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Effects of an Interannular Bridge on Spectral and Electronic Properties of Bis(cyclopentadienyl)- and Bis(indenyl)zirconium(IV) Complexes

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Interconnection of the indenyl ligands of bis(indenyl)zirconium dichloride complexes by a 1,1′-positioned Me_2Si or $(CH_2)_2$ bridge causes pronounced bathochromic shifts of the longest wavelength UV/vis absorption bands by ca. 50 nm, while much smaller shifts are caused by a Me_2Si bridge in otherwise analogous bis(cyclopentadienyl) complexes. Extended Hückel MO calculations show that overlap between the empty 4d orbitals of the $ZrCl_2^{2+}$ fragment and the highest filled π orbitals of the indenyl anions is decreased when a Me_2Si bridge forces the indenyl ligands into a lateral orientation. Consequences of this orbital mismatch, e.g. on electron densities at the Zr center, are discussed.

Introduction

In a previous study[1] on the effects of substituents and bridging units on electron densities at the Zr centers of bis(cyclopentadienyl)- and bis(indenyl)zirconium complexes, unexpected deviations were noted between these classes of complexes. While bis(cyclopentadienyl)zirconium complexes become distinctly more electron-rich by introduction of a Me_2Si bridge, such an effect is not observed for bis(indenyl)zirconium complexes. Likewise, the electron-donating property of methyl substituents is found to be strongly attenuated in Me_2Si-bridged bis(indenyl) complexes. Since the presence and the nature of these substituent and bridging units profoundly influence the performance of the resulting catalyst system,[2] it would appear desirable to clarify their effects on the electronic properties of these *ansa*-zirconocene species.

Recent studies have shown that useful information on zirconocene-based catalyst systems can be derived from their UV/vis spectra.[3,4] We have thus studied the effects of an interannular bridge on the electronic properties of a series of zirconocene dichloride complexes (Chart 1) by comparing the UV/vis spectra of otherwise equivalent bridged and unbridged complexes and by molecular-orbital calculations using the extended Hückel method.

Table 1. Longest Wavelength Absorption Bands of Complexes 1−10 in Toluene Solution

complex	λ (nm)	$\Delta\lambda$ (nm)
$(Cp)_2ZrCl_2$ (**1**)	333	
$(MeCp)_2ZrCl_2$ (**2**)	337	4[a]
$(Me_4Cp)_2ZrCl_2$ (**3**)	350	17[a]
$Me_4C_2(Cp)_2ZrCl_2$ (**4**)	345	12[a]
$Me_2Si(Cp)_2ZrCl_2$ (**5**)	356	23[a]
$(Ind)_2ZrCl_2$ (**6**)	385	
$H_4C_2(Ind)_2ZrCl_2$ (**7**)	426	41[b]
$Me_2Si(Ind)_2ZrCl_2$ (**8**)	444	59[b]
Me_2Si(2-Me-Ind)$_2ZrCl_2$ (**9**)	449	64[b]
Me_2Si(2-Me-BenzInd)$_2ZrCl_2$ (**10**)	433	48[b]

[a] Relative to complex **1**. [b] Relative to complex **6**.

Results and Discussion

From the UV/vis spectra of the bridged and unbridged bis(cyclopentadienyl)zirconium dichloride complexes **1−5** (Chart 1), it is apparent that the longest wavelength band of these complexes is only moderately affected by introduction of a $(CMe_2)_2$ or Me_2Si bridge (Table 1, Figure 1). These bridges shift this band from its position at 333 nm in $(Cp)_2ZrCl_2$ to higher wavelengths by 12 and 23 nm, respectively: i.e., by increments comparable to those associated with the introduction of several methyl groups into each C_5 ring.

The longest wavelength band of the bis(indenyl) complex $(Ind)_2ZrCl_2$ (**6**), however, is shifted to longer wavelengths by 41−64 nm in complexes **7−10,** where the indenyl ligands are connected by a $(CH_2)_2$ or a Me_2Si bridging unit at their 1-positions (Figure 1). These differences are even visually discernible: while com-

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[1] Wieser, U.; Babushkin, D.; Brintzinger, H. H. *Organometallics*, in press.

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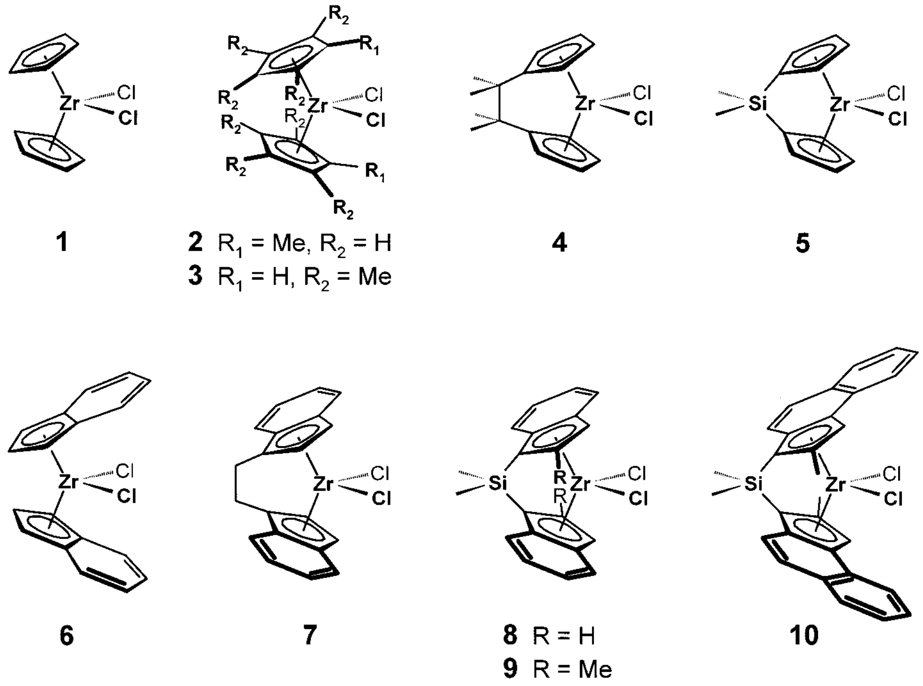
Chart 1



1

2 R$_1$ = Me, R$_2$ = H
3 R$_1$ = H, R$_2$ = Me

4

5

6

7

8 R = H
9 R = Me

10

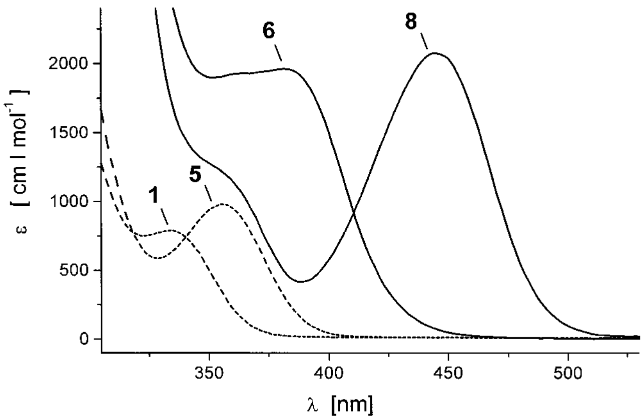


Figure 1. UV/vis spectra (molar absorbance) of unbridged and bridged zirconium bis(cyclopentadienyl) complexes (**1**, **5**) and bis(indenyl) complexes (**6**, **8**) in toluene solution.

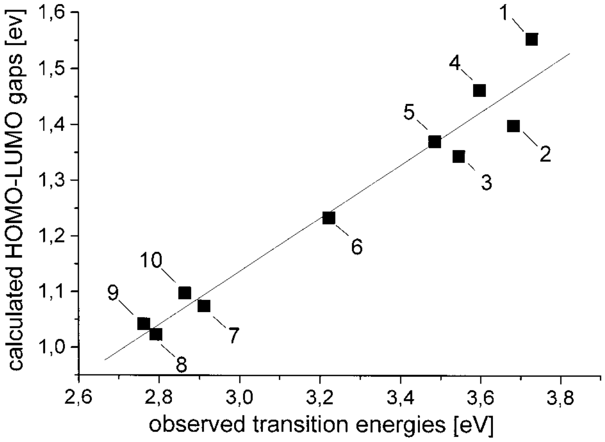


Figure 2. Calculated HOMO−LUMO energy gaps and experimentally observed transition energies of the longest wavelength absorption bands for unbridged and bridged bis(cyclopentadienyl) and bis(indenyl) complexes **1**−**10**.

plexes **1**−**6** are almost colorless in solution and as solids, complexes **7**−**10** have a distinct yellow color.

Since we suspected that these observations are related to different conformational orientations of the indenyl ligands in bridged and unbridged zirconocene complexes, we have tried to analyze the origins of the respective spectral changes by means of molecular orbital calculations. For this purpose we have used a simple extended Hückel MO analysis.[5] Despite its shortcomings, this method is known to reproduce angular overlap changes rather reliably;[6] it leads, in general, to descriptions which are intuitively understandable and, therefore, hopefully transferable to related cases.

For the complexes considered here, this method does indeed predict trends in their electronic transition energies quite reasonably: HOMO−LUMO energy gaps calculated by the EHMO method for complexes **1**−**10**—although too low by a factor of about 0.4[7]—correlate very well ($R = 0.98$) with the respective, experimentally determined longest wavelength transition energies (Figure 2).

To study the effects of changing ligand conformations on total energies and HOMO−LUMO gaps, energy profiles for C_2-symmetric $(Cp)_2ZrCl_2$ and $(Ind)_2ZrCl_2$ rotamers were calculated[8] and plotted as a function of the C(2)−centroid−centroid′−C(2′) dihedral angle ϕ

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[5] Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[6] Results of a computational study on $(Cp)_2MX_2$ complexes by the EHMO method (Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729) agree remarkably well with those of a more recent study by the Fenske−Hall SCF method (Zhu, L.; Kostic, N. M. *J. Organomet. Chem.* **1987**, *335*, 395).

[7] In a recent study,[3] HOMO−LUMO energy gaps calculated for various substituted zirconocene complexes were too high by ca. 6 eV at the Hartree−Fock level (6-31G*) and by ca. 0.6 eV at the B3LYP/6-31G* level.

[8] C_2 symmetry is assumed in order to simplify the MO analysis, even though mutual deviation of the centroid−metal−centroid and the $ZrCl_2$-bisector planes requires little energy (Burger, P.; Diebold, J.; Gutmann, S.; Hund, H. U.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 1319. Brintzinger, H. H.; Prosenc, M. H.; Schaper, F.; Weeber, A.; Wieser, U. *J. Mol. Struct.* **1999**, 409).

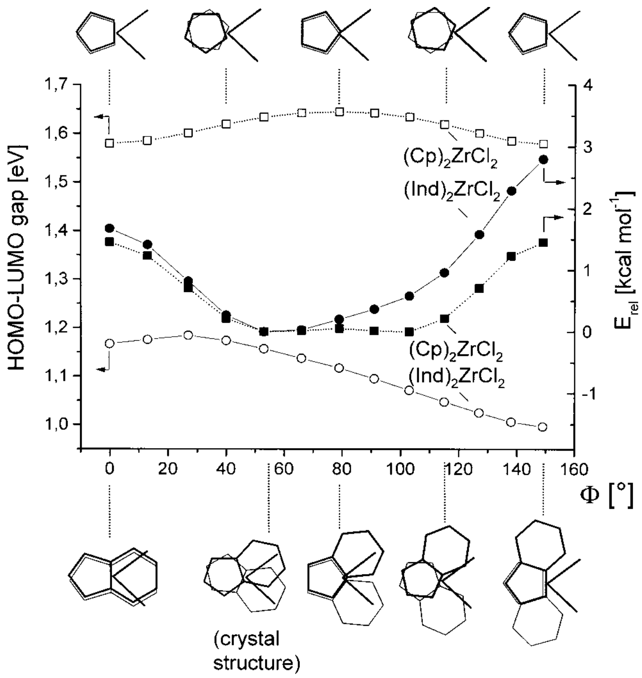

Figure 3. HOMO−LUMO energy differences (open symbols; left axis) and relative total energies (filled symbols; right axis) as functions of the interannular torsion angle ϕ for (Cp)$_2$ZrCl$_2$ (squares) and (Ind)$_2$ZrCl$_2$ (circles).

between both ligand units (Figure 3), as described in detail in the Experimental and Computational Section. In this manner, total energy changes associated with different mutual orientations of the cyclopentadienyl ligands of (Cp)$_2$ZrCl$_2$ were found to amount to only 1.5 kcal/mol. Rather shallow energy minima for staggered-ring conformations are apparent in the range of $50° < \phi < 100°$, in accord with crystallographic data.[9]

For (Ind)$_2$ZrCl$_2$, however, substantially larger changes of the total energy are found to be associated with changing orientations of the indenyl ligands. A distinct minimum is found at $\phi = 53°$, close to the crystallographically determined value of $\phi = 55°$ (Figure 3).[10] Total energies rise by ca. 3 kcal/mol in going from the minimum at $\phi = 53°$ to an eclipsed conformation with $\phi = 149°$, as is found in Me$_2$Si-bridged bis(indenyl) complexes.[11] This is mainly caused by a rise in the energy of one of the two nearly degenerate HOMO's (Figure 4, middle). This orbital consists essentially of a combination of the highest filled π orbitals of both Ind$^-$ anions with an empty 4d$_{xy}$-type orbital of the ZrCl$_2^{2+}$ fragment. It is destabilized when a rotation of the indenyl ligands to a lateral orientation reduces the overlap between filled indenyl π and empty zirconium d orbitals, due to a mismatch in the orientation of their nodal planes.

The LUMO, on the other hand, is dominated by an empty Zr 4d$_{x^2-y^2}$-type orbital, which overlaps with Cl p orbitals but is nonbonding with regard to the indenyl ligands (Figure 4, right). It is thus less affected by the orientation of these ligands than the HOMO. Due to the destabilization of the latter, the HOMO−LUMO gap decreases by 0.16 eV when ϕ increases from its value of 53° in (Ind)$_2$ZrCl$_2$ to the 150° found in Me$_2$Si(Ind)$_2$ZrCl$_2$.[12] This decrease of the HOMO−LUMO energy gap at increased values of the torsional angle ϕ thus appears to be responsible for the strong bathochromic shift of the longest wavelength ligand-to-metal charge-transfer absorption,[3,4,13] which is observed when a 1,1′-positioned Me$_2$Si or R$_4$C$_2$ bridge forces the indenyl ligands into a lateral orientation.

In (Cp)$_2$ZrCl$_2$, however, the HOMO−LUMO energy gap decreases by only 0.05 eV when the torsional angle ϕ goes from one of the staggered energy minima to the eclipsed conformation found in Me$_2$Si(Cp)$_2$ZrCl$_2$. This feature, which is based on the nearly rotation-invariant overlap between cyclopentadienyl π and zirconium 4d orbitals, explains the small bathochromic shifts caused by a Me$_2$Si bridge in bis(cyclopentadienyl) complexes.

The distinct ways in which overlap between ligand π and zirconium 4d orbitals depends on the torsional angle ϕ appear to be the cause also for the different effects of an interannular Me$_2$Si bridge on Zr electron densities in bis(cyclopentadienyl)- and bis(indenyl)zirconium complexes:[1] As discussed before, a Me$_2$Si bridge has almost the same effects on Zr electron densities in bis(cyclopentadienyl)zirconium complexes as a Me or Me$_3$Si substituent at each of the C$_5$ rings. This documents that electron donation from each of these substituents to the C$_5$-ring π system is equally well transmitted to the metal center. In a bis(indenyl)zirconium complex, however, the intrinsic electron-donating effect of a Me$_2$Si bridge appears to be compensated by a loss of Zr electron density which is caused, by way of decreased overlap between filled indenyl π orbitals and empty Zr 4d orbitals, by the lateral orientation of the indenyl rings in Me$_2$Si-bridged (Ind)$_2$Zr complexes.

This mismatch in indenyl π and Zr 4d orbital orientation is likely to contribute also to the much attenuated electron-donating effect previously found for the 2,2′-positioned CH$_3$ substituents of the bis(indenyl) complex **9**.[1] In addition, however, the 2- and 2′-positions of a bis(indenyl) zirconium complex—whether bridged or not—appear to be located close to a nodal plane in each of the near-degenerate HOMO's (Figure 4), which makes them unsuitable to transmit electron density released from the CH$_3$ groups to the Zr center.

Conclusions

A Me$_2$Si bridge induces only a moderate shift of the longest wavelength charge-transfer band but a sizable increase of the electron density at the Zr center of (Cp)$_2$Zr complexes, whereas in (Ind)$_2$Zr complexes a 1,1′-positioned Me$_2$Si bridge causes, conversely, a large bathochromic shift of the lowest charge-transfer transi-

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(11) Single-point calculations of selected rotamers using DFT methods (BP86, triple-ζ basis sets), while generally giving bigger HOMO−LUMO gaps,[7] agree qualitatively with the results of the extended Hückel calculations: Increase of the torsion angle ϕ from 55 to 150° in (Ind)$_2$ZrCl$_2$ is accompanied by a decrease of the HOMO−LUMO gap by 0.25 eV and an increase of the relative energy by ca. 2 kcal/mol. Analogous results are obtained for (Cp)$_2$ZrCl$_2$, when ϕ is increased from 80 to 150° (cf. Figure 3).

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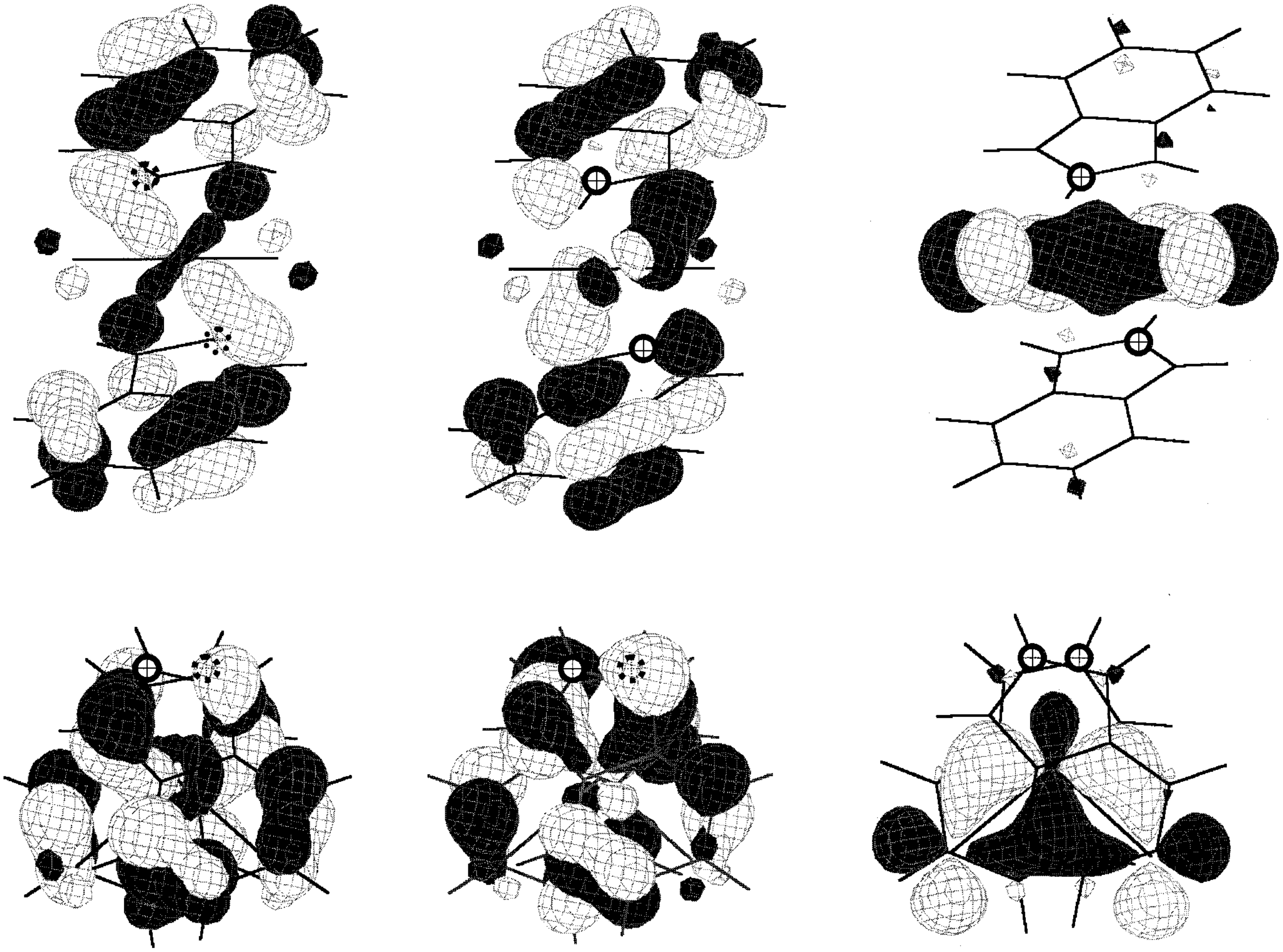

Figure 4. Contour plots of the two near-degenerate HOMO's (left and middle) and of the LUMO (right) in $(Ind)_2ZrCl_2$ with $\phi = 53°$ (projections parallel to the C_2 axis (top) and onto the $ZrCl_2$ plane (bottom), indenyl 2,2′-positions marked with crossed circles).

tion but does not significantly change the electron density at the Zr center. These observations, which run counter to the intuitive idea that transition energies and electron densities might somehow be correlated, can be reconciled by the following notion: in $(Cp)_2Zr$ complexes, any electron donation from the bridging unit into the HOMO(s) is largely passed on to the Zr center and will thus raise the energy of the HOMO orbitals only marginally. In Me_2Si-bridged $(Ind)_2Zr$ complexes, on the other hand, the lateral orientation of the indenyl rings is unfavorable for efficient π−d overlap and causes the electron density donated by the bridging unit to stay in the ligand HOMO(s) and, hence, to raise the energies of these orbitals significantly. Consequently, a strong bathochromic shift of the lowest charge-transfer transition will be associated with an essentially unchanged Zr electron density.

It is tempting to speculate that the reduced electron densities at the Zr centers of Me_2Si-bridged bis(indenyl)- as compared to bis(cyclopentadienyl)zirconium complexes are responsible for the generally higher propene-polymerization activities of catalysts derived by suitable activators from the former class of complex compounds.[2] Prior to any discussion of their effects on rates of elementary reaction steps in olefin polymerization catalyst systems, it remains to be clarified, however, whether substituent and bridge effects on electronic properties similar to those reported here for neutral dichloride and methyl chloride derivatives pertain also for the cationic zirconocene alkyl derivatives,[14] thought to be responsible for olefin polymerization catalysis.

Experimental and Computational Section

Complexes **1**−**10** were either obtained commercially or as gifts or else prepared according to previous reports.[11,15−25]

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Toluene was dried over molecular sieves, purified by refluxing over sodium metal, and distilled under dry argon.

UV/vis Measurements. Suprasil quartz cells with 1 cm path length, equipped with Teflon stoppers, were filled, in a glovebox under N_2, with solutions of the samples in toluene; their UV/vis spectra were recorded at 25 °C on a Cary 50 Varian spectrometer. Zirconocene concentrations of (2.0−6.0) $\times 10^{-4}$ mol/L were found to give appropriate absorbances in the range of 0.5−1.2.

Extended Hückel MO Calculations. The program package HYPERCHEM was used on a conventional PC (AMD Athlon), with standard parameters as given in the program. HOMO−LUMO gap energies for complexes **1**−**10** were calculated using the respective crystallographically determined geometries.[9,10,12,20,24−29] Total-energy and HOMO−LUMO gap profiles for complexes **1** and **6** were calculated as functions of the torsional angle ϕ in the following manner. With an eclipsed conformation as the starting point, the dihedral angles α and β (Figure 5) were simultaneously increased from 0 to 72° in steps of 6°. Energies were then minimized by molecular-mechanics calculations, using a previously described force field.[30] Rotational angles ϕ were read from the resulting geometries and orbital and total energies calculated by standard EHMO methods.

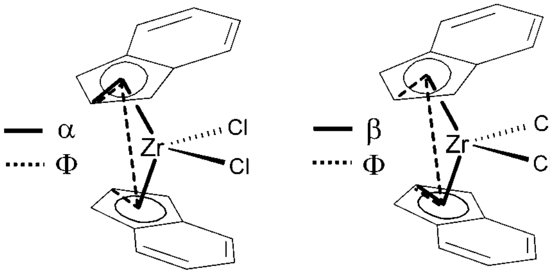

Figure 5. Torsion angles α and β (solid lines) used as variables for ligand rotation and the resulting interannular dihedral angle ϕ (dashed lines).

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