Insertion Reactions at Cyclobutylene-Bridged *ansa*-Metallocene Complexes: A Quest for the Influence of Covering Phenylene Units

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The cyclobutylene−bis(2-indenyl)zirconium dichloride complex (**4**), derived from an intramolecular photochemical [2+2] cycloaddition reaction of bis[2-(methylethenyl)indenyl]zirconium dichloride (**3**), was reacted with methyllithium or phenyllithium to yield the corresponding cyclobutylene−bis(2-indenyl)-zirconium dimethyl (**12**) or diphenyl (**13**) complex, respectively. Insertion of carbon monoxide into the Zr−phenyl linkage of **13** yielded the "O-inside" η^2-benzoyl *ansa*-zirconocene complexes **18**-*syn*/*anti*, which were characterized by X-ray diffraction. *tert*-Butyl isocyanide insertion into the Zr−CH_3 bond of **12** gave the "N-inside" η^2-iminoacyl metallocene isomers **17**-*syn* and **17**-*anti*; the latter was characterized by X-ray diffraction. Under kinetic control *tert*-butyl isonitrile insertion into **12** gave the "N-outside" η^2-iminoacyl metallocene isomers **25**-*syn*/**25**-*anti*, which rearranged to **17**-*syn*/*anti* at 243 K with Gibbs activation energies of $\Delta G^{\ddagger}_{rearr} = 18.0/17.8 \pm 0.3$ kcal·mol^{-1}, respectively. The analogous rearrangement of the "N-outside" to "N-inside" isomers of the corresponding cyclobutylene−bis(cyclopentadienyl)Zr-(η^2-iminoacyl) reference systems (**23**-*syn*/*anti* to **24**-*syn*/*anti*) is much faster (203 K: $\Delta G^{\ddagger}_{rearr} = 14.7/14.9 \pm 0.3$ kcal·mol^{-1}). Similar differences in the kinetic "N-outside" to thermodynamic "N-inside" η^2-iminobenzoyl metallocene isomerization were observed for the *tert*-butyl isonitrile insertion products of the cyclobutylene−bis(2-indenyl)$ZrPh_2$ (**13**) and cyclobutylene−bis(C_5H_4)$ZrPh_2$ (**15**) systems, which indicates a pronounced influence of the covering phenylene groups on the σ-ligand chemistry in these rigid *ansa*-metallocene systems.

Introduction

Bis(alkenyl-Cp)$ZrCl_2$ complexes (**1**) yield the *ansa*-metallocenes (**2**) by photochemical [2+2] cycloaddition.[1,2] Likewise, bis(2-alkenylindenyl)zirconium dichloride complexes **3** also readily undergo an intramolecular photochemical [2+2] cycloaddition reaction to yield the unique cyclobutylene-bridged *ansa*-metallocenes (**4**).[3−5] In these, the anellated indenyl phenylene units are rigidly held above and below the central metallocene σ-ligand plane. There is some indication that groups extending from the central plane at the front metallocene sector might interact with the covering phenylene clouds. Such indication comes from the reaction of complex **4** with "butadiene-magnesium" (**5**) to exclusively yield a single *s-trans*-η^4-butadiene metallocene isomer (**6**).[3] Complex **6** features some C−H/π-interaction[6] between the butadiene *meso*-H's and their respective covering phenylene π-systems, as judged by the pronounced "upfield" ^{1}H NMR shift[7] of the butadiene *meso*-hydrogen resonances [δ −1.45/−1.55 observed for **6** as compared to δ 1.34 for the parent (*s-trans*-η^4-butadiene)-zirconocene system]. However, the energetic magnitude of this interaction in **6** remains unknown at present.

To learn about the potential influence of the covering phenylene groups, we thought it might be useful to carry out specific reactions at the framework of **4** that at some stage would require a rotation of ligands out of the σ-plane. Comparing their rates with those of the otherwise same reactions taking place at the unobstructed frameworks **2** would provide some indication about the influence of the covering anellated phenylene rings and their potential interaction with ligand systems attached at the front sector of the bent metallocene wedge.

The reaction sequences followed upon addition of carbon monoxide or an alkyl isonitrile to σ-hydrocarbyl derivatives derived from **4** and **2** might be suited for such an assessment of potential σ-ligand/phenylene interactions along a reaction coordinate.[8] It is well established that, for example, CO adds

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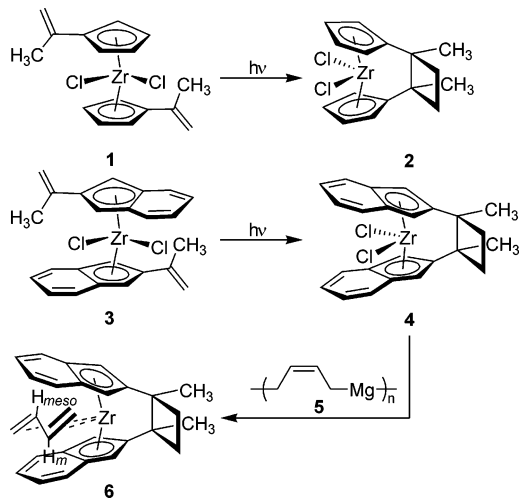
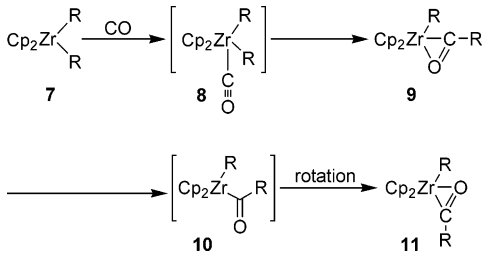
Scheme 1



Scheme 2



to the 16-electron metallocene complexes Cp_2ZrR_2 (**7**) from the side.[9−12] The resulting "lateral" carbonyl metallocene intermediate (**8**) reacts rapidly to yield the thermodynamically less favored "O-outside" η^2-acyl metallocene isomer (**9**), which has in a few cases been observed experimentally.[9] This then rearranges to the favored "O-inside" η^2-acyl metallocene isomer (**11**)[13] via rotation at the η^1-acyl metallocene (**10**) intermediate stage (see Scheme 2).[10,14] We might expect that an influence of the covering phenylene units of **4** might become noticeable in the course of this rotational process. We, therefore, have prepared a series of σ-aryl and σ-alkyl metallocene complexes derived from **4** and **2** and investigated and compared their behavior upon treatment with CO or an isonitrile reagent.

Results and Discussion

Preparation and Characterization of the Starting Materials. The cyclobutylene-bridged bis(indenyl)$ZrCl_2$ starting material (**4**) was synthesized as previously described by us (see Scheme 3).[3] Its treatment with excess methyllithium (6 molar equiv) gave the corresponding dimethyl Zr complex **12** in 72% yield (see Scheme 3). Complex **12** shows the NMR features of a C_s-symmetric *ansa*-metallocene. Its NMR spectrum features the typical AA′BB′ pattern of the cyclobutylene $-CH_2-CH_2-$ protons (δ 1.66/2.19) and a single CH_3 resonance [δ 1.17, s, 6H; ^{13}C NMR signals of the dimethylcyclobutylene bridge at δ 26.2 (CH_3), 30.6 (CH_2), 49.1 (quat. C)]. Most significantly there is a pair of Zr−CH_3 ^{1}H NMR signals both shifted considerably to high field [δ −0.23 (*syn*-CH_3), −1.75 (*anti*-CH_3); corresponding ^{13}C NMR resonances at δ 31.3 and 41.4]. The large negative shifting of the *anti*- versus the *syn*-[Zr]−CH_3 ^{1}H NMR resonance indicates a markedly unsymmetrical structure with the two σ-methyl ligands being subjected differently to the deshielding effect of the covering phenylene moieties of the cyclobutylene-bridged indenyl ligands inside this rigid *ansa*-metallocene framework (see Figure 1).

This was confirmed by the X-ray crystal structure analysis of complex **12** (single crystals were obtained from pentane at −30 °C). The structure shows a typical bent metallocene unit[15] with pertinent bond angles of Cp(centroid)−Zr(1)−Cp(centroid) = 126.0° and C(13A)−Zr(1)−C(13B) = 98.55(11)° (values for one of the three independent molecules in the crystal). The pair of η^5-indenyl ligands is linked by the 1,2-dimethylcyclobutylene bridge [typical bond lengths C(10A)−C(10B) 1.572(4) Å, C(11A)−C(11B) 1.512(5) Å, C(10A)−C(11A) 1.535(4) Å, C(10B)−C(11B) 1.593(5) Å]. In the crystal complex **12** is not strictly C_s-symmetric and, in addition, the bent metallocene is internally twisted such that the two Zr-bonded methyl groups experience distinctly different steric and electronic environments. The *syn*-CH_3 group (*syn* orientation relative to the cyclobutylene $-CH_2-CH_2-$ unit) has thus become rotated away from the covering phenylene groups, whereas the *anti*-CH_3 σ-ligand is placed between the covering π-clouds of both the indenyl phenylene groups (see Figure 2). The corresponding bond lengths Zr(1)−C(13A) (2.269(3) Å) and Zr(1)−C(13B) (2.239-(3) Å) are slightly different.[16]

Treatment of **4** with a ca. 3-fold excess of phenyllithium[17] gave the corresponding [Zr]Ph_2 complex **13** (isolated in 55% yield). It features the typical ^{1}H NMR signals of the symmetry-equivalent pair of methyl groups at the cyclobutylene bridge. The NMR chemical shifts of the Zr-bond σ-phenyl ligands are slightly but distinctively different from each other [*anti*-phenyl: δ 6.81(2H, *o*), 6.95(1H, *p*), 6.97(2H, *m*); *syn*-phenyl: δ 7.05 (2H, *m*), 7.08(2H, *o*), 7.11(1H, *p*)].

Complex **13** was characterized by X-ray diffraction (single crystals from pentane). As expected, it features two σ-phenyl groups at characteristically different positions at the rigid bent *ansa*-metallocene framework. Again, it is the *anti*-σ-ligand

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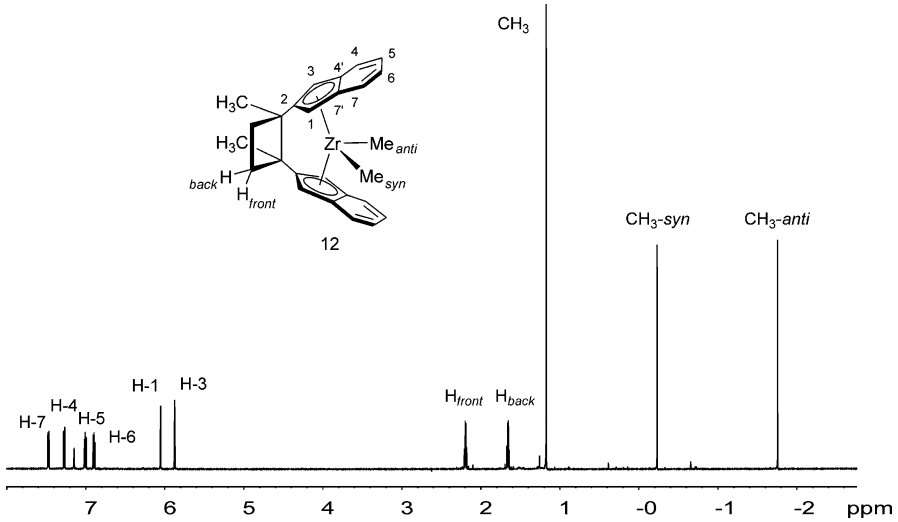
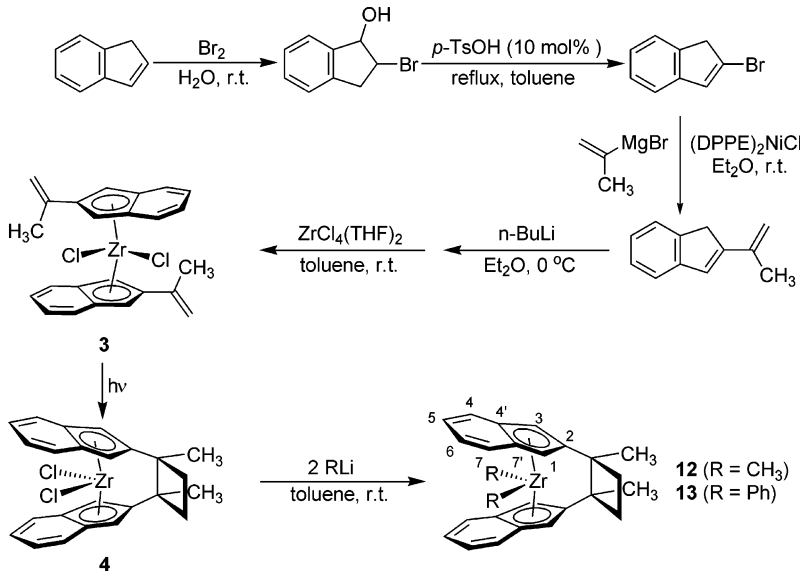


Figure 1. ^{1}H NMR spectrum (benzene-d_6, 600 MHz, 298 K) of complex **12**.

Scheme 3



(C(33)−C(38)) that is located inside between the covering phenylene groups of the indenyl ligands. The *anti*-phenyl group (Zr−C(33): 2.278(3) Å) is rotated slightly from the ideal σ-ligand plane (angle between the C(13), Zr, C(33) and the C(33)−C(38) planes: 23.0°). The *syn*-phenyl ligand (Zr−C(13): 2.300(3) Å) is oriented slightly outside the indenyl phenylene range and slightly rotated in the same direction out of σ-ligand plane (C(13), Zr, C(33) plane vs C(13)−C(18) plane: 23.6°) as its neighboring *anti*-Ph ligand. The C(13)−Zr−C(33) σ-ligand angle at the metallocene core of **13** amounts to 108.13(13)°. The bridging cyclobutylene moiety in complex **13** is slightly puckered (angle between the C(10), C(30), C(11) and C(10), C(30), C(31) planes: 19.1°).

As we will see, it was necessary to have the corresponding bis(hydrocarbyl) metallocene complexes derived from the cyclobutylene-bridged *ansa*-bis-Cp zirconium system available for comparison. The *ansa*-zirconocene dichloride starting material (**2**) was prepared by means of a variation of a fulvene route,[18,19] as we had recently described.[28] Treatment of 6,6-dimethylfulvene with LDA led to the 1-methylethenyl-CpLi reagent that was transmetalated to yield the alkenyl-functionalized zirconocene dichloride complex (**1**). This gave the *ansa*-metallocene (**2**) upon photolysis. The reaction of **2** with a slight excess of methyllithium (ca. 2.5 equiv) in ether gave the cyclobutylene-bridged *ansa*-zirconocene dimethyl complex **14** (60% isolated). The ^{1}H NMR spectrum shows that the signals of a pair of inequivalent CH_3 σ-ligands at zirconium are at δ −0.22 (*anti*-CH_3) and −0.10 (*syn*-CH_3). It should be noted that these signals are not nearly as much differentiated nor high field shifted as in the corresponding indenyl-derived system **12** (see above), which emphasizes the pronounced spectroscopic influence of the anellated covering phenylene rings in **12** (and **13**) on the σ-ligand located in the bisecting metallocene σ-plane between them.

The diphenyl *ansa*-zirconocene complex (**15**) was prepared by treatment of complex **2** with a 2-fold excess of phenyllithium

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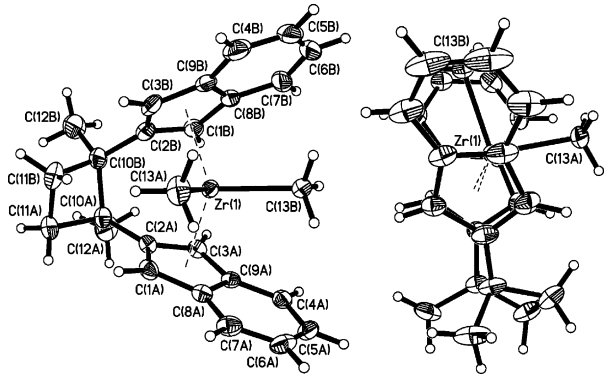

Figure 2. Two views of the molecular structure of the *ansa*-zirconocene dimethyl complex **12**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) of the three crystallographically independent molecules and angles (deg) for one: Zr(1)−C(13B) 2.239(3), Zr(1)−C(13A) 2.269(3), C(10A)−C(12A) 1.522(4), C(10A)−C(11A) 1.535(4), C(10A)−C(10B) 1.572(4), C(11A)−C(11B) 1.512(5), C(10B)−C(12B) 1.489(4), C(10B)−C(11B) 1.593(5), Zr(2)−C(13D) 2.242(3), Zr(2)−C(13C) 2.271(3), C(10C)−C(12C) 1.527(4), C(10C)−C(11C) 1.545(4), C(10C)−C(10D) 1.570(4), C(11C)−C(11D) 1.514(5), C(10D)−C(12D) 1.495(4), C(10D)−C(11D) 1.573(5), Zr(3)−C(13E) 2.235(3), Zr(3)−C(13F) 2.256(3), C(10E)−C(12E) 1.524(4), C(10E)−C(11E) 1.545(4), C(10E)−C(10F) 1.588(4), C(11E)−C(11F) 1.540(4), C(10F)−C(12F) 1.515(4), C(10F)−C(11F) 1.548(4); C(13B)−Zr(1)−C(13A) 98.55(11), C(2A)−C(10A)−C(12A) 109.8(3), C(2A)−C(10A)−C(11A) 112.1(3), C(11A)−C(10A)−C(10B) 89.4(2), C(12A)−C(10A)−C(11A) 116.7(3), C(12A)−C(10A)−C(10B) 115.3(3), C(11B)−C(11A)−C(10A) 89.6(2), C(10A)−C(10B)−C(11B) 85.5(2), C(2B)−C(10B)−C(10A) 117.4(2), C(2B)−C(10B)−C(11B) 115.7(3), C(12B)−C(10B)−C(2B) 109.8(3), C(12B)−C(10B)−C(10A) 117.0(3), C(12B)−C(10B)−C(11B) 109.5(3), C(11A)−C(11B)−C(10B) 89.5(3); for additional values see the text and the Supporting Information.

in ether and isolated as a pale yellow solid in ca. 60% yield. It shows the typical NMR features of the cyclobutylene-bridged *ansa*-bisCp[Zr] system (for details see the Experimental Section) and of two only slightly differentiated σ-phenyl groups at zirconium [δ 7.06 (*p*), 7.15 (*m*), 7.32 (*o*) of *anti*-Ph; δ 7.08 (*p*), 7.17 (*m*), 7.45 (*o*) of *syn*-Ph].

Insertion Reactions under Thermodynamic and under Kinetic Control. The reaction of the dimethyl *ansa*-zirconocene complex **12** with CO did not give sufficiently clean products, potentially because of the previously proven pronounced reversibility of the carbonylation reactions especially of many dimethyl zirconocene complexes.[7] In contrast, the reaction of the dimethyl *ansa*-zirconocene complex **12** with *tert*-butyl isonitrile (**16**) at ambient conditions proceeded cleanly to give a ca. 2:1 mixture of two stereoisomeric monoinsertion products (**17**-*syn*, **17**-*anti*, isolated in a combined yield of 56%). We assume that these products, which are formed under these conditions under thermodynamic control, are the η^2-iminoacyl zirconocene isomers that both exhibit the iminoacyl nitrogen atom coordinated to the central position in the bent metallocene σ-ligand plane ("N-inside" isomers).[20−24]

The product (**17**-*syn*), which is defined by a *cis*-relationship of the remaining [Zr]−CH_3 group with the cyclobutylene −CH_2−CH_2− side, features a Zr−CH_3 ^{1}H NMR resonance at δ 0.26 (s, 3H, ^{13}C: δ 14.4) and the CH_3 signal of the newly formed η^2-imino-acyl group at δ 2.24 (^{13}C: δ 20.8). The iminoacyl N=*C* ^{13}C NMR resonance is very typical at δ 233.1 (for additional NMR data see the Experimental Section). In contrast, the **17**-*anti* isomer features a slightly highfield shifted ^{1}H NMR [Zr]−CH_3 resonance at δ −0.42 (^{13}C: δ 19.6) that indicates some shielding by the covering indenyl phenylene π-system. The **17**-*anti* N=*C* ^{13}C NMR resonance is observed at δ 234.5.[25]

The general structural assignment of the products as "N-inside" η^2-iminoacyl *ansa*-zirconocene complexes (**17**) was confirmed by an X-ray crystal structure determination of complex **17**-*anti*. Single crystals were obtained from pentane. The structure features a cyclobutylene-bridged *ansa*-metallocene that contains a "pentacoordinated" central zirconium atom. There are two independent molecules in the crystal (parameters of the second molecule centered around Zr are given in parentheses). Both feature some structural disorder in the *ansa*-bridge that could not adequately be resolved. Therefore, the geometrical parameters of this part of the structure will not be discussed. The zirconium center is rather uniformly η^5-coordinated to the Cp subunits of the indenyl rings [Zr−C(Cp) distances ranging from 2.518(3) (2.501(2)) to 2.635(3) Å (2.641(2) Å)]. The most characteristic structural feature of complex **17** in the crystal is the presence of an η^2-iminoacyl ligand in the central metallocene σ-ligand plane that features the nitrogen atom with its bulky *tert*-butyl substituent in the central position ("N-inside" isomer) between the Zr(1)−C(14) [2.196(2) Å (2.196(2) Å)] and the Zr(1)−C(13) [2.337(3) Å (2.339(3) Å)] vectors. The short N(1)−C(14) distance [1.271(3) Å (1.267(3) Å)] lies within the typical C=N double bond range. The Zr−N bond length is 2.242(2) Å (2.234(2) Å). The angles inside the Zr, N, C three-membered ring substructure of complex **17** amount to 71.4(1)° (71.8(1)°) (Zr−N−C(14)), 75.3(1)° (75.0(1)°) (Zr−C(14)−N), and 33.3(1)° (33.2(1)°) (N−Zr−C(14)). The C(14)−N−C(16) angle amounts to 130.7(2)° (130.7(2)°), and consequently, the remaining angle at nitrogen (Zr−N−C(16)) is very large, at 157.9(2)° (157.5(2)°). The pair of the remaining angles at C(14) show a similar variation: Zr−C(14)−C(15): 153.7(2)° (153.3(2)°), N−C(14)−C(15): 130.9(2)° (131.6(2)°). The C(14)−Zr−C(13) "σ-ligand angle" in **17** is found to be 119.1(1)° (118.8(1)°). In the projection (see Figure 4) this positions the σ-CH_3 group just at the edge of the influence of the covering phenylene groups of the framework indenyl ligands, a feature that has probably led to the typical ^{1}H NMR chemical shift value observed for this isomer of **17** in solution (see above).

(20) See for example: Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41−48. Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393−5396. Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390−402, 6068−6076. Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Organometallics* **1992**, *11*, 876−884. Sebastián, A.; Royo, P.; Gómez-Sal, P.; Ramírez de Arellano, C. *Eur. J. Inorg. Chem.* **2004**, 3814−3821.

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(24) Martinez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1988**, *340*, 187−193. Carmona, E.; Palma, P.; Paneque, M.; Povera, M. L. *Organometallics* **1990**, *9*, 583−588.

(25) The **17**-*syn*/*anti* NMR signals show some solvent dependence.

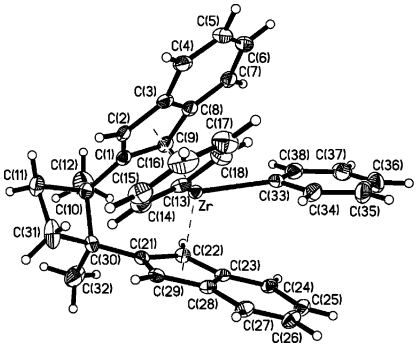


Figure 3. View of the molecular structure of complex **13**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): Zr−C(33) 2.278(3), Zr−C(13) 2.300(3), C(10)−C(12) 1.517(5), C(10)−C(11) 1.539(5), C(10)−C(30) 1.591(5), C(11)−C(31) 1.665(7), C(30)−C(31) 1.551(6), C(30)−C(32) 1.510(5); C(33)−Zr−C(13) 108.13(13), C(12)−C(10)−C(1) 110.0(3), C(12)−C(10)−C(11) 112.4(3), C(1)−C(10)−C(11) 112.2(3), C(12)−C(10)−C(30) 117.3(3), C(1)−C(10)−C(30) 112.1(3), C(11)−C(10)−C(30) 91.7(3), C(10)−C(11)−C(31) 85.9(3), C(32)−C(30)−C(21) 111.3(3), C(32)−C(30)−C(31) 112.9(4), C(21)−C(30)−C(31) 117.3(3), C(32)−C(30)−C(10) 109.9(3), C(21)−C(30)−C(10) 115.4(3), C(31)−C(30)−C(10) 88.1(3), C(30)−C(31)−C(11) 88.5(3); for additional values see the text and the Supporting Information.

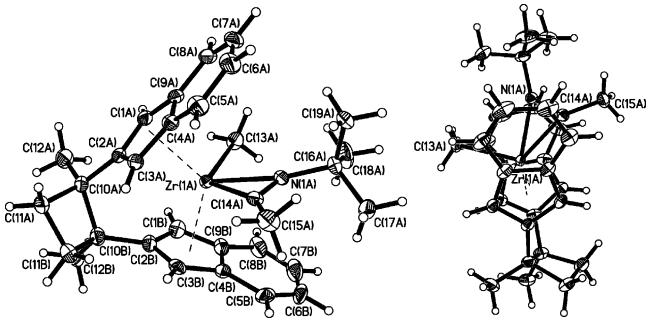


Figure 4. General view and top projection of the molecular structure of complex **17**-*anti*. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg) of the two independent molecules: C(13A)−Zr(1A) 2.337(3), C(14A)−N(1A) 1.271(3), C(14A)−C(15A) 1.506(4), C(14A)−Zr(1A) 2.196(2), N(1A)−Zr(1A) 2.242(2), C(13C)−Zr(1C) 2.339(3), C(14C)−N(1C) 1.267(3), C(14C)−C(15C) 1.503(3), C(14C)−Zr(1C) 2.196(2), N(1C)−Zr(1C) 2.234(2); N(1A)−C(14A)−C(15A) 130.9(2), N(1A)−C(14A)−Zr(1A) 75.3(1), C(15A)−C(14A)−Zr(1A) 153.7(2), C(14A)−N(1A)−C(16A) 130.7(2), C(14A)−N(1A)−Zr(1A) 71.4(1), C(16A)−N(1A)−Zr(1A) 157.9(2), C(14A)−Zr(1A)−N(1A) 33.3(1), C(14A)−Zr(1A)−C(13A) 119.1(1), N(1A)−Zr(1A)−C(13A) 86.0(1), N(1C)−C(14C)−C(15C) 131.6(2), N(1C)−C(14C)−Zr(1C) 75.0(1), C(15C)−C(14C)−Zr(1C) 153.3(2), C(14C)−N(1C)−C(16C) 130.7(2), C(14C)−N(1C)−Zr(1C) 71.8(1), C(16C)−N(1C)−Zr(1C) 157.5(2), C(14C)−Zr(1C)−N(1C) 33.2(1), C(14C)−Zr(1C)−C(13C) 118.8(1), N(1C)−Zr(1C)−C(13C) 85.8(1); additional values are given in the text and in the Supporting Information.

The carbonylation of the diphenyl *ansa*-zirconocene complex **13** (1 bar CO pressure, ambient temperature, 15 min) goes rapidly to completion and yields a ca. 45:55 mixture of the thermodynamic "O-inside" η^2-acyl zirconocene complexes **18**-*syn* and **18**-*anti* (see Scheme 6). The complexes show the typical ^{1}H and ^{13}C NMR spectra of the cyclobutylene-bridged *ansa*-metallocene frameworks. The ^{13}C NMR acyl resonances for **18**-*syn* and **18**-*anti* were found downfield at δ 298.9 and 300.8, respectively.[7]

Single crystals of the complexes **18**-*syn*/*anti* were obtained from pentane at +6 °C, which allowed the characterization of

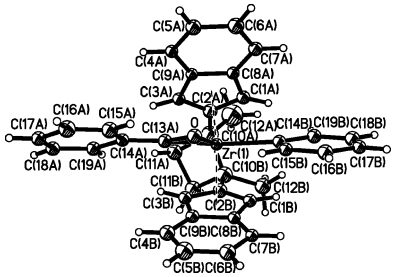
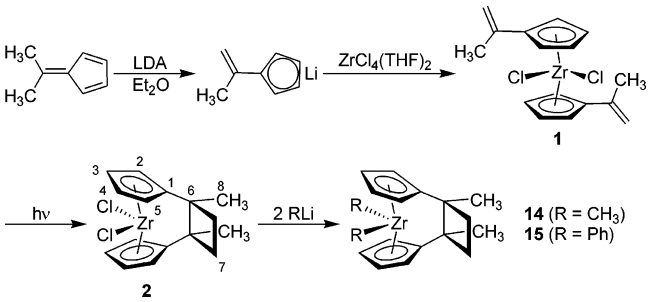


Figure 5. Front side projection of the "O-inside" η^2-benzoyl zirconocene complex **18**-*anti*. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg): C(13A)−O 1.256(3), C(13A)−C(14A) 1.468(3), C(13A)−Zr(1) 2.189(2), O−Zr(1) 2.241(2), Zr(1)−C(14B) 2.351(2); O−C(13A)−C(14A) 122.4(2), O−C(13A)−Zr(1) 75.8(1), C(14A)−C(13A)−Zr(1) 161.8(2), C(13A)−O−Zr(1) 71.3(1), C(13A)−Zr(1)−O 32.9(1), C(13A)−Zr(1)−C(14B) 114.9(1), O−Zr(1)−C(14B) 82.0(1); for additional values see the text and the Supporting Information.

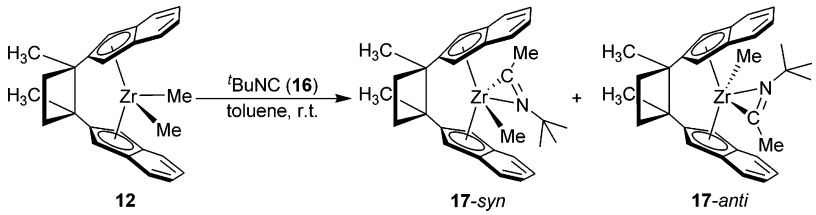
Scheme 4



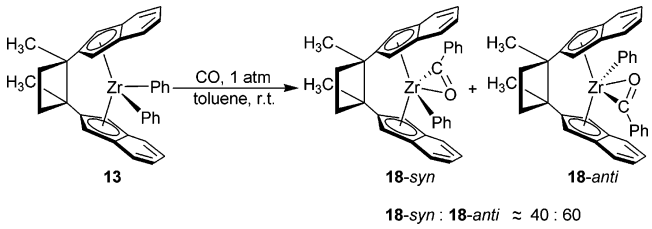
the carbonylation product by X-ray diffraction. In the crystal two molecules are found disordered that correspond to the "O-inside" (η^2-benzoyl)zirconocene isomers **18**-*syn* and **18**-*anti* (in a ca. 40:60 ratio). Both molecules show similar observed features. The molecular structure of complex **18**-*anti* features a η^2-benzoyl ligand at zirconium that is oriented coplanar with the metallocene σ-ligand plane bisecting the *ansa*-metallocene framework. The aroyl ligand is η^2-"O-inside" coordinated [bond lengths C(13A)−O: 1.256(3) Å, Zr(1)−C13A: 2.189(2) Å, Zr(1)−O: 2.241(2) Å, and C(13A)−C(14A): 1.468(3) Å; bond angles C(13A)−O−Zr(1): 71.3(1)°, O−C(13A)−Zr(1): 72.8(1)°, and C(13A)-Zr(1)−O: 32.9(1)°]. The remaining angles at the carbonyl carbon center C(13A) were found at 122.4(2)° (O−C(13A)−C(14A)) and 161.8(2)° (C(14A)−C(13A)−Zr(1)). The angle between the mean σ-ligand plane at zirconium, which contains the atoms Zr(1), O, C(13A), and C(14B), and the mean plane of the coplanar conjugated phenyl ring (C(14A) to C(19A)) amounts to 8.3°. The Zr(1)-bonded σ-phenyl ring (Zr(1)−C(14B): 2.351(2)°) is markedly rotated from the σ-ligand plane (angle 18.3°). The C(13A)−Zr(1)−C(14B) angle in complex **18**-*anti* was determined to be 114.9(1)°.

The reaction of the cyclobutylene-bridged bis(indenyl)-*ansa*-zirconocene diphenyl complex **13** with the *tert*-butylisocyanide reagent (**16**) is more complicated. At ambient temperature the reaction rapidly goes to completion with a 1:1 stoichiometry to yield a mixture of four monoinsertion products (**19**-*syn*, **19**-*anti*, **20**-*syn*, **20**-*anti*) in a ratio of 14:14:38:34, which was isolated in a combined overall yield of close to 60%. We assign the pair of the major products (**20**) the structures of the "N-inside" η^2-iminoacyl isomers (see Scheme 7). They show the typical "low-field" ^{13}C NMR resonances of the η^2-iminoacyl carbon atoms at δ 236.1 (**20**-*syn*) and δ 236.8 (**20**-*anti*), respectively. The cyclobutylene $-CH_2-CH_2-$ ^{1}H NMR resonances occur at δ 1.68/2.48 (**20**-*syn*, CH_3 signal at δ 1.12) or δ

Scheme 5



Scheme 6



1.61/2.30 (**20**-*anti*, CH_3: δ 1.16). As we will see, the ^{1}H NMR $C(CH_3)_3$ resonances are most suited to distinguish the **19**/**20** series. In **20**-*syn* (**20**-*anti*) they occur at relatively high field [δ 0.68 (δ 0.78)], which might indicate some interaction with the "anisotropy cones" of the covering indenyl phenylene π-clouds. The pair of minor products obtained from isonitrile insertion at **13** under thermodynamic control are very likely the corresponding "N-outside" η^2-iminoacyl *ansa*-metallocene isomers. The complexes **19**-*syn* and **19**-*anti* show the typical C═N ^{13}C NMR "low-field" resonances at δ 233.5 and 233.2 (the exact assignment has not been determined), both being upfield shifted relative to their **20**-*syn*/*anti* isomers (see above). The cyclobutylene ^{1}H NMR resonances are also slightly, but characteristically different from those of the "N-inside" isomers **20** [δ $-CH_2-CH_2-/CH_3$: 1.80, 2.59/1.39 (**19**-*syn*); 1.92, 2.71/1.32 (**19**-*anti*)]. Most characteristic is the marked shift of the *tert*-butyl ^{1}H NMR resonances of the "N-outside" isomers to larger δ-values [δ 1.31 (**19**-*syn*); δ 1.33 (**19**-*anti*)].

For the purpose of comparison we have reacted the cyclobutylene-bridged bis(cyclopentadienyl) zirconium dimethyl (**14**) and diphenyl (**15**) complexes with *tert*-butyl isocyanide (**16**). Under conditions of thermodynamic control, treatment of the diphenyl zirconocene complex **15** with **16** rapidly resulted in the formation of the pair of stereoisomeric η^2-iminoacyl monoisonitrile insertion products **22**-*syn* and **22**-*anti* (see Scheme 8) in a 32:68 ratio. The product mixture was isolated from the reaction on a preparative scale in a combined yield of ca. 70%. The major product (**22**-*anti*) shows very characteristic η^2-iminoacyl ^{13}C NMR resonance at δ 236.5. The minor isomer (**22**-*syn*) shows similar spectroscopic features [^{13}C: δ 236.0 (N═C)].

The reaction of **15** with *tert*-butyl isonitrile (**16**) was carried out at low temperature (−78 °C) in d_8-toluene to allow for the detection of the insertion products formed under kinetic control. The ^{1}H NMR spectrum at 203 K revealed the formation of a different pair of products in a similar ratio to which we have tentatively assigned the structures of the "N-outside" η^2-iminoacyl isomers **21**-*anti* (major) and **21**-*syn* (minor isomer). Both show NMR features that are typical for this general class of compounds. They are slightly, but distinctively different from those of the thermodynamic isomers (**22**-*anti*/*syn*). The complexes **21** feature, for example, ^{1}H NMR signals of the $C(CH_3)_3$ substituent at δ 1.00 (*anti*), 0.97 (*syn*), respectively. Upon warming the sample, we have observed the rearrangement of the kinetic isomers **21**-*anti*/*syn* to the thermodynamic η^2-iminoacyl products **22**-*anti*/*syn*. The reaction was kinetically followed by monitoring the decrease in intensity of two well-separated ^{1}H NMR signals of **21**-*anti* [cyclobutylene $-CH_2-CH_2-$ signal at δ 2.54 (218 K) and the lowest Ph signal at δ 7.84] and the appearance of one **22**-*anti* product signal [δ 5.52 (Cp, 218 K)]. The rearrangement kinetics of the minor "N-outside" η^2-iminoacyl isomer **21**-*syn* to **22**-*syn* was followed by the decrease of the δ 5.04 (Cp, 218 K) resonance and the increase of the δ 5.68 (Cp, 218 K) and 8.07 (lowest Ph signal at 218 K) product signal intensities. From such measurements (see Table 1, the Experimental Section, and the Supporting Information for details) the Gibbs activation energies of the respective η^2-iminoacyl "N-outside" to "N-inside" isomerization processes were calculated. They are almost identical for the two isomers. The values of the activation barriers $\Delta G^{\ddagger}_{rearr}$(218 K) of **21**-*anti* to **22**-*anti* and of **21**-*syn* to **22**-*syn* were determined to be 15.9 ± 0.2 and 15.5 ± 0.3 kcal·mol^{-1}, respectively.

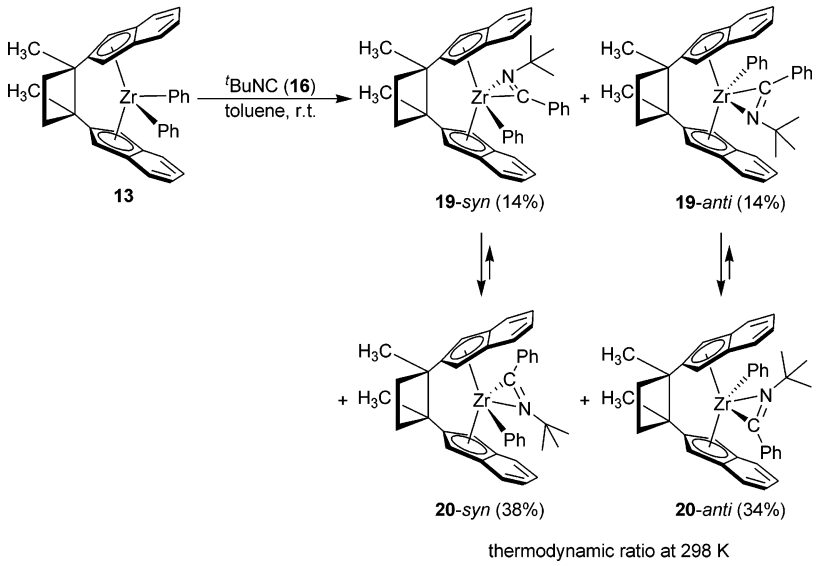
The *tert*-butylisonitrile insertion into the Zr−C σ-bond of complex **14** proceeded similarly. At ambient temperature rapid monoinsertion was observed to take place to yield a 35:65 mixture of the thermodynamic "N-inside" η^2-iminoacyl zirconocene products **24**-*syn* and **24**-*anti* (isolated yield of the mixture: 62%). Their NMR spectroscopic characterization was carried out from the mixture [^{13}C: δ 236.1 (**24**-*syn*), δ 235.2 (**24**-*anti*, C═N); ^{1}H: Zr−CH_3: δ 0.22 (*syn*), δ 0.11 (*anti*), NC−CH_3: δ 2.31 (*syn*), δ 2.39 (*anti*); $C(CH_3)_3$: δ 1.06 (*syn*), δ 1.03 (*anti*) (all values in d_8-toluene, 600 MHz, 298 K)].

At 195 K the isonitrile insertion of **14** was carried out in d_8-toluene. At 203 K the kinetic products [**23**-*syn* (minor), **23**-*anti* (major)] were directly observed, albeit admixed by some **24**-*syn*/*anti*, which was due to the relatively rapid rearrangement of the primary products (**23**) that already took place under these conditions. The systems **23**-*syn*/*anti* were identified and their structures were tentatively assigned due to a variety of characteristic ^{1}H NMR resonances (and in a comparison with their subsequent isomers **24**-*syn*/*anti*), e.g., Zr−CH_3 δ 0.49 (major **23**-*anti* product), δ 0.57 (minor, **23**-*syn*); $C(CH_3)_3$: δ 1.00 (*anti*); δ 0.95 (*syn*). The **23**-*anti* to **24**-*anti* isomerization at 203 K was kinetically followed by the intensity decrease of the ^{1}H NMR signals at δ 4.82 (Cp), 2.15 (NC−CH_3), and 0.49 (Zr−CH_3) of **23**-*anti* and the increasing intensity of the product signals of **24**-*anti* at δ 4.50 (Cp at 203 K) and 2.30 (NC−CH_3 at 203 K). From these data a Gibbs activation energy of $\Delta G^{\ddagger}_{rearr}$(203 K) = 14.9 ± 0.3 kcal·mol^{-1} was calculated[26] for the **23**-*anti* to **24**-*anti* isomerization (see Scheme 8 and Table 1). The kinetics of the rearrangement of the minor components, i.e., **23**-*syn* to **24**-*syn*, were more difficult to follow because of the low intensity of the signals in the mixture and extensive ^{1}H NMR signal overlap. Eventually we were able to estimate the corresponding $\Delta G^{\ddagger}_{rearr}$(203 K) = 14.7 ± 0.5 kcal·mol^{-1} value from monitoring the increasing intensity of the **24**-*syn* ^{1}H NMR signals at δ 4.98 (Cp at 203 K) and δ 2.23 (NC−CH_3 at 203 K).

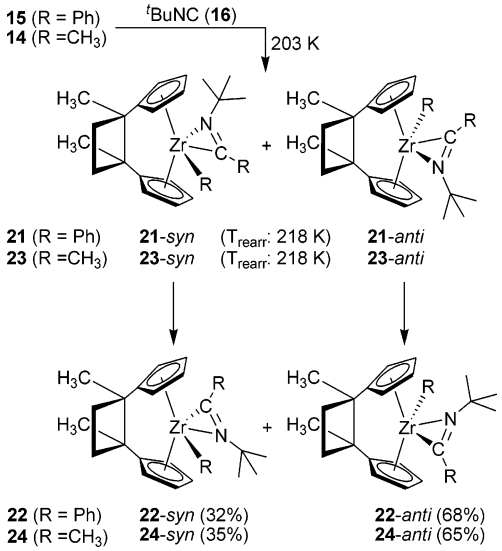
The *tert*-butylisocyanide insertion into the Zr−CH_3 linkage of the cyclobutylene−bis(indenyl) *ansa*-zirconocene dimethyl

(26) Jackman, L. M., Cotton, F. A., Eds. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1975.

Scheme 7



Scheme 8



Scheme 9

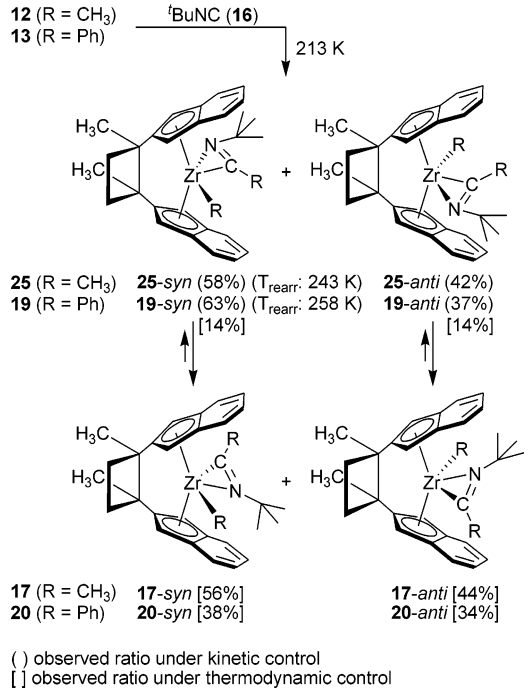


Table 1. Comparison of the Gibbs Activation Energies of the "N-Outside" to "N-Inside" Rearrangement of Cyclobutylene−Bis(2-indenyl)- and Cyclobutylene−Bis(cyclopentadienyl)zirconium Iminoacyl Complexes[a]

	complexes	T (K)	$\Delta G^{\ddagger}_{rearr}$(*syn*)	$\Delta G^{\ddagger}_{rearr}$(*anti*)
indenyl				
R = Ph	**19/20**	258	19.5	19.1
R = CH_3	**25/17**	243	18.0	17.8
cyclopentadienyl				
R = Ph	**21/22**	218	15.5	15.9
R = CH_3	**23/24**	203	14.7	14.9

[a] $\Delta G^{\ddagger}_{rearr}$ values in kcal·mol^{-1} (±0.2 to ±0.3).

complex (**12**) was then carried out under the conditions of kinetic control. The reaction was performed at 195K in d_8-toluene and then monitored by ^{1}H NMR at 213 K. The NMR analysis revealed that two new products were formed, to which we assign the structures of the "N-outside" η^2-iminoacyl zirconocenes **25**-*syn* and **25**-*anti* (see Scheme 9). The former isomer is characterized by a ^{1}H NMR signal of the Zr−CH_3 group at δ 0.06, whereas the latter shows the corresponding resonance at δ −0.28. The N═C−CH_3 signals occur at δ 1.41 (**25**-*syn*) and 1.45 (**25**-*anti*), respectively; those of the C$(CH_3)_3$ substituent, at δ 1.14 (*syn*)/δ 1.17 (*anti*).

The pair of kinetic products was formed in a **25**-*syn*/**25**-*anti* ratio of 58:42 under these conditions, which is very close to the observed ratio of the thermodynamic products **17**-*syn*/**17**-*anti* of 56:44 as it was obtained from carrying out the insertion reaction of **12** with **16** at ambient temperature (see Scheme 5). Consequently, upon warming the sample, we have observed the rearrangement of the **25**-*syn*/*anti* 58:42 mixture to the ca. 56:44 mixture of the products **17**-*syn*/**17**-*anti*, which supported the structural assignment. It turned out that the kinetic cyclobutylene−bis(indenyl)Zr "N-outside" η^2-iminoacyl products (**25**-*syn*/*anti*) are thermally considerably more stable than the corresponding cyclobutylene−bis(cyclopentadienyl)Zr reference compounds **23**-*syn* and **23**-*anti* (see Scheme 8). The rearrangement was kinetically followed at 243 K. Two series of experiments were carried out where the rate of the **25** to **17** rearrangement was determined in the presence of 2 molar equiv

and of more than 10 more equiv of *tert*-butyl isocyanide. Both series gave practically identical values, which serves as an indication to rule out dissociative reaction routes of "N-outside" to N-inside" isomerization. By ^{1}H NMR integration the disappearance of **25**-*syn* was followed by the intensity decrease of the δ 0.04 (Zr−CH_3 at 243 K) signal and the appearance of the **17**-*syn* signals at 0.42 (Zr−CH_3), 0.62 (CMe_3), and 2.20 (NC−CH_3 at 243 K). The resulting Gibbs activation barrier of the **25**-*syn* to **17**-*syn* rearrangement was calculated to be $\Delta G^{\ddagger}_{rearr}$(243 K) = 18.0 ± 0.2 kcal·mol^{-1}. Similarly monitoring of the ^{1}H NMR intensity increase of the **17**-*anti* Zr−CH_3 resonance at δ −0.35 (Zr−CH_3 at 243 K) and δ 0.67 (CMe_3) resulted in a Gibbs activation energy of $\Delta G^{\ddagger}_{rearr}$(243 K) = 17.8 ± 0.3 kcal·mol^{-1} for the corresponding **25**-*anti* to **17**-*anti* rearrangement (see Scheme 9).

We had shown that the reaction of the cyclobutylene−bis(indenyl)$ZrPh_2$ complex **13** with *tert*-butylisocyanide (**16**) at room temperature (e.g., under thermodynamic control) resulted in the formation of a mixture of all four possible stereoisomeric monoinsertion products (see above and Scheme 7). The reaction at low temperature (195 to 213 K) resulted in the observation of only a mixture of two of these products, to which we assign the structures of the "N-outside" η^2-iminoacyl *ansa*-zirconocene isomers **19**-*syn* and **19**-*anti*. Under these conditions of kinetic control the product ratio was found to be ca. 63:37. For some as yet unknown reason this ratio is slightly different from the expected 52:48 (i.e., 14+38/14+34) ratio, potentially caused by different solubilities of the stereoisomers at the low monitoring temperature. The kinetic products **19**-*syn*/*anti* are the most stable "N-outside" η^2-iminoacyl complexes studied in this series. Their rearrangement was kinetically followed by ^{1}H NMR spectroscopy at 258 K [decrease of the **19**-*syn* δ 1.37 (CH_3) and 2.54 (−CH_2−CH_2−) vs increase of the **20**-*syn* δ 1.09 (CH_3), 0.67 (CMe_3), and 2.45 (−CH_2−CH_2−) signals/decrease of the **19**-*anti* δ 1.91, 2.68 (−CH_2−CH_2−) and 6.05 (indenyl 3-H) vs increase of the **20**-*anti* δ 1.13 (CH_3) ^{1}H NMR resonances]. For the **19**-*syn* to **20**-*syn* rearrangement a Gibbs activation energy of $\Delta G^{\ddagger}_{rearr}$(258 K) = 19.5 ± 0.3 kcal·mol^{-1} was calculated. For the corresponding **19**-*anti* to **20**-*anti* isomerization (for a structural description see Scheme 7) $\Delta G^{\ddagger}_{rearr}$(258 K) = 19.1 ± 0.3 kcal·mol^{-1} was obtained.

Conclusions

The cyclobutylene−bis(2-indenyl)zirconocene dimethyl (**12**) and diphenyl (**13**) complexes both feature molecular structures where the four-membered carbocyclic bridge is found at the narrow backside and the anellated phenylene rings of indenyl moieties are oriented toward the open front side of the bent metallocene wedge.[27] The overall frameworks of the complexes **12** and **13** are slightly rotated from the ideal central position so that the σ-ligands are covered by the phenylene rings to a different degree. This shows up in the X-ray crystal structure analyses of these compounds and also in their spectroscopic features (e.g., by a different deshielding of the H_3C−Zr−CH_3 methyl groups in complex **12**).

Energetically this is probably a marginal effect. Insertion of *tert*-butyl isocyanide takes place rapidly under thermodynamic control to yield the "N-inside" η^2-iminoacyl metallocenes as the only (from **12**) or the major (from **13**) product. The framework of the product **17**-*anti* responds markedly to the increased steric bulk of the ligands in the σ-place by shifting the covering phenylene groups to the central position, thereby opening their bite angle and vertical separation to better accommodate the complex σ-ligand systems between them.

A quantitative assessment of the effects brought about by the covering phenylene rings comes from the determination of the activation barrier ($\Delta G^{\ddagger}_{rearr}$) of the intramolecular rearrangement of the kinetic "N-outside" to thermodynamic "N-inside" η^2-iminoacyl metallocene isomers in the cyclobutylene−bis(2-indenyl)Zr systems (**19/20**; **25/17**, see Table 1) relative to their unhindered cyclobutylene−bis(cyclopentadienyl)Zr reference systems (**21/22**; **23/24**). The compilation of the $\Delta G^{\ddagger}_{rearr}$ values (see Table 1) reveals that the pair of covering phenylene rings stabilizes the η^2-iminoacetyl system **25** by ca. 3 kcal·mol^{-1} from rearrangement to the favored isomer **17**. In the corresponding η^2-iminobenzoyl system **19** this stabilizing effect is even larger [ca. 3.2 (*anti*) to 4.0 (*syn*) kcal·mol^{-1}]. We assume that this marked increase in the activation energy of the rearrangement process is probably due to steric hindrance in the corresponding transition states by building up unfavorable interactions between the large rotating σ-moieties and the covering phenylene groups of the indenyl ligands of the rigid bent metallocene frameworks. An increase of the isomerization barrier by 3 to 4 kcal·mol^{-1} must be regarded as a large effect. It shows that the design of specific *ansa*-metallocene framework structures has a pronounced influence on the chemistry in the metallocene σ-ligand plane and may potentially more often than presently be used to control the chemical features of reactive early metallocene systems and the active catalysts derived from them.[3]

Experimental Section

General Considerations. All manipulations were carried out under argon using Schlenk-type glassware or in a glovebox unless otherwise noted. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use according to standard procedures. Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument. NMR spectra were measured using a Bruker AC200 P, a Varian 500 MHz INOVA, or a Varian Unity Plus 600 NMR spectrometer. Most assignments were based on a series of NOE, TOCSY, and 2D NMR experiments. Variable-temperature ^{1}H NMR experiments were conducted on a Varian Unity Plus 600 NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to solvents. Photochemical reactions were carried out with a Philipps HPK 125 high-pressure mercury lamp using a Pyrex filter (300−350 nm maximum). The complexes **2** and **4** were prepared according to literature procedures[3,28] (Scheme 3).

X-ray crystallography data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection, COLLECT (Nonius B.V., 1998), data reduction, Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol*. **1997**, *276*, 307−326), absorption correction, SORTAV (Blessing, R. H. *Acta Crystallogr*. **1995**, *A51*, 33−37; Blessing, R. H. *J. Appl. Crystallogr*. **1997**, *30*, 421−426), structure solution, SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467−473), structure refinement, SHELXL-97 (Sheldrick, G. M.), graphics XP (Bruker AXS, 2000).

Preparation of dimethyl *ansa*-Bisindenyl Zirconium Complex 12. Zirconium complex **4** (300 mg, 0.63 mmol) and methyllithium (79 mg, 3.6 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 20 mL of chilled toluene was added. The mixture was slowly warmed to room temperature and stirred for

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another 20 h. The suspension turned pale yellow and was filtered into another Schlenk tube to give a colorless solution. The toluene solvent was removed under vacuum, and the residue was washed with pentane and dried in vacuo to afford 188 mg of colorless product. Yield: 72%. From a concentrated solution of **12** in pentane kept at −30 °C single crystals could be obtained that were suitable for X-ray analysis. Anal. Calcd for $C_{26}H_{28}Zr$: C, 72.33; H, 6.54. Found: C, 71.67; H, 6.43. ^{1}H NMR (599.7 MHz, 298 K, benzene-d_6): δ −1.75 (s, 3H, Zr−CH_3(*anti*)), −0.23 (s, 3H, Zr−CH_3(*syn*), *syn* to the cyclobutylene bridge), 1.17 (s, 6H, CH_3), 1.66 (AA′BB′, 2H, CH_3CCH_{back}), 2.19 (AA′BB′, 2H, CH_3CCH_{front}), 5.88 (d, J = 2.3 Hz, 2H, H-3 in indenyl), 6.06 (d, J = 2.3 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.90 (m, 2H, H-6 in indenyl), 7.01 (m, 2H, H-5 in indenyl), 7.27 (m, 2H, H-4 in indenyl), 7.47 (m, 2H, H-7 in indenyl). ^{13}C NMR (150.8 MHz, 298 K, benzene-d_6): δ 26.2 (CH_3), 30.6 (CH_2), 31.3 (Zr−CH_3(*syn*)), 41.4 (Zr−CH_3(*anti*)), 49.1 (CH_3C), 95.4 (C-3 in indenyl), 98.1 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 123.3 (C-4′ in indenyl), 124.0 (C-5 in indenyl), 124.2 (C-7 in indenyl), 124.2 (C-6 in indenyl), 125.2 (C-4 in indenyl), 125.7 (C-7′ in indenyl), 138.6 (C-2 in indenyl).

X-ray crystal structure analysis of complex 12: formula $C_{26}H_{28}Zr$, M = 431.70, light yellow crystal 0.25 × 0.25 × 0.15 mm, a = 9.361(1) Å, b = 19.117(1) Å, c = 34.323(1) Å, β = 95.72(1)°, V = 6111.7(7) Å^3, ρ = 1.408 g cm^{-3}, μ = 0.547 mm^{-1}, empirical absorption correction (0.875 ≤ T ≤ 0.922), Z = 12, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198-(2) K, ω and φ scans, 62 986 reflections collected (±h, ±k, ±l), [(sin θ)/λ]) 0.66 Å^{-1}, 14 533 independent (R_{int} = 0.056) and 10 344 observed reflections [$I \geq 2\sigma(I)$], 753 refined parameters, R = 0.041, wR_2 = 0.098, max. residual electron density 0.67 (−0.43) e Å^{-3}, three almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

Preparation of Diphenyl *ansa*-Bisindenyl Zirconium Complex 13. Zirconium complex **4** (200 mg, 0.42 mmol) and phenyllithium (200 mg, 2.4 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled toluene was added. The mixture was slowly warmed to room temperature and stirred overnight. The afforded light yellow suspension was filtered into another Schlenk tube to give a yellow solution, the solvent of which was removed under vacuum to give a sticky residue. Then 10 mL of pentane was added and the mixture was stirred for 1 h at rt, to give a pale yellow precipitate. The mother liquid was removed and the light yellow product was dried in vacuo and collected in the amount of 123 mg. Yield: 55%. From a concentrated solution of **13** in pentane kept at −30 °C crystals could be obtained that were suitable for X-ray analysis. Anal. Calcd for $C_{36}H_{32}Zr$: C, 77.79; H, 5.80. Found: C, 77.72; H, 6.28. ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.21 (s, 6H, CH_3), 1.73 (AA′BB′, 2H, CH_3CCH_{back}), 2.45 (AA′BB′, 2H, CH_3CCH_{front}), 6.12 (dd, J = 2.46 Hz, J = 0.72 Hz, 2H, H-3 in indenyl), 6.24 (dd, J = 2.46 Hz, J = 0.72 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.28 (m, 2H, H-5 in indenyl), 6.36 (m, 2H, H-6 in indenyl), 6.65 (m, 2H, H-7 in indenyl), 6.71(m, 2H, H-4 in indenyl), 6.81 (m, 2H, *o*-H in *anti*-Ph), 6.95 (m, 1H, *p*-H in *anti*-Ph), 6.97 (m, 2H, *m*-H in *anti*-Ph), 7.05 (m, 2H, *m*-H in *syn*-Ph, *syn* to the cyclobutylene bridge), 7.08 (m, 2H, *o*-H in *syn*-Ph), 7.11 (m, 1H, *p*-H in *syn*-Ph). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.5 (CH_3), 31.0 (CH_2), 49.3 (CH_3C), 97.6 (C-3 in indenyl), 99.7 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 123.8 (C-5 in indenyl), 123.9 (C-6 in indenyl), 124.5 (C-7 in indenyl), 124.9 (C-7′ in indenyl), 125.5 (C-4 in indenyl), 125.5 (*p*-C in *anti*-Ph), 126.0 (*m*-C in *syn*-Ph), 126.4 (*m*-C in *anti*-Ph), 126.4 (*p*-C in *syn*-Ph), 127.7 (C-4′ in indenyl), 134.0 (*o*-C in *syn*-Ph), 135.5 (*o*-C in *anti*-Ph), 141.8 (C-2 in indenyl), 188.6 (Zr−C in *syn*-Ph), 188.6 (Zr−C in *anti*-Ph).

X-ray crystal structure analysis of complex 13: formula $C_{36}H_{32}Zr$, M = 555.84, light yellow crystal 0.25 × 0.10 × 0.05 mm, a = 14.611(1) Å, b = 9.583(1) Å, c = 18.948(1) Å, β = 90.62(1)°, V = 2652.9(4) Å^3, ρ = 1.392 g cm^{-3}, μ = 0.438 mm^{-1}, empirical absorption correction (0.898 ≤ T ≤ 0.978), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198-(2) K, ω and φ scans, 9870 reflections collected (±h, ±k, ±l), [(sin θ)/λ]) 0.64 Å^{-1}, 5866 independent (R_{int} = 0.0474) and 4358 observed reflections [$I \geq 2\sigma(I)$], 336 refined parameters, R = 0.051, wR_2 = 0.117, max. residual electron density 1.13 (−0.59) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Dimethyl *ansa*-Biscyclopentadienyl Zirconium Complex 14. Zirconocene complex **2** (200 mg, 0.54 mmol) and methyllithium (30 mg, 1.37 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled diethyl ether was added at −78 °C. Then the cooling bath was removed and the suspension was stirred at room temperature for 1.5 h. After the solvent of Et_2O was removed directly under vacuum to give a yellowish residue, 15 mL of pentane was used to extract the product and the filtration afforded a colorless solution. The evaporation of pentane gave a colorless solid, which was dried in vacuo to afford 108 mg of product. Yield: 60%. Anal. Calcd for $C_{18}H_{24}Zr$: C, 65.20; H, 7.29. Found: C, 64.99; H, 7.36. ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ −0.22 (s, 3H, Zr−CH_3(*anti*)), −0.10 (s, 3H, Zr−CH_3(*syn*), *syn* to the cyclobutylene bridge), 0.96 (s, 6H, CH_3), 1.50 (AA′BB′, 2H, CH_3CCH_{back}), 1.94 (AA′BB′, 2H, CH_3CCH_{front}), 5.31 (m, 2H, H-2 in Cp), 5.66 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge), 6.20 (m, 2H, H-4 in Cp), 6.38 (m, 2H, H-3 in Cp). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.5 (CH_3), 28.2 (Zr−CH_3(*anti*)), 29.2 (Zr−CH_3(*syn*)), 30.6 (CH_2), 48.8 (CH_3C), 104.7 (C-2 in Cp), 106.7 (C-5 in Cp, *syn* to the cyclobutylene bridge), 113.4 (C-4 in Cp), 116.7 (C-3 in Cp), 134.1 (C-1 in Cp).

Preparation of Diphenyl *ansa*-Biscyclopentadienyl Zirconium Complex 15. Zirconocene complex **2** (200 mg, 0.54 mmol) and phenyllithium (182 mg, 2.16 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled diethyl ether was added at −78 °C. The Schlenk tube was shielded from light by aluminum foil. Then the cooling bath was removed and the suspension was stirred at room temperature for 1.5 h. After the solvent of Et_2O was removed directly under vacuum to give a yellow residue, 10 mL of toluene was used to extract the product and the filtration afforded a yellow solution. The evaporation of toluene gave a yellow solid, and 20 mL of pentane was used for the second extraction. Then the filtration gave a light yellow solution, the solvent of which was removed and the pale yellow solid was dried in vacuo to afford 153 mg of product. Yield: 62%. Anal. Calcd for $C_{28}H_{28}Zr$: C, 73.79; H, 6.19. Found: C, 73.28; H, 6.08. ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.02 (s, 6H, CH_3), 1.58 (AA′BB′, 2H, CH_3CCH_{back}), 2.15 (AA′BB′, 2H CH_3CCH_{front}), 5.60 (m, 2H, H-2 in Cp), 5.86 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge), 6.07 (m, 2H, H-4 in Cp), 6.26 (m, 2H, H-3 in Cp), 7.06 (m, 1H, *p*-H in *anti*-Ph), 7.08 (m, 1H, *p*-H in *syn*-Ph, *syn* to the cyclobutylene bridge), 7.15 (m, 2H, *m*-H in *anti*-Ph), 7.17 (m, 2H, *m*-H in *syn*-Ph), 7.32 (m, 2H, *o*-H in *anti*-Ph), 7.45 (m, 2H, *o*-H in *syn*-Ph). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.3 (CH_3), 30.8 (CH_2), 49.1 (CH_3C), 106.3 (C-2 in Cp), 108.0 (C-5 in Cp, *syn* to the cyclobutylene bridge), 116.1 (C-4 in Cp), 119.4 (C-3 in Cp), 125.8 (*p*-C in *anti*-Ph), 126.1 (*p*-C in *syn*-Ph), 126.8 (*m*-C in *syn*- and *anti*-Ph), 135.9 (*o*-C in *syn*-Ph), 136.1 (*o*-C in *anti*-Ph), 137.0 (C-1 in Cp), 182.5 (Zr−C in *anti*-Ph), 183.0 (Zr−C in *syn*-Ph).

Preparation of η^2-*N*-*tert*-Butyliminoacetyl Methyl *ansa*-Bisindenyl Zirconium Complexes 17. Zirconium complex **4** (150 mg, 0.35 mmol) and methyllithium (39.5 mg, 1.8 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 10 mL of chilled toluene was added. The mixture was slowly warmed to room temperature and stirred for another 15 h. The suspension turned pale yellow and was filtered into another Schlenk tube to

give a colorless solution, to which 0.2 mL of ^{t}BuNC (146 mg, 1.7 mmol) was added, and the mixture was stirred at room temperature for 1 h. The toluene solvent was removed under vacuum, and 10 mL pentane was added to extract the product. The evaporation of all volatiles under vacuum gave a foam-like solid, which was dried in vacuo and stored in a glovebox for a few days. A total of 86 mg of pale yellow product was collected. From a concentrated solution of **17** in pentane kept at −30 °C light yellow single crystals could be obtained, which were suitable for X-ray analysis. Yield: 56%. Anal. Calcd for $C_{31}H_{37}NZr$: C, 72.32; H, 7.24; N, 2.72. Found: C, 72.51; H, 7.22; N, 2.47. **17**-*syn* (Zr−CH_3 is *syn* to the cyclobutylene bridge, major product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8, small amount of ^{t}BuNC): δ 0.26 (s, 3H, Zr−CH_3), 0.58 (s, 9H, ^{t}BuN═C−Zr), 1.22 (s, 6H, CH_3), 1.72 (AA′BB′, 2H, CH_3CCH_{back}), 2.24 (s, 3H CH_3C−Zr), 2.46 (AA′BB′, 2H CH_3CCH_{front}), 5.95 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-3 in indenyl), 6.10 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.39 (m, 2H, H-5 in indenyl), 6.49 (m, 2H, H-6 in indenyl), 6,76 (m, 2H, H-4 in indenyl), 7.30 (m, 2H, H-7 in indenyl). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8, small amount of ^{t}BuNC): δ 14.4 (Zr−CH_3), 20.8 (CH_3C−Zr), 25.8 (CH_3), 30.8 (CH_2), 31.4 (CH_3 in ^{t}Bu), 48.1 (CH_3C), 63.9 (Me_3C in ^{t}Bu), 87.5 (C-3 in indenyl), 97.7 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 121.1 (C-7′ in indenyl), 121.5 (C-6 in indenyl), 121.6 (C-4 in indenyl), 123.0 (C-5 in indenyl), 124.4 (C-7 in indenyl), 125.6 (C-4′ in indenyl), 139.5 (C-2 in indenyl), 233.1 (N═C−Zr). **17**-*anti* (Zr−CH_3 is *anti* to the cyclobutylene bridge, minor product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8, small amount of ^{t}BuNC): δ −0.42 (s, 3H, Zr−CH_3, *anti* to the cyclobutylene bridge), 0.63 (s, 9H, ^{t}BuN═C−Zr), 1.21 (s, 6H, CH_3), 1.77 (AA′BB′, 2H, CH_3CCH_{back}), 2.45 (s, 3H, CH_3C−Zr), 2.50 (AA′BB′, 2H, CH_3CCH_{front}), 5.88 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-3 in indenyl), 6.10 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.44 (m, 2H, H-6 in indenyl), 6,59 (m, 2H, H-7 in indenyl), 6.65 (m, 2H, H-5 in indenyl), 7.33 (m, 2H, H-4 in indenyl). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8, small amount of ^{t}BuNC): δ 19.6 (Zr−CH_3), 22.4 (CH_3C−Zr), 25.4 (CH_3), 31.0 (CH_2), 31.2 (CH_3 in ^{t}Bu), 48.2 (CH_3C), 63.8 (Me_3C in ^{t}Bu), 88.9 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 93.8 (C-3 in indenyl), 121.9 (C-5 in indenyl), 122.0 (C-7 in indenyl), 122.7 (C-6 in indenyl), 122.4 (C-7′ in indenyl), 124.8 (C-4′ in indenyl), 124.9 (C-4 in indenyl), 139.4 (C-2 in indenyl), 234.5 (N═C−Zr).

X-ray crystal structure analysis of complexes 17: formula $C_{31}H_{37}NZr$, M = 514.84, light yellow crystal 0.5 × 0.40 × 0.20 mm, a = 16.358(1) Å, b = 19.860(1) Å, c = 16.023(1) Å, β = 93.60(1)°, V = 5195.1(5) Å^3, ρ = 1.316 g cm^{-3}, μ = 0.442 cm^{-1}, empirical absorption correction (0.809 ≤ T ≤ 0.917), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198-(2) K, ω and φ scans, 44 962 reflections collected (±h, ±k, ±l), [(sin θ)/λ]) 0.67 Å^{-1}, 12 557 independent (R_{int} = 0.053) and 10 962 observed reflections [$I \geq 2\sigma(I)$], 609 refined parameters, R = 0.040, wR_2 = 0.113, max. residual electron density 2.02 (−0.87) e Å^{-3}, two molecules in the asymmetric unit, cyclobutylene bridges in disorder, hydrogens calculated and refined as riding atoms.

Preparation of η^2-Benzoyl Phenyl *ansa*-Bisindenyl Zirconium Complexes 18. Zirconium complex **4** (200 mg, 0.36 mmol) and phenyllithium (200 mg, 2.4 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled toluene was added. The mixture was slowly warmed to room temperature and stirred overnight. The afforded light yellow suspension was filtered into another Schlenk tube to give a yellow solution, which was concentrated to about 5 mL. The Schlenk tube was charged with CO at the pressure of 1 bar, and the solution was magnetically stirred at room temperature. An orange precipitate appeared after 15 min, and the mixture was stirred for another 15 min. Then 10 mL of pentane was added into the Schlenk tube, and filtration gave an orange solid, which was dried in vacuo. A total of 191 mg of product was collected. Yield: 82%. From a concentrated solution of **18** in pentane kept in the refrigerator at +6 °C orange single crystals could be obtained, which were suitable for X-ray analysis. Anal. Calcd for $C_{37}H_{32}OZr$: C, 76.11; H, 5.52. Found: C, 76.28; H, 5.67. **18**-*syn* (Zr−Ph is *syn* to the cyclobutylene bridge, minor product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.29 (s, 6H, CH_3), 1.81 (AA′BB′, 2H, CH_3CCH_{back}), 2.68 (AA′BB′, 2H, CH_3CCH_{front}), 6.24 (m, 2H, H-3 in indenyl), 6.53 (m, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 7.30 (m, 1H, *p*-H in Ph−Zr), 7.42 (m, 2H, *m*-H in Ph−Zr), 7.23 (m, 2H, *m*-H in PhC−Zr), 7.25 (m, 1H, *p*-H in PhC−Zr), 7.98 (m, 2H, *o*-H in PhC−Zr), 8.25 (d, J = 6.6 Hz, 2H, *o*-H in Ph−Zr), the remaining ^{1}H NMR signals are located in the range δ 7.30−6.00 as multiplets. ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.6 (CH_3), 31.0 (CH_2), 49.1 (CH_3C), 89.8 (C-3 in indenyl), 98.6 (C-1 in indenyl), 124.5 (*p*-C in Ph−Zr), 126.4 (*m*-C in PhC−Zr), 126.5 (*m*-C in Ph−Zr), 131.3 (*o*-C in PhC−Zr), 140.3 (*o*-C in Ph−Zr), 140.8 (C-2 in indenyl), 180.6 (Zr−C in Ph−Zr), 298.9 (Zr−C═O). **18**-*anti* (Zr−Ph is *anti* to the cyclobutylene bridge, major product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.30 (s, 6H, CH_3), 1.80 (AA′BB′, 2H, CH_3CCH_{back}), 2.56 (AA′BB′, 2H, CH_3CCH_{front}), 6.35 (d, J = 2.3 Hz, 2H, H-3 in indenyl), 6.48 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-1 in indenyl, the same side with the cyclobutylene bridge), 7.25 (m, 1H, *p*-H in Ph−Zr), 7.26 (m, 1H, *p*-H in PhC−Zr), 7.27 (m, 2H, *m*-H in PhC−Zr), 7.36 (m, 2H *m*-H in Ph−Zr), 8.07 (m, 2H, *o*-H in PhC−Zr), 8.09 (b, 2H *o*-H in Ph−Zr); the remaining ^{1}H NMR signals are within δ 7.30−6.00 as multiplets. ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.0 (CH_3), 31.0 (CH_2), 49.1 (CH_3C), 90.6 (C-1 in indenyl), 96.7 (C-3 in indenyl), 124.4 (*p*-C in Ph−Zr), 126.5 (*m*-C in Ph−Zr), 131.2 (*o*-C in PhC−Zr), 139.9 (*o*-C in Ph−Zr), 140.5 (C-2 in indenyl), 181.3 (Zr−C in Ph−Zr), 300.8 (Zr−C═O).

X-ray crystal structure analysis of complexes 18: formula $C_{37}H_{32}OZr\cdot 0.22N(C_2H_5)_3$, M = 606.32, yellow-orange crystal 0.30 × 0.20 × 0.20 mm, a = 18.133(1) Å, b = 18.133(1) Å, c = 15.654-(1) Å, γ = 120°, V = 4457.5(4) Å^3, ρ = 1.355 g cm^{-3}, μ = 0.400 mm^{-1}, empirical absorption correction (0.890 ≤ T ≤ 0.924), Z = 6, trigonal, space group $P\bar{3}$ (No. 147), λ = 0.71073 Å, T = 198(2) K, ω and φ scans, 15 781 reflections collected (±h, ±k, ±l), [(sin θ)/λ]) 0.67 Å^{-1}, 7285 independent (R_{int} = 0.032) and 5641 observed reflections [$I \geq 2\sigma(I)$], 397 refined parameters, R = 0.040, wR_2 = 0.100, max. residual electron density 0.83 (−0.62) e Å^{-3}, cyclobutylene with 0.59:0.41(1) disordered, triethylamine only occupied by 66%, hydrogens calculated and refined as riding atoms.

Preparation of η^2-*N*-*tert*-Butyliminobenzoyl Phenyl *ansa*-Bisindenyl Zirconium Complexes 19 and 20. Zirconium complex **4** (200 mg, 0.36 mmol) and phenyllithium (200 mg, 2.4 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled toluene was added. The mixture was slowly warmed to room temperature and stirred overnight. The afforded light yellow suspension was filtered into another Schlenk tube to give a yellow solution, to which 0.3 mL of ^{t}BuNC (219 mg, 2.6 mmol) was added. The solution was stirred at room temperature for 1 h, and the solvent of toluene was removed under vacuum to give a sticky solid. Then 10 mL of pentane was added to the Schlenk tube, and the mixture was stirred for 1 h at rt to afford a pale yellow precipitate, which was separated from the mother liquid and was dried in vacuo. A total of 149 mg of product was collected as a mixture of four stereoisomers. Yield: 58%. Anal. Calcd for $C_{41}H_{41}$-NZr: C, 77.06; H, 6.47; N, 2.19. Found: C, 76.57; H, 6.59; N, 1.92. **19**-*syn* (N-outside, Zr−Ph is *syn* to the cyclobutylene bridge): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.31 (s, 9H, ^{t}BuN═C−Zr), 1.39 (s, 6H, CH_3), 1.80 (AA′BB′, 2H, CH_3CCH_{back}), 2.59 (AA′BB′, 2H CH_3CCH_{front}), 6.22 (dd, J = 2.5 Hz, J = 0.7 Hz, 2H, H-3 in indenyl), 6.37 (dd, J = 2.5 Hz, J = 0.7 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge). ^{13}C NMR (150.8

MHz, 298 K, toluene-d_8): δ 25.0 (CH_3), 31.3 (CH_2), 32.0 (CH_3 in ^{t}Bu), 49.3 (CH_3C), 63.5 (Me_3C in ^{t}Bu), 89.2 (C-3 in indenyl), 97.4 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 145.5 (C-2 in indenyl). **19**-*anti* (N-outside, Zr−Ph is *anti* to the cyclobutylene bridge): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 1.32 (s, 6H, CH_3), 1.33 (s, 9H, ^{t}BuN═C−Zr), 1.92 (AA′BB′, 2H, CH_3CCH_{back}), 2.71 (AA′BB′, 2H, CH_3CCH_{front}), 6.08 (dd, J = 2.5 Hz, J = 0.8 Hz, 2H, H-3 in indenyl), 6.34 (dd, J = 2.5 Hz, J = 0.8 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.56 (2H, H-4 in indenyl), 6.86 (2H, H-7 in indenyl). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.9 (CH_3), 31.4 (CH_2), 31.9 (CH_3 in ^{t}Bu), 50.0 (CH_3C), 63.5 (Me_3C in ^{t}Bu), 89.7 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 96.0 (C-3 in indenyl), 145.6 (C-2 in indenyl). For some important ^{13}C NMR signals the relative assignment between **19**-*syn* and -*anti* has remained open: δ 143.5 (C_5H_5C−CZr), 144.1 (C_5H_5C−CZr), 181.0 (Zr−C in Ph−Zr), 181.3 (Zr−C in Ph−Zr), 233.2 (N═C−Zr), 233.5 (N═C−Zr). **20**-*syn* (N-inside, Zr−Ph *syn* to the cyclobutylene bridge): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.68 (s, 9H, ^{t}BuN═C−Zr), 1.12 (s, 6H, CH_3), 1.68 (AA′BB′, 2H, CH_3CCH_{back}), 2.48 (AA′BB′, 2H, CH_3CCH_{front}), 6.10 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-3 in indenyl), 6.35 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.87 (2H, H-4 in indenyl), 7.06 (2H, H-7 in indenyl), 7.09 (m, 1H *p*-H in PhC−Zr), 7.19 (m, 1H *p*-H in Ph−Zr), 7.25 (m, 2H *m*-H in Ph−Zr), 7.29 (m, 2H *m*-H in PhC−Zr), 7.44 (m, 2H *o*-H in PhC−Zr), 7.82 (m, 2H *o*-H in Ph−Zr). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.0 (CH_3), 31.1 (CH_2), 31.8 (CH_3 in ^{t}Bu), 48.2 (CH_3C), 63.8 (Me_3C in ^{t}Bu), 89.5 (C-3 in indenyl), 96.4 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 123,6 (*p*-C in Ph−Zr), 124.9 (*o*-C in PhC−Zr), 125.2 (*m*-C in Ph−Zr), 126.5 (*p*-C in PhC−Zr), 128.2 (*m*-C in PhC−Zr), 143.3 (*o*-C in Ph−Zr), 143.0 (*o*-C in Ph−Zr), 144.2 (ZrC−C in PhC−Zr), 179.5 (Zr−C in Ph−Zr), 236.1 (N═C−Zr). **20**-*anti* (N-inside and Zr−Ph *anti* to the cyclobutylene bridge): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.78 (s, 9H, ^{t}BuN═C−Zr), 1.16 (s, 6H, CH_3), 1.61 (AA′BB′, 2H, CH_3CCH_{back}), 2.30 (AA′BB′, 2H, CH_3CCH_{front}), 6.14 (dd, J = 2.3 Hz, J = 0.7 Hz, 2H, H-3 in indenyl), 6.23 (dd, J = 2.3 Hz, J = 0.8 Hz, 2H, H-1 in indenyl, *syn* to the cyclobutylene bridge), 6.87 (2H, H-7 in indenyl), 6.90 (2H, H-4 in indenyl), 7.08 (m, 1H *p*-H in PhC−Zr), 7.12 (m, 1H *p*-H in Ph−Zr), 7.14 (m, 2H *m*-H Ph−Zr), 7.31 (m, 2H *m*-H in PhC−Zr), 7.38 (m, 2H *o*-H in PhC−Zr), 7.58 (m, 2H *o*-H in Ph−Zr), the other ^{1}H NMR signals of the complexes **19** and **20** are within δ 7.32−6.20 as multiplets. ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.6 (CH_3), 31.0 (CH_2), 32.0 (CH_3 in ^{t}Bu), 48.5 (CH_3C), 64.4 (Me_3C in ^{t}Bu), 93.3 (C-3 in indenyl), 91.5 (C-1 in indenyl, *syn* to the cyclobutylene bridge), 122.6 (*o*-C in PhC−Zr), 123,4 (*p*-C in Ph−Zr), 125.4 (*m*-C in Ph−Zr), 126.6 (*p*-C in PhC−Zr), 128.6 (*m*-C in PhC−Zr), 142.7 (C-2 in indenyl), 142.9 (*o*-C in Ph−Zr), 146.9 (ZrC−C in PhC−Zr), 181.2 (Zr−C in Ph−Zr), 236.8 (N═C−Zr).

Preparation of η^2-*N*-*tert*-Butyliminobenzoyl Phenyl *ansa*-Biscyclopentadienyl Zirconium Complexes 22. Zirconocene complex **2** (200 mg, 0.54 mmol) and phenyllithium (182 mg, 2.16 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled diethyl ether was added at −78 °C. The Schlenk tube was shielded from light by aluminum foil. Then the cooling bath was removed and the suspension was stirred at room temperature for 1.5 h. After the solvent of Et_2O was removed directly under vacuum to give a yellow residue, 10 mL of toluene was used to extract the product and filtration afforded a yellow solution. The evaporation of toluene gave a yellow solid, and 20 mL of pentane was used for the second extraction. The filtration gave a colorless solution. Then 0.12 mL of ^{t}BuNC (89.8 mg, 1.08 mmol) was added into the solution, and the yellow mixture was stirred for 10 min. The evaporation of all volatiles under vacuum gave a yellow solid, which was dried in vacuo to afford 206 mg of product. Yield: 71%. Anal. Calcd for $C_{33}H_{37}NZr$: C, 73.55; H, 6.92; N, 2.60. Found: C, 73.43; H, 7.06; N, 2.38. **22**-*syn* (Zr−Ph is *syn* to the cyclobutylene bridge, minor product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.84 (s, 9H, ^{t}BuN═C−Zr), 1.04 (s, 6H, CH_3), 1.56 (AA′BB′, 2H, CH_3CCH_{back}), 2.21 (AA′BB′, 2H, CH_3CCH_{front}), 5.36 (m, 2H, H-3 in Cp), 5.53 (m, 2H, H-2 in Cp), 5.76 (m, 2H, H-4 in Cp), 6.09 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge), 6,78 (m, 2H, *o*-H in PhC−Zr), 6.94 (m, 2H, *p*-H in PhC−Zr), 7.13 (m, 1H, *m*-H in PhC−Zr), 7.17 (m, 2H, *p*-H in Ph−Zr), 7.29 (m, 1H, *m*-H in Ph−Zr), 7.96 (m, 2H, *o*-H in Ph−Zr). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.3 (CH_3), 30.7 (CH_2), 30.9 (CH_3 in ^{t}Bu), 48.1 (CH_3C), 62.3 (Me_3C in ^{t}Bu), 99.6 (C-2 in Cp), 105.6 (C-5 in Cp, *syn* to the cyclobutylene bridge), 110.1 (C-4 in Cp), 112.0 (C-3 in Cp), 121.4 (*o*-C in PhC−Zr), 123.7 (*p*-C in Ph−Zr), 125.9 (*p*-C in PhC−Zr), 126.2 (*m*-C in Ph−Zr), 128.6 (*m*-C in PhC−Zr), 135.6 (C-1 in Cp), 142.7 (*o*-C in Ph−Zr), 147.0 (ZrC−C in PhC−Zr), 176.5 (Zr−C in Ph−Zr), 236.0 (N═C−Zr). **22**-*anti* (Zr−Ph is *anti* to the cyclobutylene bridge, major product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.95 (s, 9H, ^{t}BuN═C−Zr), 1.06 (s, 6H, CH_3), 1.56 (AA′BB′, 2H, CH_3CCH_{back}), 2.16 (AA′BB′, 2H, CH_3CCH_{front}), 4.97 (m, 2H, H-4 in Cp), 5.61 (m, 2H, H-2 in Cp), 5.86 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge), 6.14 (m, 2H, H-3 in Cp), 6.80 (m, 2H, *o*-H in PhC−Zr), 6.94 (m, 2H, *p*-H in PhC−Zr), 7.14 (m, 1H, *m*-H in PhC−Zr), 7.16 (m, 2H, *p*-H in Ph−Zr), 7.27 (m, 1H, *m*-H in Ph−Zr), 7.85 (m, 2H, *o*-H in Ph−Zr). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 25.7 (CH_3), 30.7 (CH_2), 30.9 (CH_3 in ^{t}Bu), 48.4 (CH_3C), 62.1 (Me_3C in ^{t}Bu), 100.7 (C-2 in Cp), 100.8 (C-5 in Cp, *syn* to the cyclobutylene bridge), 107.7 (C-4 in Cp), 118.3 (C-3 in Cp), 121.0 (*o*-C in PhC−Zr), 123.6 (*p*-C in Ph−Zr), 125.8 (*p*-C in PhC−Zr), 126.0 (*m*-C in Ph−Zr), 128.7 (*m*-C in PhC−Zr), 136.0 (C-1 in Cp), 142.6 (*o*-C in Ph−Zr), 147.4 (ZrC−C in PhC−Zr), 176.3 (Zr−C in Ph−Zr), 236.5 (N═C−Zr).

Preparation of η^2-*N*-*tert*-Butyliminoacetyl Methyl *ansa*-Biscyclopentadienyl Zirconium Complexes 24. Zirconocene complex **2** (200 mg, 0.54 mmol) and methyllithium (30 mg, 1.37 mmol) were added into a Schlenk tube with a magnetic stir bar inside, to which 15 mL of chilled diethyl ether was added at −78 °C. Then the cooling bath was removed, and the suspension was stirred at room temperature for 1.5 h. After the solvent of Et_2O was removed directly under vacuum to give a yellowish residue, 15 mL of pentane was used to extract the product and filtration afforded a colorless solution. Then 0.12 mL of ^{t}BuNC (89.8 mg, 1.08 mmol) was added into the solution, and the mixture was stirred for 10 min. The evaporation of all volatiles gave a colorless solid, which was dried in vacuo to afford 140 mg of product. Yield: 62%. Anal. Calcd for $C_{23}H_{33}NZr$: C, 66.61; H, 8.02; N, 3.38. Found: C, 66.24; H, 8.02; N, 3.11. **24**-*syn* (Zr−CH_3 is *syn* to the cyclobutylene bridge, minor product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.22 (s, 3H Zr−CH_3), 1.06 (s, 9H, ^{t}BuN═C−Zr), 1.19 (s, 6H, CH_3), 1.67 (AA′BB′, 2H, CH_3CCH_{back}), 2.31 (s, 3H, CH_3C−Zr), 2.33 (AA′BB′, 2H, CH_3CCH_{front}), 4.93 (m, 2H, H-3 in Cp), 5.33 (m, 2H, H-4 in Cp), 5.49 (m, 2H, H-2 in Cp), 5.88 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 9.4 (Zr−CH_3), 23.0 (CH_3C−Zr), 25.7 (CH_3), 29.9 (CH_3 in ^{t}Bu), 30.6 (CH_2), 48.4 (CH_3C), 61.6 (Me_3C in ^{t}Bu), 97.4 (C-2 in Cp), 106.6 (C-5 in Cp, *syn* to the cyclobutylene bridge), 107.8 (C-4 in Cp), 109.0 (C-3 in Cp), 132.8 (C-1 in Cp), 236.1 (N═C−Zr). **24**-*anti* (Zr−CH_3 is *anti* to the cyclobutylene bridge, major product): ^{1}H NMR (599.7 MHz, 298 K, toluene-d_8): δ 0.11 (s, 3H, Zr−CH_3, the side opposite the cyclobutylene bridge), 1.03 (s, 9H, ^{t}BuN═C−Zr), 1.16 (s, 6H, CH_3), 1.77 (AA′BB′, 2H, CH_3CCH_{back}), 2.39 (s, 3H, CH_3C−Zr), 2.43 (AA′BB′, 2H, CH_3CCH_{front}), 4.56 (m, 2H, H-4 in Cp), 5.45 (m, 2H, H-2 in Cp), 5.70 (m, 2H, H-5 in Cp, *syn* to the cyclobutylene bridge), 5.90 (m, 2H, H-3 in Cp). ^{13}C NMR (150.8 MHz, 298 K, toluene-d_8): δ 8.6 (Zr−CH_3), 23.0 (CH_3C−Zr), 26.0 (CH_3), 29.9 (CH_3 in ^{t}Bu), 30.9 (CH_2), 48.6 (CH_3C), 61.5 (Me_3C in ^{t}Bu), 98.5 (C-5 in Cp, *syn* to the

cyclobutylene bridge), 101.3 (C-2 in Cp), 105.0 (C-4 in Cp), 116.2 (C-3 in Cp), 132.7 (C-1 in Cp), 235.2 (N═C−Zr).

General Procedure for Preparation of Samples for NMR Experiments. An amount of 25 mg of the respective dimethyl or diphenyl *ansa*-zirconocene complex was added into a NMR tube, and then it was dissolved by several drops of d_8-toluene. The solution was cooled to −78 °C, and the appropriate amount of ^{t}-BuNC in 0.4 mL of d_8-toluene, which was also first cooled to −78 °C, was slowly added into the NMR tube. The mixture was stirred mechanically until it became homogeneous. Then the NMR tube was sealed at −78 °C and kept at the same temperature for the NMR measurement. The ^{1}H NMR of the sample was measured every 2 min at the corresponding temperature within a period of 2 h. Then several suitable resonances of protons in each complex were selected for integration, and the $\tau = k^{-1}$ values were calculated by exponential fit of the kinetic data (the first order) with "vnmr" from Varian.

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Supporting Information Available: Preparation of starting materials. Additional NMR data for complexes **12**−**15** and **17**−**25**. Preparation of kinetic products at low temperatures. Detailed kinetic data and results.

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