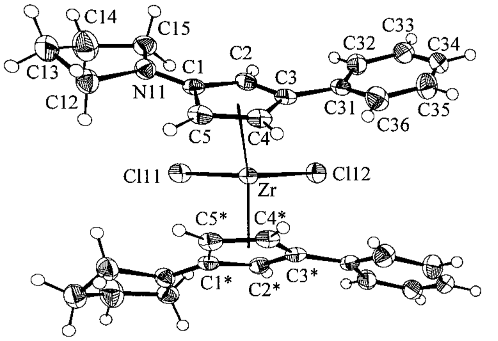

Figure 1. Molecular structure of *meso*-**4b** (with unsystematical atom-numbering scheme). Selected bond lengths (Å) and angles (deg): Zr−Cl11 2.442(1), Zr−Cl12 2.441(1), $Zr{-}C_{Cp}$ 2.537, C1−C2 1.413(3), C1−C5 1.422(3), C2−C3 1.425(3), C3−C4 1.407(3), C4−C5 1.429(3), C1−N11 1.349(3), N11−C12 1.451(3), N11−C15 1.456(3), C12−C13 1.509(4), C13−C14 1.490(4), C14−C15 1.514(4), C3−C31 1.475(4); Cl11−Zr−Cl12 99.03(4), C1−N11−C12 123.4(2), C1−N11−C15 122.8(2), N11−C12−C13 103.3(2), N11−C15−C14 103.2(2), C12−C13−C14 104.4(2), C13−C14−C15 105.9(3), C2−C3−C31 125.8(3), C4−C3−C31 126.9(2), C3−C31−C32 121.1(2), C3−C31−C36 121.2(2).

The reagent **3b** was treated with $ZrCl_4$ in toluene for 3 days at reflux temperature. Crystallization from the concentrated hot solution furnished a red microcrystalline solid (33% isolated) that turned out to be a ca. 5:95 mixture of the respective *rac*- and *meso*-**4b** isomers. Single crystals of complex *meso*-**4b** suited for the X-ray crystal structure analysis were obtained by recrystallization from dichloromethane.

In the crystal, complex *meso*-**4b** is C_s-symmetric, with the mirror plane passing through the two chlorine atoms and zirconium. The two bulky substituents are oriented toward the front side of the eclipsed bent metallocene, where they occupy the sectors above and below the chlorine atoms. The Cl(11)−Zr−Cl(12) and Cp(centroid)−Zr−Cp(centroid) angles are 99.03(4)° and 132.7°, respectively. The frameworks of the phenyl substituent, the central η^5-C_5H_3 ring, and the pyrrolidine ring system at C(1) are arranged almost coplanar at each ligand. The NC_4H_8 ring attains a twist conformation. The carbon−carbon bond lengths inside the disubstituted Cp ring are within a narrow range between 1.407(3) and 1.429(3) Å. The Zr−C(Cp) bond lengths are in a larger range. The Zr−C(1) distance (2.658(2) Å) is notably longer than the Zr−C(2) to Zr−C(5) lengths (2.555(2), 2.531(2), 2.459(2), 2.483(2) Å). Thus, the C(1)−N vector in *meso*-**4b** is slightly bent away from the idealized plane defined by the C(2)−C(5) carbon atoms (angle between the C2−C5 and C1−N11−C12−C15 planes: 6.4°).

Complex *meso*-**4b** behaves as C_s-symmetric in solution. At "high" temperature (298 K in benzene-d_6) it shows a single ^{1}H NMR set of Ph signals (600 MHz) and three separated Cp resonances at δ 5.62 (H-2), 6.27 (H-4), and 4.83 (H-5) (corresponding ^{13}C NMR resonances at δ 89.7, 108.0, and 92.9 ppm). Complexes *rac*- and *meso*-**4a** show analogous NMR features of the central $C_5H_3R_2$ ligand systems (see Table 1). The complexes **4** show dynamic NMR features of the *sec*-amino substituent derived signals. For the pure compound *meso*-**4b** the temperature-dependent dynamic ^{1}H NMR spectra were followed in two solvents (toluene-d_8

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Table 1. $^1H/^{13}C$ NMR Data[a] of the Central $C_5H_3R_2$ Core of the Complexes 4

	rac-**4a**	*meso*-**4a**	*meso*-**4b**
$-NR_2$	morpholine	morpholine	pyrrolidine
H-2	5.61	5.52	5.62
H-4	6.12	6.10	6.27
H-5	4.88	5.04	4.83
C1	151.1	150.8	150.6
C2	92.4	93.9	89.7
C3	122.8	123.3	123.6
C4	109.5	108.5	108.0
C5	94.9	94.7	92.9

[a] In benzene-d_6 at 298 K, 600/150 MHz; **4a** data obtained from the ca. 1:1 *rac*/*meso* mixture, tentative relative assignment of the **4a** isomers.

and a $CDFCl_2/CDF_2Cl$ mixture); the corresponding ^{13}C NMR spectra were recorded only in the aromatic solvent. In all cases the $Ph-C_5H_3$-derived NMR signals were practically temperature invariant, whereas the $-NC_4H_8$ resonances exhibited a very pronounced dependent averaging and coalescence behavior.

At 273 K the ^1H NMR spectrum of *meso*-**4b** in toluene-d_8 shows two broad signals at δ 2.80 and 1.52 corresponding to the α- and β-protons of the pyrrolidino substituent. Lowering of the temperature resulted in a splitting of the low-field signal into a well-resolved set of four resonances in an equal intensity ratio at δ 3.36, 2.85, 2.80, and 2.71 (223 K in toluene-d_8). The high-field signal also undergoes splitting into several signals, but these remained overlapped. Likewise, the two $-NC_4H_8$ ^{13}C NMR signals of *meso*-**4b** that are observed at high temperature decoalesce upon decreasing the monitoring temperature to eventually give four separate resonances at δ 47.2, 46.5, 25.3, and 24.6.

No additional changes of the spectral appearance occurred for *meso*-**4b** upon lowering the temperature further (in the Freon solvent). This spectral behavior indicates that the complex *meso*-**4b** has retained C_s-symmetry throughout the investigated temperature range. The observed dynamic features were confined to the Cp−(*sec*-amino) substituent linkage and indicate freezing of the $Cp-NR_2$ rotation on the NMR time scale. At the coalescence temperature of the respective pairs of ^1H NMR signals, a Gibbs activation energy of $\Delta G^{\ddagger}_{(CN-rot)}(248\ K) = 12.1 \pm 0.2\ kcal\ mol^{-1}$ was obtained, a value in the typical enamine $\Delta G^{\ddagger}_{(CN-rot)}$ range.[10]

Treatment of 2-indanone with morpholine in toluene at 60 °C in the presence of dry 3 Å molecular sieves resulted in an almost quantitative conversion to the enamine **5a** (98% isolated). Treatment with *n*-butyllithium cleanly resulted in the formation of the corresponding morpholino-substituted indenyllithium reagent (**6a**, isolated and spectroscopically characterized in a separate experiment). The subsequent reaction (3 days, toluene reflux) with zirconium tetrachloride gave the bis(2-morpholinoindenyl)$ZrCl_2$ complex **7a** in >70% yield (see Scheme 2). Crystallization from toluene furnished single crystals of **7a** suited for the X-ray crystal structure analysis (see Figure 2).

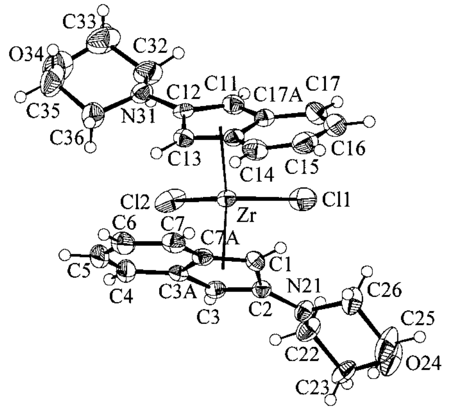
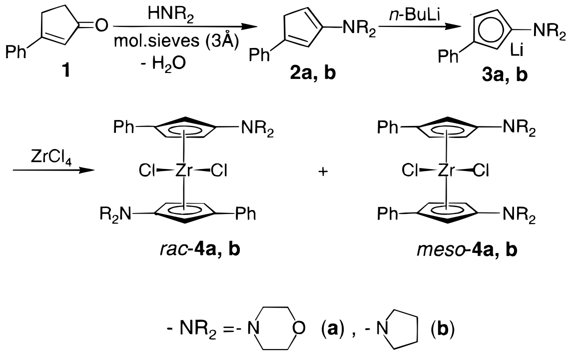
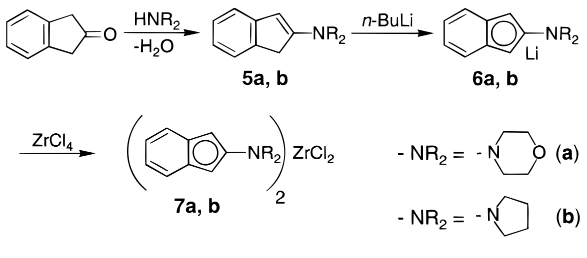


Figure 2. View of the molecular structure of complex **7a** (with unsystematical atom-numbering scheme). Selected bond lengths (Å) and angles (deg): Zr−Cl1 2.430(1), Zr−Cl2 2.462(1), Zr−C_{Cp} 2.532, C1−C2 1.445(5), C11−C12 1.419(6), C2−C3 1.408(6), C12−C13 1.416(6), C2−N21 1.349(5), C12−N31 1.381(5), C3−C3A 1.432(6), C13−C13A 1.443(6), C3A−C7A 1.424(6), C13A−C17A 1.419(6), C7A−C1 1.439(6), C17A−C11 1.431(6), N21−C22 1.467(5), N31−C32 1.468(6), N21−C26 1.453(6), N31−C36 1.463(6), C22−C23 1.503(6), C32−C33 1.518(7), C23−O24 1.409(6), C33−O34 1.412(8), O24−C25 1.421(6), O34−C35 1.417(7), C25−C26 1.510(7), C35−C36 1.495(7); Cl1−Zr−Cl2 95.84(5), C1−C2−C3 107.1(4), C11−C12−C13 108.3(4), C1−C2−N21 125.9(4), C11−C12−N31 126.0(4), C3−C2−N21 127.0(4), C13−C12−N31 125.7(4), C2−N21−C22 119.5(3), C12−N31−C32 118.2(4), C2−N21−C26 122.9(4), C12−N31−C36 120.3(4).

Scheme 1. Synthesis of the Complexes 4



Scheme 2



Complex **7a** adopts a chiral metallocene conformation in the solid state, which is close to C_2-symmetric. The two morpholino residues are arranged toward the forward upper right and lower left quadrants (relative to each other) at the front side of the bent metallocene wedge. They occupy the respective positions above and below the Zr−Cl vectors (Zr−Cl(1) 2.430(1) Å, Zr−Cl(2) 2.462(1) Å, Cl(1)−Zr−Cl(2) 95.84(5)°). Consequently the anellated phenylene rings are found oriented toward the respective opposite positions at the bent metallocene

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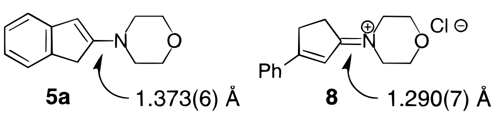
[10] Mannschreck, A.; Koelle, U. *Tetrahedron Lett.* **1967**, *10*, 863−867. Müller, K.; Previdoli, F.; Desilvestro, H. *Helv. Chim. Acta* **1981**, *64*, 2497−2507. Anderson, J. E.; Casarini, D.; Lunazzi, L. *Tetrahedron Lett.* **1988**, *29*, 3141−3144. Erker, G.; Ahlers, W.; Fröhlich, R. *J. Am. Chem. Soc.* **1995**, *117*, 5853−5854. Ahlers, W.; Erker, G.; Fröhlich, R.; Zippel, F. *Chem. Ber./Recl.* **1997**, *130*, 1079−1084.

Chart 1



sectors (see Figure 2). The Cp(centroid)−Zr−Cp(centroid) angle in **7a** is 132.5°. The bonding of the indenyl five-membered ring to zirconium is rather unsymmetric, featuring short Zr−C1/3 contacts (Zr−C(1) 2.488(4) Å, Zr−C(11) 2.519(4) Å, Zr−C(3) 2.470(4) Å, Zr−C(13) 2.453(4) Å), slightly longer Zr−C(3a/7a) distances (Zr−C(3a) 2.496(4) Å, Zr−C(13a) 2.543(4) Å, Zr−C(7a) 2.545(4) Å, Zr−C(17a) 2.551(4) Å), and a rather long metal to C(2) linkage (Zr−C(2) 2.646(4) Å, Zr−C(12) 2.612(4) Å). Carbon atom C(2), having the morpholino substituent attached to it, is placed markedly outside the C(1), C(3), C(3a), C(7a) plane. The morpholino substituent shows a chairlike conformation with an almost trigonal-planar nitrogen atom (sum of angles at N(21) 355.6°, at N(31) 352.4°). The C(2)−N(21) bond length is 1.349(5) Å (C(12)−N(31) 1.381(5) Å), which is identical to the corresponding value found in **4b** (see above) and only slightly longer than observed by Plenio and Burth in the related bis(2-pyrrolidinoindenyl)ZrCl$_2$ complex **7b**.[6b] These aminoindenyl C−N bond lengths should be compared with the corresponding values of the parent enamine (**5a**) and a related iminium salt (**8**, see Chart 1); both compounds were characterized as references by X-ray diffraction in the course of our study (for details see the Experimental Section).[11]

The enamine **5a** exhibits a trigonal-planar nitrogen atom (sum of angles at N 360.1° and a C(5)−N(4) bond length of 1.373(6) Å).[12,13] The N−C(sp^2) distance in the iminium salt **8** is 1.290(7) Å. Thus, the N−C(sp^2) bond lengths observed in the zirconium complexes **4b**, **7a** (both this study), and **7b** are close to the **5a** value, which indicates a conjugative interaction between the nitrogen lone pair and the cyclopentadienyl or indenyl π-system in these complexes, similar to or only slightly larger than present in a *tert*-enamine.

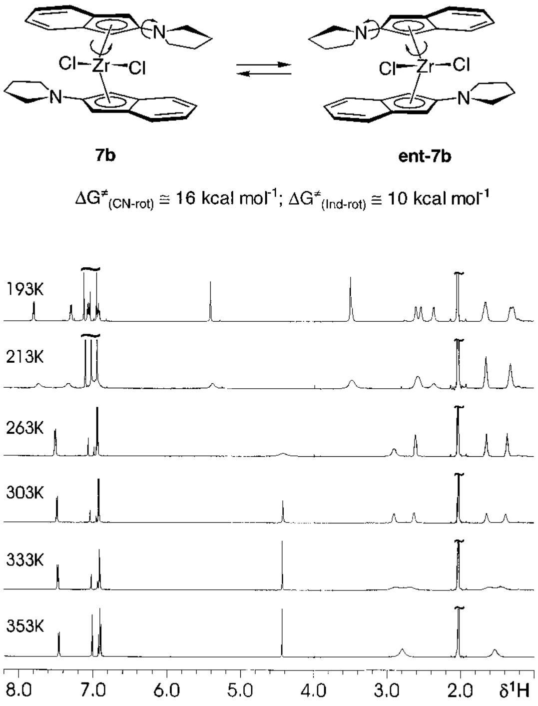


Figure 3. Dynamic ^{1}H NMR spectra of complex **7b** (in toluene-d_8, 600 MHz).

Bis(2-pyrrolidinoindenyl)zirconium dichloride **7b** shows temperature-dependent dynamic ^{1}H NMR spectra. At high temperature (353 K in toluene-d_8, 600 MHz) the complex exhibits the reported[6b] simple spectrum, featuring two aromatic methine hydrogen resonances at δ 7.45 (H-5, H-6) and 6.90 (H-4, H-7), a sharp singlet at δ 4.43 (H-1, H-3), and two broad signals of the pyrrolidino α- and β-hydrogens at δ 2.79 and 1.54 ppm (see Figure 3, bottom spectrum). Lowering the monitoring temperature reveals two different dynamic processes becoming subsequently frozen on the 600 MHz ^{1}H NMR time scale. First, the rotation about the C2(indenyl)−N(pyrrolidino) partial double bond becomes slow. This is revealed by splitting of the two broad pyrrolidino hydrogen resonances into two pairs of sharp multiplets, which are eventually observed at 303 K at δ 2.92, 2.64, 1.65, and 1.39 ppm. At the coalescence temperature of the respective pairs a Gibbs activation energy of $\Delta G^{\ddagger}_{(\mathrm{CN-rot})}(338\ \mathrm{K}) = 16.4 \pm 0.2$ kcal mol^{-1} was determined[14] for the C−N rotational barrier of **7b**. Lowering the temperature further results in a broadening and eventually a splitting of all the signals into equal intensity pairs of ^{1}H NMR resonances (see Figure 3). Except for the pyrrolidino β-H signals, which are partially overlapping, all these signal pairs are clearly separated. This low-temperature decoalescence phenomenon is due to the freezing of the (η^5-indenyl)−Zr rotation, eventually resulting in a static situation featuring a single metallocene rotamer in solution at low temperature within the limits of the ^{1}H NMR detection. Structurally this is probably equivalent to the C_2-symmetric structure of **7b**, observed previously by Plenio et al. in the solid state.[6b] From the NMR spectra we have obtained an activation energy of the (η^5-indenyl)−Zr rotational process of complex **7b** of $\Delta G^{\ddagger}_{(\mathrm{Ind-rot})} = 9.8 \pm 0.5$ kcal mol^{-1} (at $T_c = 223$ K in toluene-d_8, this value in CDFCl$_2$/CDF$_2$Cl is decreased to 9.1 ± 0.5 kcal mol^{-1} at $T_c = 198$ K).

The bis(2-morpholinoindenyl)zirconium dichloride complex **7a** shows a similar NMR behavior, but slightly different values of the respective activation energies. Splitting of the two broad room-temperature α- and β-morpholino CH$_2$ resonances takes place below the coalescence temperature of 268 K to lead to two pairs

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(11) Single crystals of compound **8** were obtained in the course of the hydrolysis of the lithium compound **3a** with aqueous HCl/dichloromethane. The single crystals used for the structural determination were recrystallized subsequently from chloroform. This compound was only characterized by X-ray diffraction. For details see the Supporting Information.

(12) For compilations of general enamine structural features see for example: Cook, A. G. In *Enamines: Synthesis, Structure and Reactions*, 2nd ed.; Marcel Dekker: New York, NY, 1988. Brown, K. L.; Damm, L.; Dunitz, J. D.; Eschenmoser, A.; Hobi, R.; Kratky, C. *Helv. Chim. Acta* **1978**, *61*, 3108−3135. Kowalski, D.; Fröhlich, R.; Erker, G. *Z. Naturforsch.* **1996**, *51B*, 1053−1059.

(13) For a comparison with conjugated primary enamine structures see for example: Erker, G.; Pfaff, R.; Krüger, C.; Nolte, M.; Goddard, R. *Chem. Ber.* **1992**, *125*, 1669−1673. Erker, G.; Pfaff, R.; Kowalski, D.; Würthwein, E.-U.; Krüger, C.; Goddard, R. *J. Org. Chem.* **1993**, *58*, 6771−6778. Erker, G.; Kowalski, D.; Noe, R.; Krüger, C.; Nolte, M. *Tetrahedron Lett.* **1994**, *35*, 6665−6668. Erker, G.; Wingbermühle, D.; Grehl, M.; Fröhlich, R. *Chem. Ber.* **1994**, *127*, 1331−1332.

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Table 2. Rotational Barriers[a] of the Complexes 4 and 7

cmpd	$\Delta G^{\ddagger}_{\text{(CN-rot)}}$	T (K)	$\Delta G^{\ddagger}_{\text{(Ind-rot)}}$	T (K)
meso-**4b**[c]	12.1 ± 0.2	248		
7a[b]	12.9 ± 0.2	268	7.6 ± 0.5	178[d]
7b[c]	16.4 ± 0.2	338	9.1 ± 0.5	198[d]

[a] In kcal mol^{-1} obtained by dynamic ^{1}H NMR spectroscopy; in toluene-d_8 if not otherwise noted. [b] $-NR_2$ = morpholino. [c] $-NR_2$ = pyrrolidino. [d] In $CDFCl_2/CDF_2Cl$.

of well-resolved $-N(CH_2{}^{\alpha})_2(CH_2{}^{\beta})_2O$ resonances at 223 K in toluene-d_8 (δ 3.75, 3.36, 3.08, and 2.80 ppm). A Gibbs activation energy of $\Delta G^{\ddagger}_{\text{(CN-rot)}}$(268 K) = 12.9 ± 0.2 kcal mol^{-1} was thus obtained. In the $CDFCl_2/CDF_2Cl$ solvent mixture the (η^5-indenyl)−Zr rotation of **7a** eventually became frozen on the 600 MHz ^{1}H NMR time scale. Again this resulted in a splitting of all remaining resonances into 1:1 intensity pairs. The activation energy of the (η^5-indenyl)−Zr rotation was determined as $\Delta G^{\ddagger}_{\text{(Ind-rot)}}$(178 K) = 7.6 ± 0.5 kcal mol^{-1} for complex **7a**. Again only a single metallocene rotamer was observed at low temperature under static conditions by ^{1}H NMR spectroscopy in solution.

Conclusions

There are several remarkable features about the conformational properties of the amino−cyclopentadienyl and amino−indenyl zirconium complexes investigated in this study. First, in each case there seems to be only a single favored conformer present in solution. We have frozen out the major conformational movements in all of these representative examples of this class of compounds and have not obtained indications for the presence of pairs of metallocene conformers (or rotamers) of principally different molecular symmetries, such as they were proposed by Waymouth et al. for the bis(2-arylindenyl)$ZrCl_2$ series and observed there in the solid state[3] but so far never in solution.[4]

The two conformational processes that were frozen out at low temperature on the ^{1}H NMR time scale are the rotation about the C−N bond followed by the metallocene rotation (i.e., the rotation about the Zr−Cp(centroid) vector) within a single degenerate pair of metallocene conformers in the bis(2-aminoindenyl)$ZrCl_2$ cases. It turned out that the C−N rotational barriers for the two compounds **4b** and **7a**, which were characterized by X-ray diffraction in this study, are very close in energy (see Table 2). The height of this barrier ($\Delta G^{\ddagger}_{\text{(CN-rot)}}$) probably directly reflects the bond strength of the enamine-like C−N bond involved and is thus a much more accurate measure for the small Cp−N(amino) π-component than the X-ray crystal structure analysis.

It is more difficult to describe accurately the characteristics of the low-energy indenyl−Zr rotational barrier of the complexes **7a** and **7b**. Typically two energy barriers must be quantitatively estimated. The second highest corresponds to the actually observed rotational barrier (see Figure 4), since the highest overall barrier is of course avoided and circumvented in the case of the conformational equilibrium process. We assume that passing of the two phenylene rings of the compounds **7** at the narrow backside of the bent metallocene wedge (as it is schematically represented by the possible transition state geometry I in Figure 4) probably generates the maximum barrier on the energy surface, whereas passing of the two R_2N- amino substituents at the backside affords the less crowded more favorable transition state geometry II, shown in Figure 4. This would be in accord with the pronounced dependence of the actually observed $\Delta G^{\ddagger}_{\text{(Ind-rot)}}$ values from the nature of the amino substituent (see Table 2) and would be supported by the structural bending of the C(Cp)−N vectors from the center of the metallocenes as observed in the X-ray crystal structure analysis.

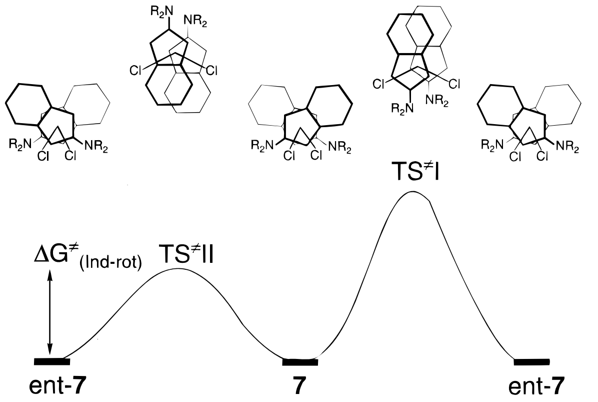

Figure 4. Schematic qualitative representation of the potential conformational energy profile of the metallocene complexes **7**.

The attachment of the amino substituents has a remarkable effect on the metallocene rotational barrier of the bis(indenyl)zirconium dichlorides with the $\Delta G^{\ddagger}_{\text{(Ind-rot)}}$ values of the 2-substituted-indenyl complexes varying from very low (i.e., not observed) to a measurable range of 7.6−9.8 kcal mol^{-1}. In contrast to a variety of bis(1-substituted-indenyl)$ZrCl_2$ compounds,[1,2] bis(2-substituted-indenyl)$ZrCl_2$ complexes had to the best of our knowledge up to this study not been conformationally characterized in solution due to these very low rotational barriers.[4,15,16] The combined steric and electronic features of the amino substituents employed in this study seem to be well suited to slow down this rotational process considerably. Therefore, amino groups and related substituents may provide an easy means to influence substantially the conformational properties of these metallocene complexes and their catalytically active derivatives. The extent that electronically active substituents can influence the chemical behavior of

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metallocene systems remains an area of further investigation in our laboratory.

Experimental Section

Reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The $CDFCl_2/CDF_2Cl$ solvent mixture was prepared as described in the literature.[17] NMR spectra were recorded on a Bruker AC 200 P NMR spectrometer (^{1}H 200 MHz, ^{13}C 50 MHz) at 300 K or a Varian Unity Plus NMR spectrometer (^{1}H 600 MHz, ^{13}C 150 MHz) at variable temperature. 3-Phenylcyclopent-2-enone (**1**) was synthesized as described in the literature.[18] Complex **7b** was prepared analogously as described by Plenio et al.[6b]

3-*N*-Morpholino-1-phenylcyclopenta-1,3-diene (2a). 3-Phenylcyclopent-2-enone (**1**) (5.0 g, 31.6 mmol) was added to a stirred suspension of activated molecular sieves (10.0 g, 3 Å) in toluene (70 mL). After the addition of morpholine (9.08 g, 104.3 mmol) the reaction mixture was stirred for 3 days at 70 °C. Then the liquid phase was decanted off, the molecular sieves were extracted with 30 mL of toluene, and the liquid was again decanted. The solvent was then removed from the combined orange-red extracts, whereupon the orange solid remained behind. The crude product was recrystallized from ether to yield 4.81 g (67%) of an orange-brown solid. Mp: 114 °C. HRMS calcd for $C_{15}H_{17}NO$: 227.1310. Found: 227.1303. ^{1}H NMR ($CDCl_3$): δ 2.58 (m, 4H, morpholine), 2.98 (s, 2H, 5-H), 3.45 (m, 4H, morpholine), 5.16 (d, 1H, 2-H), 6.85 (dt, 1H, 4-H), 7.21−7.41 (m, 5H, Ph-H). ^{13}C NMR ($CDCl_3$): δ 35.2 (C-5), 48.3, 66.3, 101.7 (C-2), 122.8, 123.3, 126.6, 131.1 (C-4), 132.0 (C-3), 136.7, 157.8 (C-1).

1-Phenyl-3-*N*-pyrrolidinocyclopenta-1,3-diene (2b). 3-Phenylcyclopent-2-enone (**1**) (3.50 g, 22.1 mmol) was reacted with pyrrolidine (4.72 g, 66.4 mmol) analogously as described above. The crude product was recrystallized from pentane. Yield: 3.94 g (84%) orange-brown solid. Mp: 95 °C. HRMS calcd for $C_{15}H_{17}N$: 211.1361. Found: 211.1366. ^{1}H NMR ($CDCl_3$): δ 1.85 (m, 4H, pyrrolidine), 3.08 (m, 4H, pyrrolidine), 3.21 (s, 2H, 5-H), 4.81 (d, 1H, 2-H), 6.74 (dt, 1H, 4-H), 7.06−7.23 (m, 5H, Ph-H). ^{13}C NMR ($CDCl_3$): δ 25.5, 39.2 (C-5), 48.6, 96.2 (C-2), 122.8, 123.7, 125.7 (C-4), 128.3, 130.3 (C-3), 137.4, 156.0 (C-1).

1-Morpholino-3-phenylcyclopentadienyllithium (3a). A solution of *n*-butyllithium (0.58 mL, 0.92 mmol, 1.6 M in hexane) was slowly added at 0 °C to a solution of **2a** (0.21 g, 0.92 mmol) in toluene (100 mL). The reaction mixture was allowed to warm to room temperature and then stirred for an additional 12 h. The resulting white suspension was filtered. The residue was washed twice with 10 mL of pentane and dried in vacuo to yield 0.17 g (98%) of a white solid. ^{1}H NMR (benzene-d_6/THF-d_8 = 8:1): δ 2.84 (m, 4H, morpholine), 3.64 (m, 4H, morpholine), 5.42 (m, 1H, Cp−H), 5.74 (m, 1H, Cp−H), 6.02 (m, 1H, Cp−H), 6.69 (m, 1H, Ph−H), 7.02−7.42 (m, 4H, Ph−H). ^{13}C NMR (benzene-d_6/THF-d_8 = 8:1): δ 53.1, 67.5, 88.0 (C−Cp), 93.0 (C−Cp), 97.9 (C−Cp), 117.1 (C-3), 120.8, 122.8, 128.1, 140.4, 142.0 (C-1).

X-ray Crystal Structure Analysis of 8. Single crystals were obtained from the hydrolysis of **3a** in dichloromethane followed by crystallization from chloroform:[11] formula $C_{15}H_{18}NO^{+}Cl^{-}\cdot CHCl_3$, $M = 383.12$, yellow crystal, 0.10 × 0.10 × 0.10 mm, $a = 11.534(2)$ Å, $b = 19.290(6)$ Å, $c = 8.156(1)$ Å, $\beta = 95.41(1)°$, $V = 1806.6(7)$ Å^3, $\rho_{calc} = 1.409$ g cm^{-3}, $F(000) = 792$ e, $\mu = 6.55$ cm^{-1}, empirical absorption correction via φ scan data ($0.974 \le C \le 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3305 reflections collected ($\pm h$, $-k$, $+l$), [(sin θ)/λ] = 0.59 Å^{-1}, 3070 independent and 1165 observed reflections [$I \ge 2\ \sigma(I)$], 199 refined parameters, $R = 0.054$, $wR2 = 0.098$, max residual electron density 0.30 (−0.34) e Å^{-3}, hydrogens calculated and refined as riding atoms.

3-Phenyl-1-pyrrolidinocyclopentadienyllithium (3b). Compound **2b** (3.12 g, 14.76 mmol) in toluene (100 mL) was treated with *n*-butyllithium (9.23 mL, 14.76 mmol, 1.6 M in hexane) at 0 °C analogously as described above to yield 3.15 g (98%) of **3b** as a white solid. ^{1}H NMR (benzene-d_6/THF-d_8 = 8:1): δ 1.52 (m, 4H, pyrrolidine), 3.09 (m, 4H, pyrrolidine), 5.57 (m, 1H, Cp−H), 5.84 (m, 1H, Cp−H), 6.26 (m, 1H, Cp−H), 6.78−7.65 (m, 5H, Ph−H). ^{13}C NMR (benzene-d_6/THF-d_8 = 8:1): δ 25.4, 51.9, 87.2 (C−Cp), 92.6 (C−Cp), 98.1 (C−Cp), 115.1 (C-3), 120.4, 123.0, 128.2, 139.5, 142.7 (C-1).

Bis(1-morpholino-3-phenylcyclopentadienyl)dichlorozirconium (*rac-/meso*-4a). A solution of **2a** (2.0 g, 8.79 mmol) in toluene (100 mL) was treated with *n*-butyllithium (5.50 mL, 8.79 mmol) at 0 °C to generate **3a** in situ. After 3 h stirring at room temperature $ZrCl_4$ (1.03 g, 4.40 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot dark red solution was then filtered. The volatiles were evaporated and the residue recrystallized from toluene to yield 1.45 g (53%) of a red-colored solid containing a ca. 1:1 mixture of *rac*- and *meso*-**4a**. Anal. Calcd for $C_{30}H_{32}N_2O_2ZrCl_2$ (614.7): C, 58.62; H, 5.25; N, 4.56. Found: C, 59.68; H, 5.74; N, 4.57. ^{1}H NMR (benzene-d_6) *rac*-**4a**: δ 2.70 (m, 2H, morpholine), 2.90 (m, 2H, morpholine), 3.21 (m, 2H, morpholine), 3.38 (m, 2H, morpholine), 4.88 (m, 1H, 5-H), 5.61 (m, 1H, 2-H), 6.12 (m, 1H, 4-H), 6.91−7.33 (m, 5H, Ph-H). *meso*-**4a**: δ 2.40 (m, 2H, morpholine), 2.77 (m, 2H, morpholine), 3.33 (m, 2H, morpholine), 3.36 (m, 2H, morpholine), 5.04 (m, 1H, 5-H), 5.52 (m, 1H, 2-H), 6.10 (m, 1H, 4-H), phenyl signals similar to *rac*-**4a**. ^{13}C NMR (benzene-d_6) *rac*-**4a**: δ 46.8 (morpholine), 66.3 (morpholine), 92.4 (C-2), 94.9 (C-5), 109.5 (C-4), 122.8 (C-3), 125.6, 126.0, 128.2, 134.7 (C−Ph), 151.1 (C-1). *meso*-**4a**: δ 47.1 (morpholine), 66.4 (morpholine), 93.9 (C-2), 94.7 (C-5), 108.5 (C-4), 123.3 (C-3), 125.3, 125.7, 127.1, 134.8 (C−Ph), 150.8 (C-1).

Bis(1-pyrrolidino-3-phenylcyclopentadienyl)dichlorozirconium (*meso*-4b). A suspension of **3b** (2.5 g, 11.5 mmol) in toluene (100 mL) was treated with $ZrCl_4$ (1.34 g, 5.75 mmol) for 3 days at reflux temperature. The hot red solution was then filtered. The volatiles were removed in vacuo and the residue recrystallized from toluene to yield 1.10 g (33%) of a red-colored microcrystalline solid containing a 5:95 mixture of *rac*- and *meso*-**4b**. Anal. Calcd for $C_{30}H_{32}N_2ZrCl_2$ (582.7): C, 61.84; H, 5.54; N, 4.81. Found: C, 62.59; H, 5.67; N, 4.51. ^{1}H NMR (benzene-d_6, 298 K) *meso*-**4b**: δ 1.78 (m, 4H, pyrrolidine), 2.95 (m, 2H, pyrrolidine), 3.07 (m, 2H, pyrrolidine), 4.83 (m, 1H, 5-H), 5.62 (m, 1H, 2-H), 6.27 (m, 1H, 4-H), 7.03−7.45 (m, 5H, Ph−H). ^{13}C NMR (benzene-d_6, 298 K) *meso*-**4b**: δ 25.9 (pyrrolidine), 48.1 (pyrrolidine), 89.7 (C-2), 92.9 (C-5), 108.0 (C-4), 123.6 (C-3), 125.5, 126.8, 128.6, 135.1 (C−Ph), 150.6 (C-1).

X-ray Crystal Structure Analysis of 4b. Single crystals were obtained by recrystallization from dichloromethane: formula $C_{30}H_{32}N_2Cl_2Zr\cdot CH_2Cl_2$, $M = 667.62$, red-yellow crystal, 0.40 × 0.15 × 0.10 mm, $a = 24.417(2)$ Å, $b = 18.554(1)$ Å, $c = 6.426(1)$ Å, $V = 2911.2(5)$ Å^3, $\rho_{calc} = 1.523$ g cm^{-3}, $F(000) = 1368$ e, $\mu = 7.69$ cm^{-1}, empirical absorption correction via φ scan data ($0.978 \le C \le 0.999$), $Z = 4$, orthorhombic, space

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group $Pnma$ (No. 62), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3038 reflections collected ($-h$, $-k$, $+l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3038 independent and 2222 observed reflections [$I \geq 2\ \sigma(I)$], 181 refined parameters, $R = 0.031$, $wR2 = 0.065$, max residual electron density 0.39 (−0.51) e Å^{-3}, hydrogens calculated and refined as riding atoms.

2-(*N*-Morpholino)indene (5a). Analogously as described for the preparation of **2a**, 2-indanone (4.0 g, 30.3 mmol) was reacted with morpholine (3.38 g, 38.4 mmol) to yield **5a**. The molecular sieves were extracted with dichloromethane (40 mL). The crude product was recrystallized from ether. Yield: 6.0 g (98%) of colorless crystals. Anal. Calcd for $C_{13}H_{15}NO$ (201.3): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.63; H, 7.58; N, 7.07. ^{1}H NMR (benzene-d_6): δ 2.58 (m, 4H, morpholine), 2.90 (s, 2H, 1-H), 3.40 (m, 4H, morpholine), 5.42 (s, 1H, 3-H), 7.02−7.30 (m, 4-H, Ar−H). ^{13}C NMR (benzene-d_6): δ 37.0 (C-3), 48.3, 66.3, 100.8 (C-1), 118.3, 121.4, 123.1, 127.1, 137.5, 147.3, 157.3 (C-2).

X-ray Crystal Structure Analysis of 5a. Single crystals were obtained from diethyl ether: formula $C_{13}H_{15}NO$, $M = 201.26$, colorless crystal, 0.15 × 0.10 × 0.10 mm, $a = 14.931(3)$ Å, $b = 11.542(2)$ Å, $c = 12.178(2)$ Å, $V = 2098.7(7)$ Å^3, $\rho_{calc} = 1.274$ g cm^{-3}, $F(000) = 864$ e, $\mu = 6.31$ cm^{-1}, empirical absorption correction via φ scan data ($0.960 \leq C \leq 0.998$), $Z = 8$, orthorhombic, space group $Fdd2$ (No. 43), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 1125 reflections collected (-h, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 838 independent and 774 observed reflections [$I \geq 2\ \sigma(I)$], 71 refined parameters, $R = 0.064$, $wR2 = 0.188$, max residual electron density 0.27 (−0.26) e Å^{-3}, Flack parameter 0.1(11), C(6) refined as 50% sp^2-C and 50% sp^3-C, hydrogens calculated and refined as riding atoms.

Bis(2-*N*-morpholinoindenyl)dichlorozirconium (7a). A solution of 2-(*N*-morpholino)indene (**5a**) (4.5 g, 22.4 mmol) in toluene (100 mL) was treated with *n*-butyllithium (13.97 mL, 22.4 mmol) at 0 °C. After 3 h stirring at room temperature $ZrCl_4$ (2.60 g, 11.2 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot yellow solution was then filtered. The volatiles were evaporated and the residue recrystallized from toluene to yield 4.66 g (74%) of a yellow colored powder. Anal. Calcd for $C_{26}H_{28}N_2O_2ZrCl_2$ (562.6): C, 55.50; H, 5.02; N, 4.98. Found: C, 55.54; H, 6.16; N, 5.30. ^{1}H NMR (dichloromethane-d_2, 298 K): δ 3.03 (m, 4H, morpholine), 3.60 (m, 4H, morpholine), 4.84 (s, 2H, 1-H/3-H), 7.18 (m, 2H, 4-H/7-H), 7.65 (m, 2H, 5-H/6-H). ^{13}C NMR (dichloromethane-d_2, 298 K): δ 46.2 (morpholine), 66.5 (morpholine), 85.2 (C-1/C-3), 123.8 (C-4/C-7), 123.9 (C-3a/C-7a), 125.5 (C-5/C-6), 157.3 (C-2).

X-ray Crystal Structure Analysis of 7a. Single crystals were obtained by recrystallization from toluene: formula $C_{26}H_{28}N_2O_2Cl_2Zr\cdot C_7H_8$, $M = 654.76$, yellow crystal, 0.20 × 0.20 × 0.10 mm, $a = 10.538(2)$ Å, $b = 16.030(2)$ Å, $c = 17.856(3)$ Å, $V = 3016.3(9)$ Å^3, $\rho_{calc} = 1.442$ g cm^{-3}, $F(000) = 1352$ e, $\mu = 5.74$ cm^{-1}, empirical absorption correction via φ scan data ($0.949 \leq C \leq 0.999$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3430 reflections collected ($+h$, $+k$, $+l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3430 independent and 2763 observed reflections [$I \geq 2\ \sigma(I)$], 362 refined parameters, $R = 0.030$, $wR2 = 0.066$, max residual electron density 0.35 (−0.46) e Å^{-3}, Flack parameter −0.12(6), hydrogens calculated and refined as riding atoms.

Bis(2-*N*-pyrrolidinoindenyl)dichlorozirconium (7b).[6b] A solution of 2-(*N*-pyrrolidino)indene (5.0 g, 27.0 mmol) in toluene (100 mL) was treated at 0 °C with *n*-butyllithium (16.9 mL, 27.0 mmol). After 3 h stirring at room temperature $ZrCl_4$ (3.15 g, 13.5 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot yellow solution was then filtered. The volatiles were evaporated and the residue recrystallized from toluene to yield 4.66 g (74%) of a yellow-colored powder. Anal. Calcd for $C_{26}H_{28}N_2ZrCl_2$ (530.6): C, 58.85; H, 5.32; N, 5.28. Found: C, 58.60; H, 5.79; N, 5.23. ^{1}H NMR (toluene, 298 K): δ 1.39 (m, 2H, pyrrolidine), 1.65 (m, 2H, pyrrolidine), 2.64 (m, 2H, pyrrolidine), 2.92 (m, 2H, pyrrolidine), 4.42 (s, 2H, 1-H/3-H), 6.95 (m, 2H, 4-H/7-H), 7.49 (m, 2H, 5-H/6-H). ^{13}C NMR (toluene, 298 K): δ 25.8 (pyrrolidine), 48.0 (pyrrolidine), 85.4 (C-1/C-3), 122.6 (C-4/C-7), 124.1 (C-3a/C-7a), 126.3 (C-5/C-6), 154.6 (C-2).

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Supporting Information Available: Additional NMR data of the complexes **4b** and **7a**. Details on the X-ray crystal structure determinations of the complexes *meso*-**4b**, **5a**, **7a**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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