# Formation and Structures of [1,2–Bis(*N-tert*-butylcarbamoyl)cyclopentadienyl]zirconium Complexes – Coordination Chemistry of a "Fulvenologous" Malonic Amide Anion Ligand System

**Katrin Klaß,[a] Lothar Duda,[a] Nina Kleigrewe,[a] Gerhard Erker,*[a] Roland Fröhlich,[a] and Elina Wegelius[a]**

*Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday*

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Treatment of sodium cyclopentadienide with two molar equivalents of *tert*-butyl isocyanate yields sodium 1,2-bis(*N-tert*-butylcarbamoyl)cyclopentadienide (**6**). The $[C_5H_3(1,2\text{-}CONHCMe_3)_2]Na$ reagent **6** adds to $Cp_2Zr(CH_3)Cl$ (**8**) to yield $Cp_2Zr(CH_3)[C_5H_3(CONHCMe_3)_2]$ (**9**). In **9** the $C_5H_3(CONHCMe_3)_2$ ligand is bonded to zirconium through one of its carboxamido-oxygen atoms (κ*O*-coordination). Treatment of **6** with $CpZrCl_3(THF)_2$ yields $CpZrCl_2[C_5H_3(CONHCMe_3)_2](THF)$ **11**. In **11** the 1,2-bis(*N-tert*-butylcarbamoyl)cyclopentadienide moiety serves as a $C_s$-symmetric chelate ligand, binding to zirconium through both carbamoyl oxygens (κ²*O*,*O*′-coordination). The same seven-membered metallacyclic structural type is found in the reaction products of **6** with $ZrCl_4(THF)_2$ in 1:1 and 2:1 molar ratios. The former yields the distorted octahedral complex $ZrCl_3[C_5H_3(CONHCMe_3)_2](THF)$ (**12**), the latter gives the chiral octahedral system $ZrCl_2[C_5H_3(CONHCMe_3)_2]_2$ (**13**). In solution, complex **13** undergoes a thermally induced enantiomerization process ($\Lambda \rightleftharpoons \Delta$ interconversion), for which a Gibbs activation energy of $\Delta G^{\ddagger}_{\mathrm{enant}} = 14.0 \pm 0.3$ kcal mol⁻¹ was determined by dynamic ¹H-NMR spectroscopy. The κ²*O*,*O*′-coordination of the $[C_5H_3(1,2\text{-}CONHCMe_3]^-$ ligand in the complexes **11**, **12**, and **13** was secured by X-ray crystal structure analyses.

## Introduction

Compounds derived from mono- and especially from bis(η-cyclopentadienyl) group 4 metal complexes have become of enormous importance in organometallic chemistry and catalysis.[1] Numerous variations at the Cp-ring systems have been devised and carried out, many of those in the development of improved homogeneous metallocene Ziegler catalysts and related systems. Most of the variations involved the attachment or anellation of hydrocarbyl moieties.[2] Functional groups have much less frequently been used for derivatising the Cp-rings, although there has been a variety of group 4 metallocene examples bearing Cp-side chains that contain amino-, phosphanyl-, or borane (and borate) substituents.[3] However, the more reactive carbonyl-derived functional groups are still very rarely found attached to Cp-type ring systems in group 4 metallocene and related chemistry. Following the pioneering work by M. D. Rausch et al.[4] we have searched for new ways of introducing reactive carbonyl substituents, especially carboxamide-derived groups at Cp-ligands, and then to attach them to the electropositive, oxophilic early transition metals.

We had previously shown that the cyclopentadienyl anion rapidly adds to a variety of alkyl- and arylisocyanates.[5][6] Subsequent to the carbon-carbon coupling step a rapid proton transfer takes place and the respective *N*-aryl- or *N*-alkylcarboxamido-substituted cyclopentadienides were obtained with moderate to good yields and selectivities. Formally these systems constitute carbamoyl-substituted cyclopentadienyl anion systems, but their fulvenoid mesomeric resonance structures must probably be taken into account for their ample structural and electronic description.[7] Nevertheless, transmetallation of the $[C_5H_4{-}CONHR^-]$anion equivalents to e.g. titanium straightforwardly led to the selective formation of $(\eta^5\text{-}C_5H_4{-}CONHR)[Ti]$ complexes, such as e.g. **4**. Only coordination of the ligand system through the five cyclopentadienyl ring carbon atoms was observed. The carboxamide functional group did not participate in the bonding of this ligand type to the central group 4 metal center. This was unequivocally shown by an X-ray crystal structure analysis of a representative example.[5]

This raises the question about the structural consequences that arise from attaching more than one electron-withdrawing carboxamido-substituent at the anionic Cp ligand. Especially in the case of two "*ortho*"-positioned carbonyl substituents,[8] that can cooperatively remove cyclopentadienide electron density, a situation might arise where the remaining Cp-nucleophilicity is not sufficient to warrant binding of the carbocyclic ring system to an early transition

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[a] Organisch-Chemisches Institut der Universität Münster,
Corrensstr. 40, D-48149 Münster, Germany
Fax: (internat.) +49 (0)251/ 83 36503
E-mail: erker@uni-muenster.de

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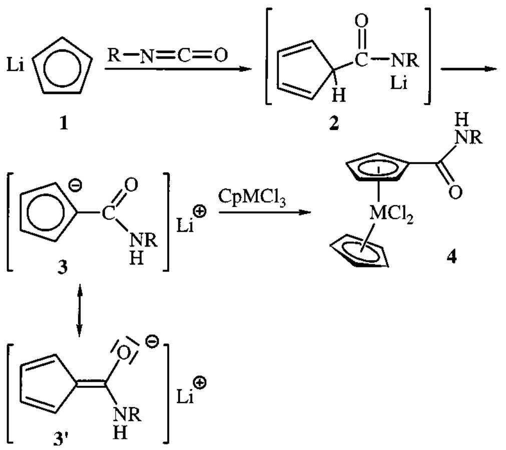
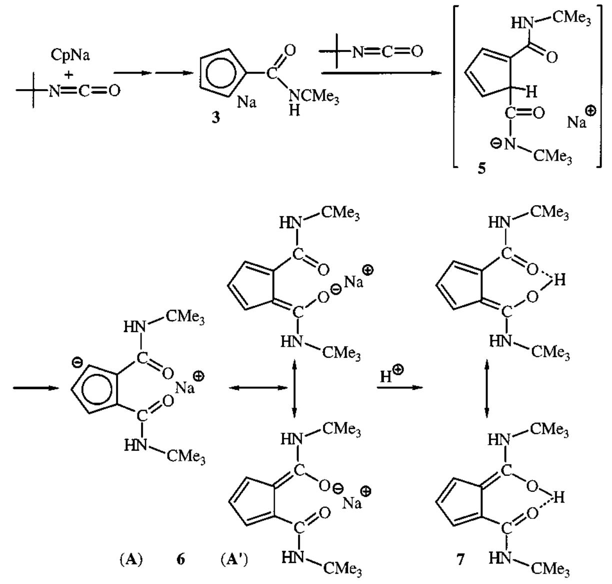


Scheme 1. Formation and metal coordination of the $[C_5H_4CONHR]^-$ ligand

metal center. Then a situation is conceivable where a switching of the preferred coordination mode from $\eta^5$-$CpX_2$ to potentially favored chelate bonding through the substituent nitrogen or, more likely, oxygen atoms might occur. We have prepared such a ligand system and attached it to a series of organometallic zirconium containing frameworks of decreasing overall electronic unsaturation to see which of the possible coordination modes, $\eta^5$-cyclopentadienyl or bis(carboxamide) substituent $\kappa^2 O,O'$-chelate is favored.

## Results and Discussion

The 1,2-biscarbamoyl-Cp ligand system employed in this study was selectively prepared by treatment of sodium cyclopentadienide with two molar equivalents of *tert*-butyl isocyanate in tetrahydrofuran. The twofold addition took place readily at temperatures between 0°C and room temperature. In view of our earlier work[5] it must be assumed that the reaction sequence proceeds through the monofunctionalized intermediates **2** and **3** (see Scheme 1, but in this case with the $Na^+$ counterion). Apparently, the anion **3** still contains a sufficiently nucleophilic substituted cyclopentadienide ring system to allow for a rapid subsequent attack at the strongly electrophilic sp-hybridized carbon atom of the *tert*-butyl isocyanate reagent present in the solution. Again, proton transfer seems to be rapid at the stage of the intermediate resulting from the addition reaction (compound **5** in Scheme 2) to give the doubly carbamoyl substituted anionic ligand system **6**. The twofold *tert*-butyl isocyanate addition reaction sequence is strictly 1,2-selective. This is probably due to a pronounced anion-stabilization in **6**, as it is illustrated by the fulvenoid resonance forms **6A/6A'** (see Scheme 2).[8] Indeed, the NMR spectra of **6** indicate a delocalized $C_{2v}$-symmetric structure in solution. There is only one set of $^1H/^{13}C$ NMR signals for the pair of symmetry-equivalent $-CONHCMe_3$ substituents (for details see the Experimental Section). Also, complex **6** exhibits an apparent $AX_2$ $^1H$-NMR spin pattern of the central $C_5H_3$ unit ($\delta$ 6.73, d, 2 H; 6.25, t, 1 H; $^3J$ = 3.6 Hz; corresponding $^{13}C$ NMR **C**H signals at $\delta$ 115.1 and 108.8). Hydrolysis of **6** gives the neutral system **7**. The spectroscopic features (e.g. $^1H$ NMR $-OH$ signal at $\delta$ 19.7 in $CDCl_3$) indicate the presence of a fully enolized tautomer with $C=O\cdots H-O-$ bridging hydrogen. Again, the obtained product **7** exhibits NMR spectra that are consistent with a fully delocalized $C_{2v}$-symmetric species in solution. It thus seems justified to consider the compound **7** (and the anion **6** derived from it) as fulvene-expanded analogues of the respective malonic amides. One might, therefore, term such systems "fulvenologous" β-dicarbonyl compounds. The compounds **7** and **6** may then be regarded as a fulvenologous malonic amide or malonic amide anion, respectively.



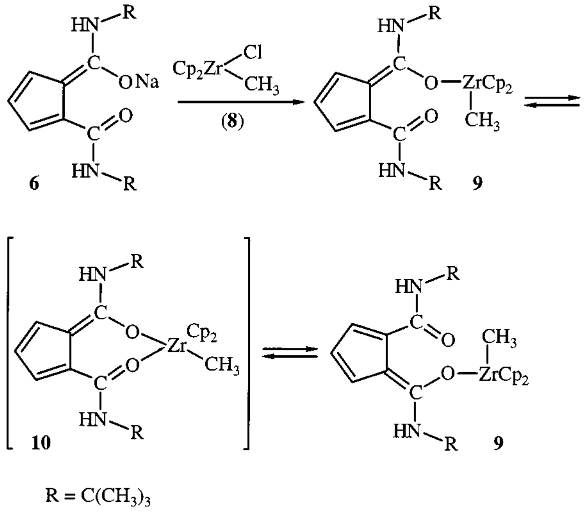
Scheme 2. Preparation of a $[C_5H_3(CONHR)_2]^-$ ligand

The anion **6** was then reacted with a variety of zirconium complexes with a varying degree of coordinative unsaturation and electrophilicity. We first treated the reagent **6** with $Cp_2Zr(CH_3)Cl$ (**8**).[9]

Complex **8** reacts rapidly with **6** in a 1:1 molar ratio in toluene solution. The product **9** of the composition $Cp_2Zr(CH_3)[C_5H_3(CONHCMe_3)_2]$ was isolated in ca. 60% yield. The NMR spectra of **9** are in accord with a $C_s$-symmetric structure in solution. The complex contains a pair of symmetry-equivalent $\eta^5$-cyclopentadienyl ligands ($^1H/^{13}C$ NMR signals observed at $\delta$ 6.22/112.1) and a single metal-bound $CH_3$ group ($\delta$ 0.38/29.7 in $CD_2Cl_2$ solution). The $C_5H_3(CONHCMe_3)_2$ ligand is unsymmetrically coordinated to zirconium. It exhibits two sets of $^1H$- and $^{13}C$-NMR resonances of the $-CONHCMe_3$ groups, five separated $^{13}C$-NMR resonances of the carbon atoms of the $C_5H_3$ ring and an ABC-type $^1H$-NMR pattern for the $C_5H_3$ hydrogen resonances (at 213 K, 150/600 MHz). This spectroscopic behavior is incompatible with the formation of a complex containing an $\eta^5$-$C_5H_3X_2$ ligand in addition to a pair of $\eta^5$-$C_5H_5$ moieties. We must assume that the $C_5H_3(CONHCMe_3)_2$ ligand in **9** is bonded to zirconium through oxygen. We assume that complex **9** contains one uncomplexed $-CONHCMe_3$ substituent, i.e. that the $C_5H_3(CONHCMe_3)_2$ ligand is only attached to the

$Cp_2ZrCH_3$ unit through one of the carbonyl oxygen atoms (i.e. κ$^1$*O*-coordination). This structural interpretation seems to be called for in view of the observation of two very different $^1$H-NMR chemical shifts of the respective NH amido hydrogen atoms (at 213 K and 600 MHz in $CD_2Cl_2$ observed at δ 12.91 and 6.00, respectively). The IR spectrum is in accord with this interpretation: in this series of $[C_5H_3(CONHCMe_3)_2]$zirconium complexes (see below) only complex **9** exhibits a band (at 1643 cm$^{-1}$) that can be attributed to a free uncoordinated carboxamido functional group.

Complex **9** shows dynamic NMR spectra. Raising the temperature from 213 K rapidly leads to coalescence of the pairs of diastereotopic groups at the $C_5H_3(CONHCMe_3)_3$ ligand. From the $^1$H NMR coalescence of the $C(CH_3)_2$ resonances (200 MHz, $T_c = 289$ K, $\Delta\nu = 22$ Hz) a Gibbs activation energy of $\Delta G^{\neq}{}_{\text{exchange}} = 14.9 \pm 0.3$ kcal mol$^{-1}$ was determined.[10] We assume that a pentacoordinate $Cp_2Zr(CH_3)[C_5H_3(CONHCMe_3)_2]$ structure (**10**) is likely to be formed as an intermediate which has both carbonyl oxygen atoms coordinated at the available coordination sites at the front of the bent metallocene wedge.[11] Opening and closing these bonds similarly as it has been shown to proceed in $\eta^2 \rightleftarrows \eta^1 \rightleftarrows \eta^2$-acyl group 4 metallocene isomerizations and related processes[12] probably provides an ample mechanistic scheme for describing the automerization process observed to take place in complex **9** (see Scheme 3).

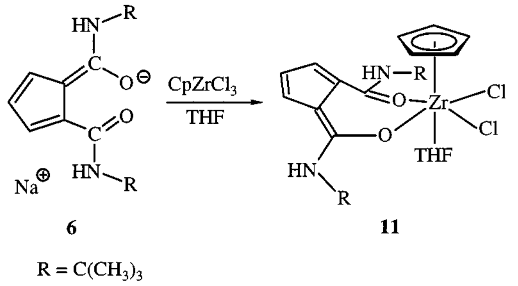


Scheme 3. Formation and dynamic behavior of **9**

We next reacted (η-cyclopentadienyl)zirconium trichloride[13] (as the bis-THF adduct) with the ligand system **6**. The chloride substitution reaction proceeds cleanly in a 1:1 stoichiometry, and we have isolated the product **11** in >70% yield as a solid from the reaction mixture. Single crystals of **11** suited for an X-ray crystal structure analysis were obtained by letting pentane diffuse through the gas phase into a toluene/dichloromethane solution of **11**. Complex **11** can be regarded as chemically $C_s$-symmetric, but not strictly so crystallographically. The unsubstituted cyclopentadienyl ligand is η$^5$-coordinated to zirconium with Zr−C(Cp) bond lengths ranging from 2.490(5) to 2.555(4) Å. The $[C_5H_3(CONHCMe_3)_2]$ ligand is bonded to the early transition metal center only through its carboxamido-oxygen atoms (Zr−O1: 2.093(3), Zr−O2: 2.081(2)Å). The ligand is part of a seven-membered metallacycle, that contains large bonding angles at the oxygen atoms[14] [C1−O1−Zr: 145.3(2)°, C2−O2−Zr: 145.0(2)°] and a rather small σ-ligand angle at zirconium (O1−Zr−O2: 82.7(1)°]. The anellated $C_5H_3$-ring system has no close contact to zirconium. It is in principle oriented in the $C_4O_2Zr$ seven-membered ring plane, but bent slightly in the direction toward the adjacent η$^5$-cyclopentadienyl ring because of a boat-like distortion of the seven-membered metallacycle from planarity.[14a] Because of this distortion the (η$^5$-Cp)[κ$^2$*O,O′*-$C_5H_3(CONHCMe_3)_2]Cl_2Zr$ moiety may be regarded as a square-pyramidal subunit inside the overall octahedral coordination polyhedron around the central zirconium atom (see Figure 1). A weakly bound tetrahydrofuran ligand [Zr−O31 2.365(3)Å] trans to the η$^5$-Cp group completes the ligand sphere around Zr in **11**. Both the Zr−O1/O2 and the Zr−Cl1/Cl2 bonds are bent toward this THF ligand [angles O1−Zr−O31: 75.0(1)°, O2−Zr−O31: 75.2(1)°, Cl1−Zr−Cp(centroid): 104.1°, Cl2−Zr−Cp(centroid): 102.8°].

Inside the σ-bonded $C_5H_3(CONHCMe_3)_2$ ligand the double bonds are fully delocalized. There seems to be a pronounced difference in C−C bond lengths with shorter values being favored at the distal end away from zirconium, but this effect is equal for both ligand sides [e.g. C6−C5/C6−C7: 1.385(6), 1.387(3) Å; C5−C4/C7−C3: 1.398(5)/1.401(5) Å; C3−C1/C4−C2: 1.445(3)/1.436(5) Å; the length of the central conjugated C3−C4 bond is 1.440(5) Å].

The C−C(=O)−N(H)−C carboxamido groups are trans-configurated. Therefore, the bulky *tert*-butyl substituents at the carbamoyl-nitrogen atoms are oriented toward the chlorine atoms in the central $O_2Cl_2Zr$ containing plane of the complex **11**. The corresponding bond angles at nitrogen are 128.8(4)° (C2−N2−C21) and 127.8(3)° (C1−N1−C11), respectively.



The structure of **11** in solution seems to be similar. Complex **11** shows static NMR spectra. The $C_5H_3(CONHCMe_3)_2$ ligand is $C_s$-symmetrically bonded to zirconium. In $CD_2Cl_2$ solution the single $^1$H-NMR N*H* resonance occurs at δ 6.41 (br s, 2 H), and the $C_5H_3$ unit is characterized by $^1$H-NMR resonances at δ 6.70 (d, 2 H) and 6.10 (t, 1 H, $^3J = 3.8$ Hz). The observed carboxamide IR features [ṽ = 3412 and 3322 cm$^{-1}$ (NH), 1570 and 1529 cm$^{-1}$ (CONH)] also indicate *O*-coordination of the delocalized $C_5H_3(CONHCMe_3)_2$ ligand system to zirconium.

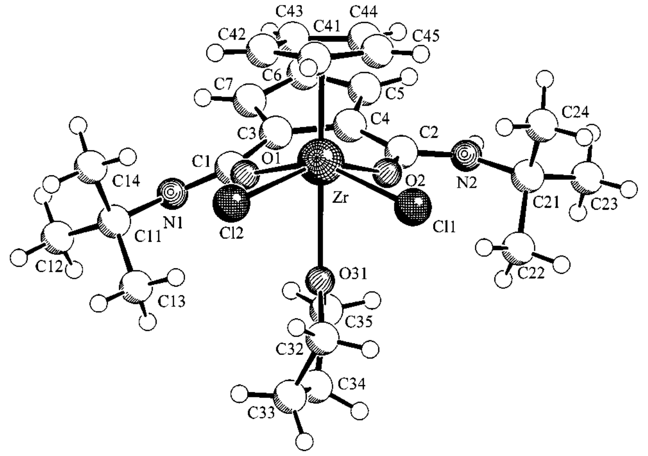
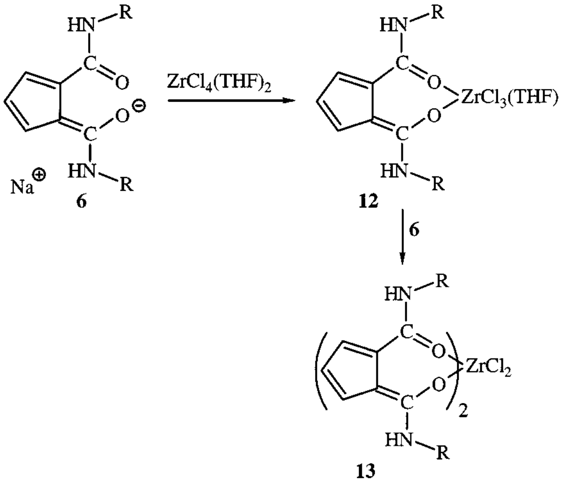


Figure 1. A view of the molecular structure of **11**; selected bond lengths and angles: Zr−O1 2.092(3), Zr−O2 2.081(2), O1−C1 1.280(4), O2−C2 1.291(4), C1−N1 1.322(5), C2−N2 1.325(5), N1−C11 1.489(5), N2−C21 1.492(5), C1−C3 1.445(5), C2−C4 1.436(5), C3−C4 1.440(5), C3−C7 1.401(5), C4−C5 1.398(5), C5−C6 1.385(6), C6−C7 1.387(5), Zr−Cl1 2.4892(11), Zr−Cl2 2.5067(10), Zr−Cp(centroid) 2.230, Zr−O31 2.365(3); O1−Zr−O2 82.73(10), O1−Zr−O31 74.96(10), O2−Zr−O31 75.18(9), O1−Zr−Cl1 152.02(8), O1−Zr−Cl2 86.07(7), O1−Zr−Cp(centroid) 103.8, O2−Zr−Cl1 91.86(6), O2−Zr−Cl2 168.54(6), O2−Zr−Cp(centroid) 102.7, O31−Zr−Cl1 77.08(7), O31−Zr−Cl2 79.18(7), O31−Zr−Cp(centroid) 177.6, Cl1−Zr−Cl2 89.93(4), Cl1−Zr−Cp(centroid) 104.1, Cl2−Zr−Cp(centroid) 102.8, Zr−O1−C1 145.3(2), Zr−O2−C2 145.0(2), O1−C1−N1 118.1(3), O2−C2−N2 117.2(3), O1−C1−C3 123.1(3), O2−C2−C4 122.6(3), N1−C1−C3 118.8(3), N2−C2−C4 120.2(3), C1−N1−C11 127.8(3), C2−N2−C21 128.8(4), C1−C3−C4 132.0(3), C2−C4−C3 129.3(3), C1−C3−C7 121.3(3), C2−C4−C5 124.1(3), C4−C3−C7 106.6(3), C3−C4−C5 106.5(3), C3−C7−C6 109.4(3), C4−C5−C6 109.7(4), C5−C6−C7 107.7(3)

We have then reacted **6** with zirconium tetrachloride. The group 4 metal halide was introduced as its tetrahydrofuran adduct (i.e. $ZrCl_4 \cdot 2$ THF), and the reaction was performed in toluene. The outcome was dependent on the chosen ratio of the reagents and it relied somewhat on the reaction conditions. Employing the reagents **6** and $ZrCl_4 \cdot 2$ THF in a 1:1 molar ratio and heating the mixture for ca. 1 d at 60°C gave a precipitate (after cooling) from which the mono-substitution product **12** was obtained by extraction with dichloromethane (35% isolated). There was a small amount of the di-substitution product **13** recovered from the toluene filtrate of this reaction. However, the complex **13** is easier prepared by treatment of **6** with $ZrCl_4 \cdot 2$ THF directly in a 2:1 molar ratio in toluene at 60°C. In this case, the product **13** was obtained in >60% yield.

Complex **12** contains a coordinated THF molecule. According to the NMR and IR spectra is exhibits very similar bonding features of the $[C_5H_3(CONHCMe_3)_2]$ ligand as found in **11**. The ligand is probably symmetrically coordinated through both oxygen atoms. The characteristic $^1H$-NMR N*H* resonance of **12** is observed at δ 6.55 (br s, 2 H), and the IR features typical for this ligand arrangement are again observed ($\tilde{\nu} = 3419, 3347, 1577, 1535\ cm^{-1}$).

The $\kappa^2$*O,O′*-coordination of the $[C_5H_3(CONHCMe_3)_2]$ ligand of **12** was secured by the X-ray crystal structure analysis (see Figure 2). The (1,2-biscarbamoyl-Cp)Zr unit again forms a slightly boat-shaped seven-membered metallacycle.



Coordination of this ligand takes place solely through the $-CONHCMe_3$ oxygen atoms. The carbon framework is again fully delocalized and exhibits very similar bonding features as already observed for the analogously structured $[C_5H_3(CONHCMe_3)_2]Zr$ unit in **11**. The in-plane oriented −CONHR groups again exhibit a trans-configurated C−C(=O)−N(H)−C(Me$_3$) framework and consequently have their bulky *tert*-butyl residues oriented towards the in-plane $ZrCl_2$ section. The coordination geometry around zirconium is almost ideally octahedral. The deviations of the $O_3Cl_3Zr$ octahedral core from the ideal expected geometry are much smaller than e.g. observed for the $O_3Cl_2(Cp)Zr$ core in **11** (see above).

In **12** the Zr−O1 and Zr−O2 bond lengths are 2.063(2) and 2.036(2) Å, respectively.[15a] The Zr−Cl1/−Cl2 bonds are 2.426(1) and 2.448(1) Å in length, whereas the perpendicularly oriented Zr−Cl3 is shorter at 2.397(1) Å.[16] The coordinated THF molecule is located trans to it. The corresponding Zr−O31 bond length is 2.232(2) Å.[15b] This is considerably shorter than observed for the THF coordination in **11** as it is expected for a complex derived from the more electrophilic $LZrCl_3$ building block in comparison to the $LZrCl_2(Cp)$ moiety. The very close to octahedral arrangement of the core atoms of **12** around zirconium is illustrated by the close to linear arrangement of the O31−Zr−Cl3 moiety [178.62(5)°]. Also the O1−Zr−Cl1 [170.03(6)°] and O2−Zr−Cl2 [168.54(6)°] units are only slightly bent, and the deviation of the respective vectors from orthogonality is also very small [e.g.: O1−Zr−Cl2: 89.00(6)°, O2−Zr−Cl1: 91.86(6)°, O2−Zr−Cl3: 94.54(6), O1−Zr−Cl3: 95.58(6)°]. The anellated $C_5H_3$ ring at the $C_4O_2Zr$ boat-shaped metallacyclic core of **12** is oriented toward the coordinated THF molecule. This is opposite of what is observed in the structurally and otherwise also conformationally related complex **11**.

Crystals of **13** were obtained by letting pentane diffuse through the gasphase into a benzene/dichloromethane solution of the 2:1 reaction product. The X-ray crystal structure analysis of **13** shows that both $[C_5H_3(CONHCMe_3)_2]$ ligands in this complex are exclusively bonded to zirconium through their carbamoyl-oxygen atoms. Again the adjacent

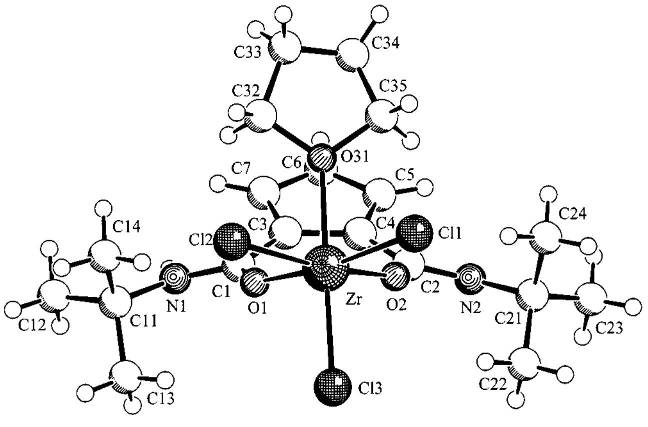


Figure 2. Molecular structure of **12**; selected bond lengths and angles: Zr−O1 2.063(2), Zr−O2 2.036(2), O1−C1 1.297(3), O2−C2 1.303(3), C1−N1 1.329(4), C2−N2 1.317(4), N1−C11 1.481(4), N2−C21 1.485(3), C1−C3 1.429(4), C2−C4 1.424(4), C3−C4 1.446(4), C3−C7 1.410(4), C4−C5 1.403(4), C5−C6 1.393(4), C6−C7 1.383(4), Zr−Cl1 2.4257(9), Zr−Cl2 2.4475(8), Zr−Cl3 2.3969(9), Zr−O31 2.232(2); O1−Zr−O2 83.73(8), O1−Zr−O31 84.70(8), O2−Zr−O31 84.15(8), O1−Zr−Cl1 170.03(6), O1−Zr−Cl2 89.00(6), O1−Zr−Cl3 95.58(6), O2−Zr−Cl1 91.86(6), O2−Zr−Cl2 168.54(6), O2−Zr−Cl3 94.54(6), O31−Zr−Cl1 85.96(6), O31−Zr−Cl2 86.37(6), O31−Zr−Cl3 178.62(5), Cl1−Zr−Cl2 93.89(3), Cl1−Zr−Cl3 93.68(4), Cl2−Zr−Cl3 94.98(3), Zr−O1−C1 144.1(2), Zr−O2−C2 146.7(2), O1−C1−N1 117.4(3), O2−C2−N2 117.5(2), O1−C1−C3 123.2(3), O2−C2−C4 122.4(3), N1−C1−C3 119.4(2), N2−C2−C4 120.0(2), C1−N1−C11 129.3(2), C2−N2−C21 128.2(2), C1−C3−C4 130.2(3), C2−C4−C3 131.0(3), C1−C3−C7 122.9(3), C2−C4−C5 122.5(3), C4−C3−C7 105.8(3) C3−C4−C5 106.5(2), C3−C7−C6 109.0(3), C4−C5−C6 109.3(3), C5−C6−C7 108.4(3).

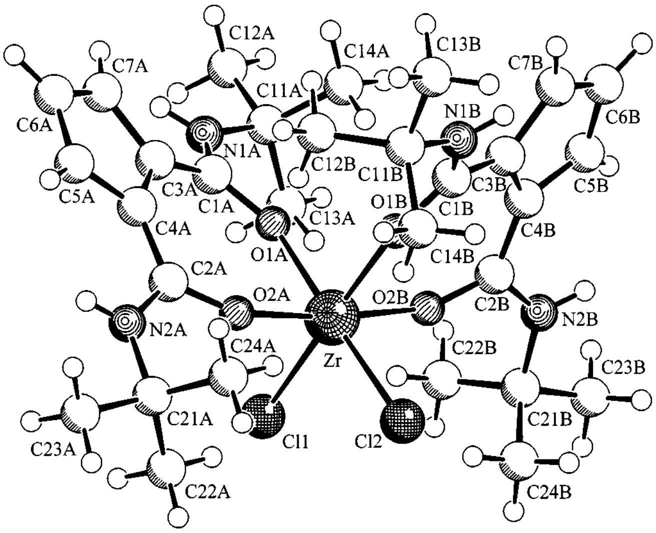


Figure 3. A view of the molecular structure of complex **13**; selected bond lengths [Å] and angles [°]: Zr−O1A 2.037(2), Zr−O1B 2.045(2), Zr−O2A 2.044(2), Zr−O2B 2.050(2), O1A−C1A 1.284(3), O1B−C1B 1.277(3), O2A−C2A 1.291(3), O2B−C2B 1.284(3), C1A−N1A 1.322(4), C1B−N1B 1.325(4), C2A−N2A 1.326(4), C2B−N2B 1.336(3), N1A−C11A 1.480(4), N1B−C11B 1.488(4), N2A−C21A 1.483(4), N2B−C21B 1.478(4), C1A−C3A 1.432(4), C1B−C3B 1.429(4), C2A−C4A 1.426(4), C2B−C4B 1.430(4), C3A−C4A 1.449(4), C3B−C4B 1.454(4), C3A−C7A 1.406(4), C3B−C7B 1.398(4), C4A−C5A 1.411(4), C4B−C5B 1.402(4), C5A−C6A 1.380(5), C5B−C6B 1.382(4), C6A−C7A 1.385(5), C6B−C7B 1.386(5), Zr−Cl1 2.4489(9), Zr−Cl2 2.4435(8); O1A−Zr−O2A 84.09(8), O1A−Zr−O1B 86.79(9), O1A−Zr−O2B 91.18(8), O1A−Zr−Cl1 90.99(7), O1A−Zr−Cl2 173.41(6), O1B−Zr−O2B 83.93(7), O1B−Zr−O2A 91.75(8), O1B−Zr−Cl1 174.66(6), O1B−Zr−Cl2 88.06(7), O2A−Zr−O2B 173.77(8), O2A−Zr−Cl1 92.85(6), O2A−Zr−Cl2 91.97(6), O2B−Zr−Cl1 91.27(6), O2B−Zr−Cl2 92.36(6), Cl1−Zr−Cl2 94.49(4), Zr−O1A−C1A 152.08(2), Zr−O1B−C1B 152.4(2), Zr−O2A−C2A 150.9(2), Zr−O2B−C2B 149.2(2), O1A−C1A−N1A 117.1(3), O1B−C1B−N1B 117.4(3), O2A−C2A−N2A 117.0(3), O2B−C2B−N2B 116.8(3), O1A−C1A−C3A 122.6(3), O1B−C1B−C3B 123.5(2), O2A−C2A−C4A 123.6(3), O2B−C2B−C4B 124.8(2), N1A−C1A−C3A 120.3(3), N1B−C1B−C3B 119.1(23), N2A−C2A−C4A 119.4(3), N2B−C2B−C4B 118.3(3), C1A−N1A−C11A 128.1(32), C1B−N1B−C11B 128.4(3), C2A−N2A−C21A 129.5(3), C2B−N2B−C21B 129.3(3), C1A−C3A−C4A 131.6(3), C1B−C3B−C4B 130.2(3), C2A−C4A−C3A 131.1(3), C2B−C4B−C3B 131.0(3), C1A−C3A−C7A 121.9(3), C1B−C3B−C7B 123.7(3), C2A−C4A−C5A 122.6(3), C2B−C4B−C5B 122.7(3), C4A−C3A−C7A 106.5(3), C4B−C3B−C7B 106.9(3), C3A−C4A−C5A 106.3(3), C3B−C4B−C5B 106.3(2), C3A−C7A−C6A 109.3(3), C3B−C7B−C6B 110.2(3), C4A−C5A−C6A 109.4(3), C4B−C5B−C6B 109.9(3), C5A−C6A−C7A 108.5(3), C5B−C6B−C7B 107.6(3).

cyclopentadienide moiety is not involved in the bonding. Chelate coordination of both ligands leads to the occurrence of two organometallic seven-membered ring systems. Their overall bonding characteristics are very similar as has already been observed for **11** and **12** (see above). The observed bond lengths (for details see the legend of Figure 3) indicate a complete π-delocalization at both the $C_5H_3CO(N)$ frameworks with individual characteristics of bond lengths and angles that have been already discussed for the related complexes **11** and **12**.

The coordination polyhedron in **13** around the central zirconium atom is close to ideally octahedral. The respective O−Zr−O, O−Zr−Cl, and Cl−Zr−Cl angles do not deviate much from the expected values of 90° or 180°, respectively (see Figure 3). In the solid state the *cis*-chelate ligands are arranged close to $C_2$-symmetric to give a chiral octahedral geometry of **13** (i.e. a racemate of the respective Λ and Δ enantiomers).

Complex **13** shows the expected characteristic IR features in KBr ($\tilde{\nu}$ = 3412, 3361 (NH), 1585, 1529 (delocalized amide)). The latter bands are almost unchanged when the IR spectrum is monitored in $CDCl_3$ solution (1585, 1531 $cm^{-1}$). This indicates that the solution structure of **13** is very similar to that observed in the solid state.

The NMR spectra indicate that the complex $[C_5H_3(CONHCMe_3)_2]_2ZrCl_2$ **13** also attains a chiral $C_2$-symmetric octahedral structure in solution. The $^1$H-NMR spectrum at 213 K in $CD_2Cl_2$ exhibits the signals of a pair of symmetry-equivalent $[C_5H_3(CONHCMe_3)_2]$ ligands whose “right and left sides” are diastereotopic due to the chiral octahedral molecular geometry.[17] This leads to an observation of an AMX-type $^1$H-NMR spin pattern of the $C_5H_3$ protons (signals at δ 6.64, 6.59, and 5.98 with coupling constants $^3J$ = 4.2 Hz and $^4J$ = 1.8 Hz). There are two N*H* resonances at δ 6.61 and 6.42 and two separate signals of the *tert*-butyl $CH_3$ groups (δ 1.52 and 1.18). The $^{13}$C-NMR spectrum shows the analogous diastereotopic splitting of the −CONH, $C_5H_3$−, and $C(CH_3)_3$ resonances (for details see the Experimental Section).

With increasing temperature the NMR signals of the respective pairs of diastereotopic groups broaden and eventu-

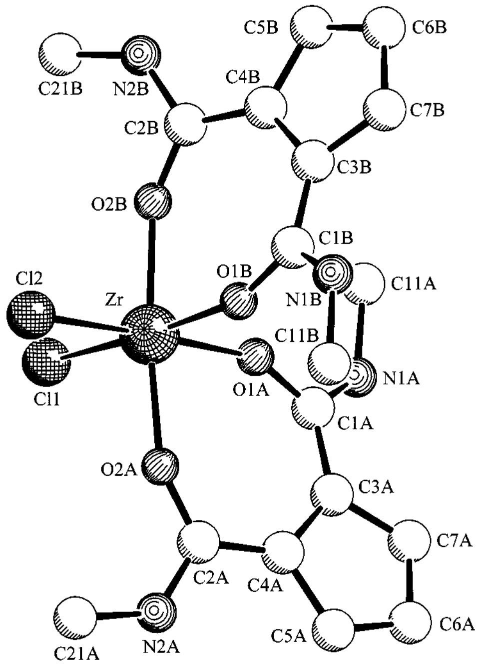
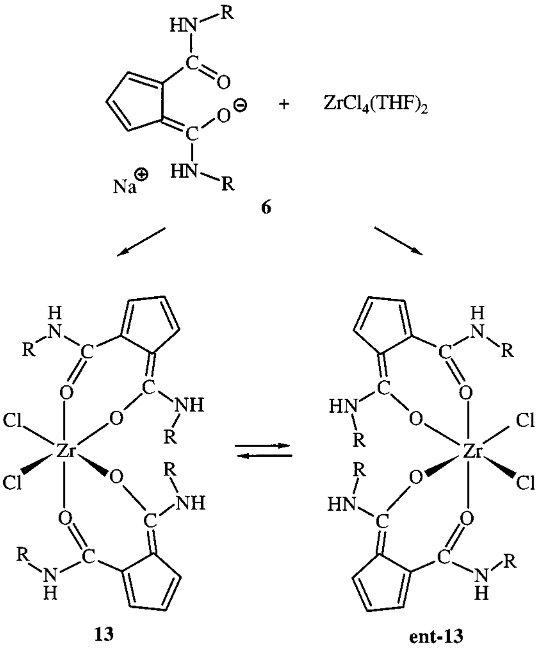


Figure 4. A projection of the octahedral core of complex **13**



Scheme 4. Formation and enantiomerization of **13**

ally undergo coalescence to give a much simplified appearance of the limiting NMR spectra at high temperature. This observation indicates a rather rapid racemization of **13**, i.e. the thermally induced interconversion of the octahedral Λ ⇄ Δ configurated enantiomers of **13** in solution. From the $^1$H-NMR coalescence of the NH resonances of **13** an enantiomerization barrier of $\Delta G^{\neq}_{\mathrm{enant}}$ (298 K) = 14.0 ± 0.3 kcal mol$^{-1}$ was determined at the coalescence temperature. Similar enantiomerization processes have previously been observed for a variety of chiral octahedral bis-chelate ligand zirconium complexes of the general types $(A-B)_2ZrX_2$ or $(A-A)_2ZrX_2$.[18] In view of the coordination properties observed in this study of the complex $[C_5H_3(CONHCMe_3)_2]$-$Cp_2ZrCH_3$ (**9**, see above), and of the properties of the literature systems,[18] it is likely that the Λ ⇄ Δ-isomerization of **13** is initiated by cleavage of one of the Zr−O linkages to generate a coordinatively unsaturated intermediate of a higher molecular symmetry.

## Conclusions

The reaction of cyclopentadienide with two molar equivalents of the alkylisocyanate very selectively leads to the formation of the 1,2-biscarbamoyl substituted cyclopentadienide ligand system. Attachment of this ligand to a variety of zirconium centered frameworks has in most cases investigated in this study led to the formation of $\kappa^2 O,O'$-bonded chelate zirconium complexes. In no case was the attached $C_5H_3$-cyclopentadienide residue involved directly in the bonding of the $[C_5H_3(CONHCMe_3)_2]$ ligand system to the oxophilic early transition metal. In contrast, we and others had previously observed that the attachment of one −COX substituent at a Cp ring does not inhibit its $\eta^5$-$C_5H_4$−COX attachment to a group 4 metal.[4][5] It may be that we here have crossed a borderline, being encountered when a second electron-withdrawing −COX substituent, suitably located at the Cp framework, removes too much additional electron density from the ligand core, beyond which the coordinative ability of the chelate system exceeds that of the normal $\eta^5$-Cp arrangement. It appears that 1,2-COX− (or similarly) substituted cyclopentadienides may be regarded as π-anellated cyclic vinylogues of the ubiquitous β-diketonates and systems derived thereof. Related bis(imino)$C_5H_3$ ligands have just recently been found to show a complexation behavior[19] analogous to our bis(carbamoyl)$C_5H_3$ systems **6**, forming seven-membered chelate complex systems. Also, a variety of troponolato chelate complexes have recently been described.[20] Their ligand systems may be regarded as structural isomers of the $C_5H_3(COX)_2^-$ or $C_5H_3[CR(=NR')]_2^-$ frameworks. Opening viable synthetic pathways to novel chelate systems such as those described here and in the related recent studies could be of interest in view of the actual development and the search for new homogeneous non-metallocene group 4 metal derived Ziegler systems.[21] The catalytic properties of complexes derived from $[C_5H_3(CONHR)_2]^-$ ligand systems are currently investigated in our laboratory.

## Experimental Section

**General Information:** All reactions with organometallic reagents or substrates were carried out under argon using Schlenk-type glassware or in a glove-box. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. − The following instruments were used for spectroscopic and physical characterization of the compounds: Bruker AC 200P ($^1$H: 200.13, $^{13}$C: 50.3 MHz), Bruker ARX 300, and Varian Unity Plus ($^1$H: 599.2, $^{13}$C: 150.8 MHz) NMR spectrometers (spectral assignments were usually secured by GCOSY, GHSQC, and

GHMBC experiments[22]); Nicolet 5 DXC FT-IR spectrometer; melting points: DSC 2010 (Texas Instruments); elemental analyses: Foss Heraeus CHN-Rapid; X-ray crystal structure analyses: Data sets were collected with Enraf Nonius CAD4 and MACH3 diffractometers, connected to sealed tube or rotating anode generators. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93 and SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102777−102779. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [Fax: int. code +44 (1223) 336-033, E-mail: deposit@ccdc.cam.ac.uk].

The reagents $CpZrCl_3(THF)_2$[13,15a] and $Cp_2Zr(CH_3)Cl$[9] were prepared according to literature procedures.

**[1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]sodium (6):** A solution of 12.8 g (129.0 mmol, 15.2 mL) of *tert*-butyl isocyanate in 30 mL of tetrahydrofuran was added dropwise at 0°C to a solution of 5.1 g (58.0 mmol) of CpNa in 80 mL of tetrahydrofuran. The dark yellow colored reaction mixture was allowed to warm to room temperature overnight. Solvent was then removed in vacuo, and the solid residue was washed once with pentane to give the product **6** as a pale yellow solid, m. p. 178°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3442 $cm^{-1}$, 3380 (NH), 1603, 1505 (CONH). − $^1H$ NMR ([$D_6$]benzene/[$D_8$]THF, 10:1.5): $\delta$ = 7.90 ( br s, 2 H, NH), 6.73 (d, $^3J$ = 3.6 Hz, 2 H), 6.25 (t, $^3J$ = 3.6 Hz, 1 H, $C_5H_3$), 1.44 (s , 18 H, $CMe_3$). − $^{13}C$ NMR ([$D_6$]benzene/[$D_8$]THF, 10:1.5): $\delta$ = 170.7 (CONH), 116.4 (*ipso*-C, Cp), 115.1, 108.8 (CH of Cp), 50.3 and 29.6 ($CMe_3$). − $C_{15}H_{23}N_2NaO_2$ (286.4): calcd. C 62.92, H 8.10, N 9.78; found: C 62.53, H 8.42, N 9.12.

**1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadiene (7):** Water (50 mL) and acetic acid (1 mL) was added to an ethereal solution (50 mL) of 304 mg (1.06 mmol) of **6** at ambient temperature. The mixture was vigorously stirred and then the organic phase was separated. The aqueous phase was extracted with ether (2× 20 mL). The combined organic solutions were dried, solvent was removed in vacuo and the residue chromatographed at silicagel to give 95 mg (34%) of **7**, which was only spectroscopically characterized. − $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 19.66 (br s, 1 H, OH), 6.53 (d, $^3J$ = 3.9 Hz, 2 H, $C_5H_3$), 6.11 (t, $^3J$ = 3.9 Hz, 1 H, $C_5H_3$), 6.09 (br s, 2 H, NH), 1.46 (s, 18 H, $CMe_3$). − $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 168.2 (C=O), 117.0, 113.6 (CH of $C_5H_3$), 112.3 (*ipso*-C of $C_5H_3$), 52.4 and 29.1 (*tert*-butyl).

**[1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]bis($\eta^5$-cyclopentadienyl)methylzirconium (9):** Chlorobis($\eta^5$-cyclopentadienyl)methylzirconium (**8**) (500 mg, 1.8 mmol) was treated with [1,2-bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]sodium (**6**) (530 mg, 1.8 mmol) at −78°C in 40 mL of toluene. The yellow colored mixture was stirred overnight and allowed to warm to room temperature. Filtration and solvent removal gives the yellow solid **9** in 60% yield (530 mg), m.p. 98°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3443 $cm^{-1}$, 3091 (NH), 1643, 1586 (CONH) (in $CDCl_3$ solution: 1648, 1580). − $^1H$ NMR (599.9 MHz, $CD_2Cl_2$, 213 K): $\delta$ = 12.91 (br s, 1 H, NH), 6.44 (dd, $^3J$ = 3.6 Hz, $^4J$ = 1.8 Hz, 1 H), 6.22 (s, 10 H, Cp), 6.03 (dd, $^3J$ = 3.6 Hz, $^4J$ = 1.8 Hz, 1 H), 6.00 (br s, 1 H, NH), 5.93 (t, $^3J$ = 3.6 Hz, 1 H, $C_5H_3$), 1.33 (s, 9 H, $CMe_3$), 1.23 (s, 9 H, $CMe_3$), 0.38 (s, 3 H, Me). − $^{13}C$ NMR (150.8 MHz, $CD_2Cl_2$, 213 K): $\delta$ = 168.6 (CONH), 168.4 (CONH), 119.1, 117.5 (CH of $C_5H_3$), 112.1 (CH of $C_5H_5$), 110.6, 110.7 (*ipso*-C of $C_5H_3$), 109.7 (CH of $C_5H_3$), 51.1, 50.4 ($CMe_3$), 29.7 (Me), 28.5, 28.3 ($CMe_3$). − $C_{26}H_{36}N_2O_2Zr$ (499.8): calcd. C 62.48, H 7.26; found: C 62.38, H 7.29.

**[1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]($\eta^5$-cyclopentadienyl)dichlorozirconium (11):** $CpZrCl_3 \cdot 2$ THF (5.77 g, 14.0 mmol) was treated with [1,2-bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]sodium (**6**) (4.06 g, 14.0 mmol) in 50 mL of tetrahydrofuran at −78°C. The reaction mixture was stirred and allowed to warm to room temperature overnight. It was filtered and the solvent was removed in vacuo to give the product **11** as a pale yellow powder in 74% yield (5.80 g), m.p. 180°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3412 $cm^{-1}$, 3322 (NH), 1570, 1529 (CONH) (in $CDCl_3$ solution: 1576, 1525). − $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 6.70 (d, $^3J$ = 3.8 Hz, 2 H, $C_5H_3$), 6.41 (br s, 2 H, NH), 6.38 (s, 5 H, $C_5H_5$), 6.10 (t, $^3J$ = 3.8 Hz, 1 H, $C_5H_3$), 4.00, 1.80 (m, each 4 H, THF), 1.46 (s, 18 H, $CMe_3$). − $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ = 169.7 (CONH), 121.4, 114.3 (CH of $C_5H_3$), 117.7 (CH of $C_5H_5$), 113.9 (*ipso*-C of $C_5H_3$), 71.1 ($CH_2$ of THF), 53.3, 29.3 ($CMe_3$), 25.5 ($CH_2$ of THF). − $C_{24}H_{36}Cl_2N_2O_3Zr$ (562.7): calcd. C 51.23, H 6.45, N 4.98; found: C 51.06, H 6.61, N 5.09.

**X-ray crystal structure analysis of 11:** Formula $C_{24}H_{36}Cl_2N_2O_3Zr$, *M* = 562.7, colorless crystal, 0.40 × 0.25 × 0.10 mm, *a* = 10.725(1), *b* = 17.410(2), *c* = 14.699(2) Å, $\beta$ = 100.25(1)°, *V* = 2700.8(5) $Å^3$, $\rho_{calc}$ = 1.384 g $cm^{-3}$, *F*(000) = 1168 e, $\mu$ = 6.31 $cm^{-1}$, empirical absorption correction via $\varphi$ scan data (0.937 $\le C \le$ 0.999), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), $\lambda$ = 0.71073 Å, *T* = 223 K, $\omega/2\theta$ scans, 5789 reflections collected (-*h*, +*k*, ±*l*), [$(\sin\theta)/\lambda$] = 0.62 $Å^{-1}$, 5493 independent and 3744 observed reflections [$I \ge 2\ \sigma(I)$], 301 refined parameters, *R* = 0.047, $wR^2$ = 0.108, max. residual electron density 0.69 (-0.74) e $Å^{-3}$, hydrogens calculated and refined as riding atoms.

**[1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]trichlorozirconium (12):** [1,2-Bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]sodium (**6**) (2.80 g, 9.8 mmol) was treated with $ZrCl_4 \cdot 2$ THF (3.70 g, 9.8 mmol) in 100 mL of toluene for 20 h at 60°C. The reaction mixture was filtered and the residue was extracted with dichloromethane to give 1.8 g (35%) of **12** as a pale yellow solid (from the toluene layer the disubstituted compound **13** was obtained as a side product). **12**: m.p. 243°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3419 $cm^{-1}$, 3347 (NH), 1577, 1535 (CONH) (in $CDCl_3$ solution: 1575, 1530). − $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 6.69 (d, $^3J$ = 3.9 Hz, 2 H, $C_5H_3$), 6.55 (br s, 2 H, NH), 6.07 (t, $^3J$ = 3.9 Hz, 1 H, $C_5H_3$), 4.16, 1.76 (m, each 4 H, THF), 1.54 (s, 18 H, $CMe_3$). − $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ = 168.7 (CONH), 123.0, 115.3 (CH of $C_5H_3$), 113.1 (*ipso*-C of $C_5H_3$), 75.5 ($CH_2$ of THF), 54.3, 29.4 ($CMe_3$) 25.7 ($CH_2$ of THF). − $C_{19}H_{31}N_2O_3Cl_3Zr$ (533.0): calcd. C 42.81, H 5.86, N 5.26; found: C 42.70, H 6.50, N 5.42.

**X-ray Crystal Structure Analysis of 12:** Formula $C_{19}H_{31}N_2O_3Cl_3Zr$, *M* = 533.0, yellow crystal, 0.25 × 0.15 × 0.10 mm, *a* = 9.805(2), *b* = 15.932(4), *c* = 16.082(3) Å, $\beta$ = 105.37(2)°, *V* = 2422.4(9) $Å^3$, $\rho_{calc}$ = 1.462 g $cm^{-3}$, *F*(000) = 1096 e, $\mu$ = 8.06 $cm^{-1}$, empirical absorption correction via $\varphi$ scan data (0.955 $\le C \le$ 0.999), *Z* = 4, monoclinic, space group $P2_1$/n (No. 14), $\lambda$ = 0.71073 Å, *T* = 223 K, $\omega/2\theta$ scans, 5214 reflections collected (+*h*, +*k*, ±*l*), [$(\sin\theta)/\lambda$] = 0.62 $Å^{-1}$, 4923 independent and 3550 observed reflections [$I \ge 2\ \sigma(I)$], 265 refined parameters, *R* = 0.032, $wR^2$ = 0.072, max. residual electron density 0.51 (−0.57) e $Å^{-3}$, hydrogens calculated and refined as riding atoms.

**Bis[1,2-bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]dichlorozirconium (13):** A reaction mixture of [1,2-bis(*N*-*tert*-butylcarbamoyl)cyclopentadienyl]sodium (**6**, 758 mg, 2.7 mmol) and $ZrCl_4 \cdot 2$ THF (500 mg, 1.3 mmol) in 50 mL of toluene was stirred for 14 h at 60°C and then filtered. Solvent was removed in vacuo to yield 600 mg (65%) of **13** as a yellow solid, m.p. 269°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3412 $cm^{-1}$, 3361 (NH), 1585, 1529 (CONH) (in $CDCl_3$ solution: 1585, 1531). − $^1$H NMR ([D$_6$]benzene): $\delta$ = 6.43 (d, $^3J$ = 3.8 Hz, 4 H, $C_5H_3$), 6.36 (t, $^3J$ = 3.8 Hz, 2 H, $C_5H_3$), 6.00 (br s, 4 H, NH), 1.25 (br, 36 H, CMe$_3$). − $^{13}$C NMR ([D$_6$]benzene): $\delta$ = 168.9 (CONH), 122.7 (CH of $C_5H_3$), 114.4 (*ipso*-C of $C_5H_3$), 114.0 (CH of $C_5H_3$), 53.1, 29.1 (CMe$_3$). − $C_{30}H_{46}N_4O_4Cl_2Zr \cdot 1/3\ C_7H_8$ (715.9): calcd. C 53.69, H 6.90, N 7.83; found: C 53.60, H 7.28, N 7.43.

**X-ray Crystal Structure Analysis of 13:** Formula $C_{30}H_{46}N_4O_4Cl_2Zr \cdot C_6H_6$, $M$ = 766.9, yellow crystal, 0.25 × 0.20 × 0.10 mm, $a$ = 13.058(2), $b$ = 12.735(3), $c$ = 24.172(3) Å, $\beta$ = 96.43(1)°, $V$ = 3994.4(12) Å$^3$, $\rho_{calc}$ = 1.275 g cm$^{-3}$, $F(000)$ = 1608 e, $\mu$ = 4.49 cm$^{-1}$, empirical absorption correction via $\varphi$ scan data ($0.981 \leq C \leq 0.999$), $Z$ = 4, monoclinic, space group $P2_1/n$ (No. 14), $\lambda$ = 0.71073 Å, $T$ = 223 K, $\omega/2\ \theta$ scans, 8282 reflections collected ($\pm h$, $-k$, $-l$), $[(\sin\theta)/\lambda]$ = 0.62 Å$^{-1}$, 8090 independent and 5503 observed reflections [$I \geq 2\ \sigma(I)$], 448 refined parameters, $R$ = 0.037, $wR^2$ = 0.085, max. residual electron density 0.40 (−0.32) e Å$^{-3}$, hydrogens calculated and refined as riding atoms.

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