# Synthesis, Structural Features, and Formation of Organometallic Derivates of $C_1$-Bridged Cp/Amido Titanium and Zirconium "CpCN-Constrained Geometry" Systems

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A series of $C_1$-bridged Cp/amido group 4 metal complexes [("CpCN")$MX_2$] was prepared. The starting compound 6-*tert*-butylfulvene (**7**) was reacted with LiNHR (R = *o*-anisyl (**a**), *p*-anisyl (**b**), phenyl (**c**), or *tert*-butyl (**d**)) to yield the Li($C_5H_4$-CH(tBu)-NHR) compounds (**8**). Subsequent deprotonation with *n*-butyllithium, followed by transmetalation with $Cl_2$-Ti($NMe_2$)$_2$, yielded the ("CpCN")Ti($NR_2$)$_2$ complexes **10** (**a**−**d**). A second synthetic series started from 6-(dimethylamino)fulvene (**11**). The reaction with the LiNHR reagents led to addition followed by $HNMe_2$ elimination to yield the respective imino-substituted cyclopentadienides Li($C_5H_4$-CH=NR) (**13**). Addition of methyllithium to **13** gave the $(Li^+)_2$($C_5H_4$-CHMe-NR)$^{2-}$, ("CpCN")$^{2-}$, ligands (**14**). Transmetalation with $Cl_2$Ti($NMe_2$)$_2$ subsequently yielded the corresponding $\mu$-CHMe-bridged Cp/amido group 4 complexes **15** (**a**−**c**). Treatment with $Me_2SiCl_2$ cleanly converted the ("CpCN")M($NR_2$)$_2$ complexes to the respective ("CpCN")-$MCl_2$ systems [**3a**−**d**, **4a**−**c** (Ti), **5a** (Zr)]. These were transformed to the ("CpCN")M($CH_3$)$_2$ complexes [$\mu$-CHCMe$_3$: **17a**−**d** (Ti), **19a** (Zr), $\mu$-CHMe: **18a**−**c** (Ti)] and the (*s-cis*-supine-$\eta^4$-butadiene)("CpCN")Ti systems **21a**−**d** and **22b**,**c**. With respect to X-ray structure analyses the (CpCN)$MX_2$ systems must be regarded as more "constrained" than their ("CpSiN")$MX_2$ analogues. The ("CpCN")$MCl_2$ and ("CpCN")M($CH_3$)$_2$ complexes were used as catalysts for ethene homopolymerization and ethene/1-octene copolymerization. All systems gave active catalysts, but these were quite different in their catalytic performance when compared with the usually applied ("CpSiN")$TiX_2$-derived catalysts. The ("CpCN")M catalyst activities and selectivities were very dependent on the specific activator components employed.

## Introduction

The silicon-bridged Cp/amido framework of the "constrained geometry" metal complexes was introduced by Bercaw et al. originally in scandium chemistry[1] and shortly thereafter applied by several groups for the preparation of the respective group 4 metal complexes.[2] The silicon-bridged "CpSiN" group 4 metal systems (**1**) have found significant use in homogeneous Ziegler−Natta catalysis, especially the titanium systems, which were shown to give excellent ethene/1-alkene copolymerization catalysts.[3] Many variations were carried out at the original framework, especially with regard to variations at the Cp ring and the substituents at the bridging silicon and the nitrogen center.[4,5] Okuda and others have described a great variety of (CpSiN)$MX_2$ derivates that contain an additional donor group that

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# X-ray crystal structure analyses.

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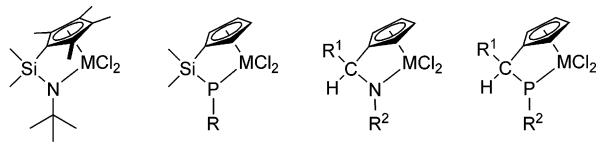
was attached directly or by a suitable linker at the amido nitrogen atom.[6]

There are much fewer reports about related systems where either the bridging group 14 or the terminal anionic group 15 element has been varied. The "Cp-SiP"$ZrCl_2$ system has been reported,[7] and synthetic entries to the related "CpCN" and "CpCP" group 4 metal complexes were developed.[8–10] "CpCN" compounds should in principle be more "constrained" than "CpSiN" and, consequently, show different catalytic behavior. This was observed, but due to the limited number of examples of these types of complexes not well understood. We here describe the synthesis and structural characterization of a larger series of "CpCN"$TiX_2$ and "CpCN"$ZrX_2$ complexes and of some organometallic derivatives that were used to arrive at a better understanding of the chemical and catalytic properties of this interesting class of compounds.[8]

**Scheme 1**




**1a** (Ti), **1b** (Zr) **2** **3** (Ti, $R^1$=$CMe_3$) **4** (Ti, $R^1$=$CH_3$) **5** (Zr, $R^1$=$CH_3$) **6**

## Results and Discussion

**Synthesis of the "CpCN" Group 4 Metal Compounds.** In this study two reaction routes to "CpCN" ligand systems were used that had previously been developed and described by us.[8,11] Both are derived from suitably substituted fulvenes as starting materials. 6-*tert*-Butylfulvene (**7**) was shown to add a variety of lithium amide reagents LiNHR at the electrophilic fulvene carbon atom C6 to yield the respective −CH(CMe$_3$)-NHR-substituted cyclopentadienides (**8**). For this study, these were not isolated, but depronotated in situ at the secondary amine nitrogen by the subsequent addition of *n*-butyllithium to yield the "CpCN" dianion equivalents (**9**). The dilithio reagents (**9**) were isolated and characterized by NMR spectroscopy. Since it was known that the reaction of some reagents **9** with $TiCl_4$ or $ZrCl_4$ led to the organometallic "spiro" complexes of the composition ("CpCN")$_2$M,[8] transmetalation was carried out with the $TiCl_2(NMe_2)_2$ reagent[12] to asure a clean reaction in a 1:1 ratio to yield the respective ("CpCN")Ti$(NMe_2)_2$ products (**10**). These complexes[8] were characterized by $^1$H NMR spectroscopy and then directly treated with $Me_2SiCl_2$ [9] to yield the corresponding ("CpCN")$TiCl_2$ products **3a**−**d** (see Scheme 2).

Both the *p*-anisyl (**3b**) and the *o*-anisyl substituted complex (**3a**) feature very similar sets of $^1$H NMR signals of diastereotype pairs of $C_5H_4$ hydrogens (**3b**: $\delta$ 6.29, 6.26, 6.23, 5.91), although two of the methine signals of the latter are shifted to larger $\delta$-values (**3a**: $\delta$ 6.75, 6.62, 6.25, 5.70). The $^{13}$C NMR resonance of the bridging carbon atom C6 of **3b** occurs at $\delta$ 70.5, of **3a** at $\delta$ 68.5. A major difference is observed between the −$OCH_3$ $^1$H NMR and $^{13}$C NMR resonances [(**3b**: $\delta$ 3.23($^1$H), $\delta$ 54.9($^{13}$C); **3a**: $\delta$ 4.35($^1$H), 59.4($^{13}$C)]. This marked

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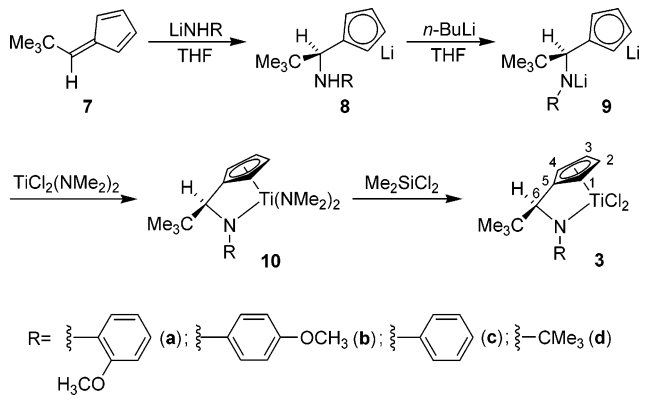
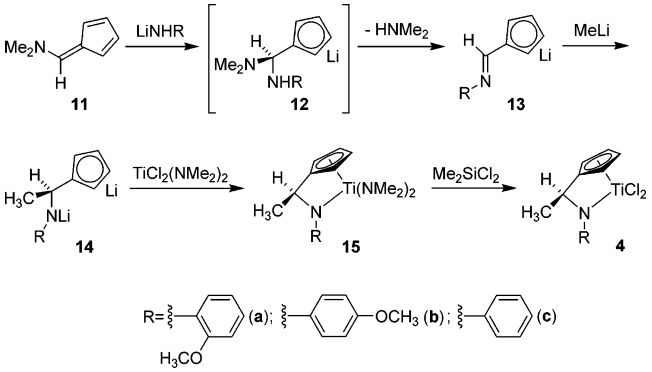
**Scheme 2**




**Scheme 3**



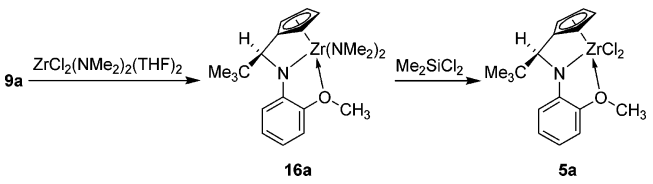

downfield shift is probably caused by the internal coordination of the oxygen atom of the methoxy group to the titanium center, as will later be supported by the X-ray crystal structure analysis (see below).

A second series of ("CpCN") titanium and zirconium complexes was prepared that featured a methyl substituent at the bridging carbon atom (C6). The synthesis of these systems required a different route, since the reaction of a strongly basic LiNHR reagent with, for example, 6-methylfulvene would have resulted in deprotonation at the methyl substituent to form an alkenylcyclopentadienide.[12] Therefore 6-(dimethylamino)fulvene (**11**)[13] was reacted with the LiNHR reagents to yield the aldimino-substituted cyclopentadienides (**13**) by means of an amide addition/dimethylamine elimination process.[11] Addition of methyllithium to **13** gave the respective "CpCN" dianion equivalents (**14**), which were subsequently transmetalated by treatment with the $TiCl_2(NMe_2)_2$ reagent to yield the ("CpCN")$Ti(NMe_2)_2$ systems (**15**). Their treatment with $Me_2SiCl_2$ eventually furnished the corresponding ("CpCN")$TiCl_2$ products (**4a**−**c**) (see Scheme 3).

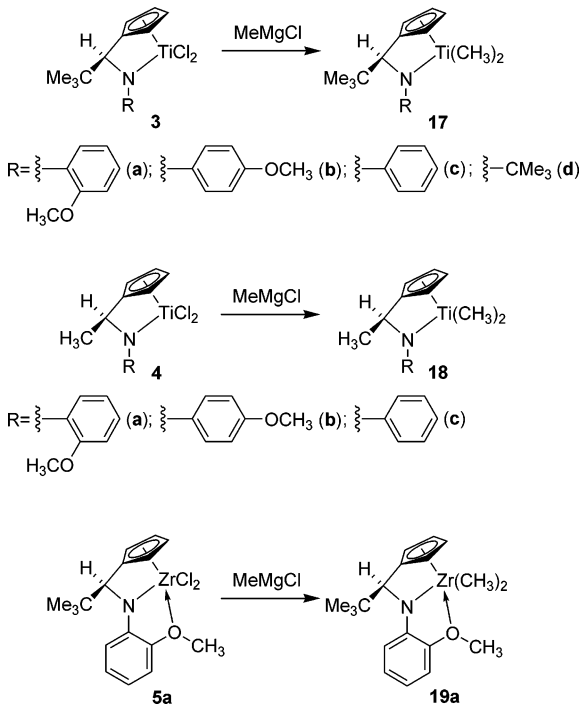
The [("CpCN")$^{2-}$]$(Li^+)_2$ reagent **9a** was also reacted with $ZrCl_2(NMe_2)_2(THF)_2$[14] to give the corresponding ("CpCN")$Zr(NMe_2)_2$ product (**16a**). Again, the reaction with $Me_2SiCl_2$ was used to exchange the dialkylamido $\sigma$-ligands at the group 4 transition metal center for chlorides. The ("CpCN")$ZrCl_2$ product (**5a**, see Scheme 4) was isolated as a pale yellow solid in ca. 80% yield.

**Formation of Organometallic Derivates of the ("CpCN")Titanium and Zirconium Complexes.** The

**Scheme 4**




**Scheme 5**




("CpCN")$TiCl_2$ complexes **3** and **4** were reacted with methylmagnesium chloride to give the corresponding ("CpCN")$Ti(CH_3)_2$ complexes (**17a**−**d** and **18a**−**c**) in yields ranging from 64% to 81%. Some of the complexes were isolated as yellow to red oils, others as yellow solids. Several of the compounds were characterized by X-ray diffraction. The ("CpCN")$ZrCl_2$ complex **5a** showed a very low solubility once it was isolated as a solid. Its reaction with the methyl Grignard reagent produced the soluble ("CpCN")$Zr(CH_3)_2$ product (**19a**), that was isolated as a yellowish solid in >80% yield (Scheme 5).

The ("CpCN")$TiMe_2$ complex **18a** features a pair of Ti-$CH_3$ $^1$H NMR signals at $\delta$ 0.29 and 0.11. The $-OCH_3$ $^1$H NMR resonance was found at $\delta$ 4.00, which is markedly shifted "downfield" as compared to its *p*-anisyl isomer **18b** ($OCH_3$: $\delta$ 3.37), which indicated coordination of the substituent oxygen atom to titanium. This was further supported by an NOE experiment: irradiation at the $^1$H NMR $-OCH_3$ resonance produced a strong response at both [Ti]$(CH_3)_2$ signals in complex **18a**. The structurally related *o*-anisyl-substituted titanium system **17a** features a $-OCH_3$ $^1$H NMR resonance at $\delta$ 4.03 and [Ti]$(CH_3)_2$ $^1$H NMR signals at $\delta$ 0.46 and 0.03. The zirconium analogue of **18a**, the ("CpCN")Zr$(CH_3)_2$ complex **19a**, shows a pair of [Zr]$(CH_3)_2$ $^1$H NMR resonances at markedly lower $\delta$ values ($\delta$ 0.09 and −0.30) and a $-OCH_3$ $^1$H NMR signal at $\delta$ 3.81. All these systems showed NOE spectra that indicated coordination of the *o*-anisyl methoxide oxygen atom to the group 4 metal center.

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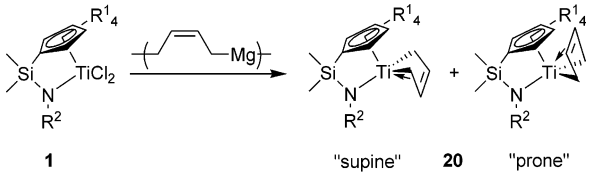
**Scheme 6**




($R^1$=$CH_3$, $R^2$=$CMe_3$: **a**)
($R^1$=H, $R^2$=$CMe_3$: **b**)

Group 4 metal dihalide complexes react readily with the "butadiene-magnesium" reagent[15] to yield the corresponding ($\eta^4$-butadiene)metal complexes. It had been shown that the conventional ("CpSiN")$TiCl_2$ and $-ZrCl_2$ systems (**1**) furnished mixtures of "prone"- and "supine" -$\eta^4$-butadiene metal complex isomers upon treatment with the butadiene-dianion equivalent (see Scheme 6). The equilibrium ratios of these isomers were dependent on the substituent pattern of the ligand framework and the metal. There was a tendency that the "prone" structures were favored for the Ti complexes and the "supine" structures for zirconium in many ("CpSiN")M-(butadiene) examples.[16,17,21] This was different in the ("CpCN")Ti(butadiene) series.

The ("CpCN")$TiCl_2$ complexes **3a**−**d**, **4b**, and **4c** were each reacted with the "butadiene-magnesium" reagent to give the respective ($\eta^4$-butadiene)titanium complexes (**21a**−**d**, **22b**, **22c**). In each case the $C_4H_6$ ligand was found to be coordinated in an *s-cis*-conformation,[16,17] and in each case only a single isomer was observed. In the case of complex **21b** (R = *p*-anisyl) a low-temperature $^1$H NMR study revealed that no rapid isomerism between prone and supine isomers[18] obscured the analysis.[19] In toluene-$d_8$ only a single set of signals was observed down to the lowest temperature studied (193 K, 600 MHz). However, in this specific case it was observed that the rotation around the N-(*p*-anisyl) vector became "frozen" on the $^1$H NMR time scale at low temperature,[20] which gave rise to a decoalescence of the pair of $-C_6H_4OCH_3$ $^1$H NMR resonances below $T_c$ = 233 K to four separate aromatic hydrogen resonances (see Figure 1 and the Experimental Section for details). From the temperature-dependent $^1$H NMR spectra an N-aryl rotational barrier of $\Delta G^{\ddagger}$(233 K) = 11.6 ± 0.3 kcal mol$^{-1}$ was calculated.

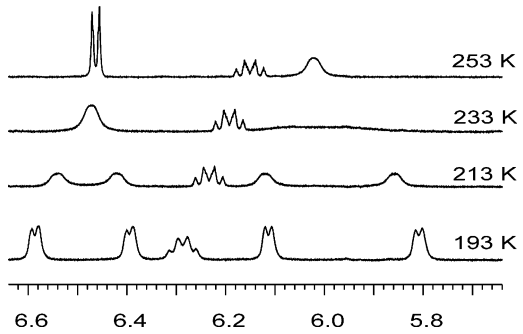



**Figure 1.** Dynamic $^1$H NMR spectra (600 MHz, $d_8$-toluene) of the aromatic region of complex **21b**, indicating a hindered rotation around the N-aryl vector.

**Scheme 7**

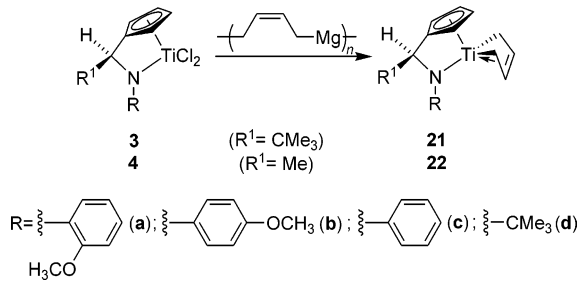



**Table 1. Comparison of the Butadiene Ligand $^1$H and $^{13}$C NMR Resonances of the ("CpCN")Ti(butadiene) Complexes 21 and 22 with Some of Their ("CpSiN")Ti($C_4H_6$) Counterparts[a]**

| compd | $\delta$ $^1H_{meso}$[d] | $\delta$ $^1H_{syn}$[d] | $\delta$ $^1H_{anti}$[d] | $\Delta\delta_H$[e] | $\delta$ $^{13}CH$[d] | $\delta$ $^{13}CH_2$[d] |
|---|---|---|---|---|---|---|
| **21a**[c] | 5.76 | 3.29 | 0.51 | 5.25 | 124.0 | 63.6 |
| | 4.95 | 3.05 | 0.36 | 4.59 | 126.4 | 64.2 |
| **21b**[b] | 6.29 | 3.67 | 0.43 | 5.86 | 124.1 | 63.3 |
| | 5.15 | 3.24 | −0.07 | 5.22 | 124.9 | 65.7 |
| **21c** | 6.16 | 3.57 | 0.47 | 5.69 | 125.1 | 64.2 |
| | 4.98 | 3.13 | −0.03 | 5.01 | 125.1 | 66.4 |
| **21d** | 5.88 | 3.20 | 0.28 | 5.60 | 116.6 | 64.2 |
| | 6.31 | 3.67 | −0.20 | 6.51 | 129.9 | 66.2 |
| **22b**[c] | 6.20 | 3.48 | 0.32 | 5.88 | 124.8 | 64.0 |
| | 5.37 | 3.11 | 0.07 | 5.30 | 124.8 | 65.2 |
| **22c** | 6.34 | 3.58 | 0.35 | 5.99 | 125.7 | 65.6 |
| | 5.44 | 3.12 | 0.13 | 5.31 | 125.4 | 66.6 |
| **20a**[f] (supine) | 6.33 | 2.84 | 0.04 | 6.29 | | |
| **20a**[f] (prone) | 4.15 | 3.01 | 1.71 | 2.44 | 111.9 | 62.0 |
| **20b**[f] (prone) | 4.20 | 3.28 | 1.82 | 2.38 | 107.2 | 62.8 |

[a] Spectra in benzene-$d_6$. [b] In toluene-$d_8$ at 193 K. [c] In toluene-$d_8$ at 298 K. [d] Each was separated into two values because of the chiral carbon of the bridge in these butadiene complexes. [e] $\delta$ $^1H_{meso}$ − $\delta$ $^1H_{anti}$. [f] From ref 17.

Because of the presence of the chiral carbon center in the $C_1$-bridge, all the complexes **21** and **22** exhibit a set of four separate $C_5H_4$ $^1$H NMR signals and a total of six butadiene $^1$H NMR resonances and four $^{13}$C NMR resonances. The three pairs of $C_4H_6$ $^1$H NMR signals are widely separated and occur in characteristic regions [e.g., **21d**: $\delta$ 5.88/6.31 ($H_{meso}$), $\delta$ 3.20/3.67 ($H_{syn}$), 0.28/−0.20 ($H_{anti}$)]. It was previously shown that the chemical shift difference $\Delta\delta$ of the $^1$H NMR $H_{meso}$ and $H_{anti}$ resonances was very different for the prone and supine isomers [e.g., **20a**: $\Delta\delta$ (prone) = 2.44, $\Delta\delta$ (supine) = 6.29 (see Scheme 7 and Table 1)].[17,21] This can be used for a spectroscopic identification of the isomer types. In the case of the complexes **21** and **22** all our examples show

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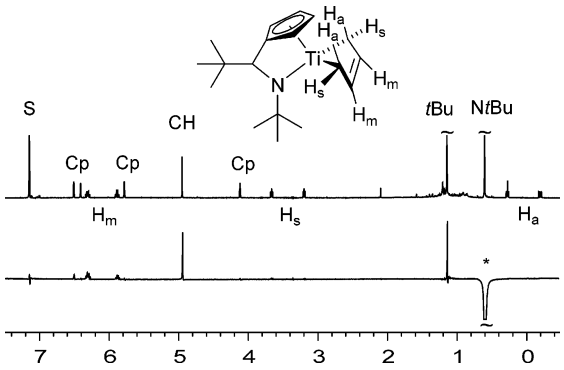


**Figure 2.** $^1$H NMR and 1D-NOE spectra of complex **21d** (in benzene-$d_6$).

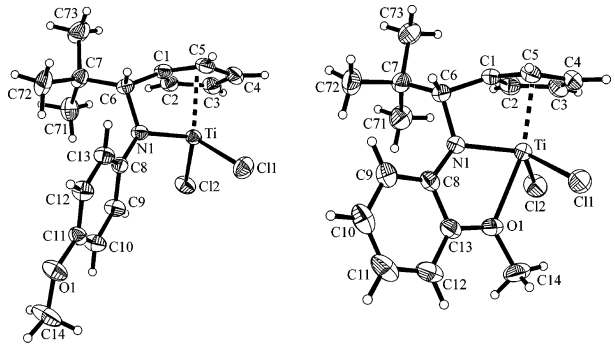


**Figure 3.** Views of the ("CpCN")$TiCl_2$ complexes **3b** (left) and **3a** (right) featuring *p*- and *o*-anisyl substituents at the ligand nitrogen atom.

very large $\Delta\delta$ ($H_{meso} - H_{anti}$) values (in a range between 4.59 and 6.51 ppm), which indicates that in contrast to the related ("CpSiN")Ti(butadiene) systems[17,21] the newly prepared ("CpCN")Ti($C_4H_6$) examples (**21**, **22**) all favored a supine structure having the $H_{meso}$ hydrogen atoms pointing away from the Cp ring.

The structural assignment of the ("CpCN")Ti(butadiene) complexes **21** and **22** as "supine" isomers was further supported by an NOE response of the $H_{meso}$ $^1$H NMR pair of resonances (and the adjacent C*H*[C($CH_3$)$_3$] signals as well) upon irradiating the N-C($CH_3$)$_3$ signal of complex **21d** (see Figure 2). Similar NOE features were also observed for the other members of this series of complexes.

The $-OCH_3$ group of the *o*-anisyl substituent of the ("CpCN")Ti(butadiene) complex **21a** seems not to be coordinated to the titanium center in contrast to its ("CpCN")$TiCl_2$ (**3a**) and ("CpCN")$TiMe_2$ (**17a**) relatives. This was concluded from the observation of an "unperturbed" $-OCH_3$ $^1$H NMR resonance of **21a** at $\delta$ 3.07 (**3a**: 4.35, **17a**: 4.03).

**X-ray Crystal Structure Analyses.** Ten of the ("CpCN")M(IV) complexes prepared in the course of this study were characterized by X-ray diffraction, among them the $\mu$-CH($CMe_3$)-bridged titanium dichlorides **3a**, **3b**, and **3d** and the corresponding [Ti]$Me_2$ system **17a**. In the $\mu$-CH($CH_3$)-bridged Cp/amido series the titanium dichlorides **4a**, **4b**, and **4c** as well as their [Ti]$Me_2$ derivates **18a** and **18b** were characterized by X-ray crystal structure analyses. In addition, the structure of the ("CpCN")zirconium dimethyl system **19a** was determined. A comparison of some general structural features is given in Table 2 together with some data of the ("CpSiN")$TiX_2$ systems. Detailed information on the structure determinations and the structural features of all 10 compounds of this study are provided with the Supporting Information. Some of the general structural characteristics of this class of ("CpCN")$MX_2$ complexes are discussed below by using selected examples.

Complex **3b** may serve as an example to outline the general characteristics of this class of compounds. The central titanium atom in **3b** is pseudotetrahedrally coordinated to a pair of chloride ligands (Ti−Cl1 2.2697(5)/2.2717(5) Å, Ti−Cl2 2.2691(5)/2.2726(6) Å), the amido nitrogen, and the Cp ligand of the CpCN ligand system. The Ti−N1 bond is rather short (1.921(1)/1.919(1) Å).[22] The Cp ligand is $\eta^5$-coordinated to titanium, but rather unsymmetrically probably because of the strain imposed on the system by the short $C_1$-bridge. The Ti−C1 linkage is markedly shorter than the Ti−C2/C5 bonds, which in turn are themselves slightly shorter than the Ti−C3/C4 linkage (for values see Table 2). The connecting C1−C6 vector between the Cp ring and the $C_1$ bridge is bent out of the Cp ligand plane toward the metal center. The corresponding Cp(centroid)−C1−C6 angle amounts to 153.3°/153.1°. The endocyclic C1−C6−N1 bond angle is 95.4° (averaged value from two independent molecules), which is far away from the tetrahedral $sp^3$-C value. The "constrained geometry" character in a series of related compounds is probably best characterized by the Cp(centroid)−metal−nitrogen angle, which responds sensitively to steric and electronic geometry changes. In **3b** it amounts to 96.0°. The coordination geometry of the ligand nitrogen atom is trigonal-planar. The *p*-anisyl substituent is rotated out of the plane of the nitrogen substituents in a direction that minimizes its steric interaction with the bulky *tert*-butyl group at C6 (dihedral angles: C1−C6−N1−C8 168.8(1)°/−164.9(1)°, C6−N1−C8−C9 143.6(2)°/−144.0(1)°, Ti−N1−C8−C9 −53.0(2)°/66.2(2)°).

The *o*-anisyl-substituted −CH($CMe_3$)-bridged ("CpCN")-$TiCl_2$ complex analogue **3a** features a similar structure, in which, however, the anisyl oxygen atom is coordinated to titanium at a position *trans* to the unsymmetrically bound $\eta^5$-Cp ligand. The overall structure may, therefore, be regarded as strongly distorted trigonal-bipyramidal. The Cp(centroid)−Ti−O angle in **3a** amounts to 164.9°. The three basal angles at titanium are 114.72(4)° (N−Ti−Cl1), 118.52(4)° (N−Ti−Cl2), and 111.25(2)° (Cl1−Ti−Cl2) [see for a comparison in **3b**: 105.94(4)°/110.26(4)° (N−Ti−Cl1), 108.27(4)°/103.22(4)° (N−Ti−Cl2), 104.51(2)°/106.76(2)° (Cl1−Ti−Cl2)]. The Ti−O bond length (2.282(1) Å) is in the typical range found in other ether adducts to $CpTiX_3$,[23] and the Ti−Cl bond lengths amount to 2.329(1) Å (Ti−Cl1) and 2.331(1) Å (Ti−Cl2), respectively, which is markedly larger than in **3b**. Again, the C1−C6 vector is oriented out of the Cp plane [Cp(centroid)−C1−C6: 156.5°, which is ca. 3° more bent than in the otherwise related complex **3b**]. The C1−C6−N angle in **3a** is 94.0(1)° and the Cp(centroid)−Ti−N angle amounts to 93.6°, i.e., even slightly smaller than found in **3b**. In contrast, the

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**Table 2. Compilation of Characteristic Structural Parameters of the ("CpCN")$MX_2$ Complexes[a]**

| | **3d** (Ti)[b] | **4c** (Ti) | **3b** (Ti)[b] | **4b** (Ti) | **18b** (Ti) | **3a** (Ti) | **17a** (Ti)[b] | **4a** (Ti) | **18a** (Ti) | **19a** (Zr) |
|---|---|---|---|---|---|---|---|---|---|---|
| M−C1 | 2.234(5)<br>2.242(5) | 2.251(2) | 2.258(2)<br>2.254(2) | 2.259(2) | 2.257(2) | 2.278(1) | 2.294(2)<br>2.298(2) | 2.290(2) | 2.312(2) | 2.427(2) |
| M−C2 | 2.278(5)<br>2.275(6) | 2.310(2) | 2.311(2)<br>2.280(2) | 2.310(2) | 2.332(3) | 2.318(2) | 2.323(2)<br>2.331(2) | 2.334(2) | 2.347(2) | 2.469(2) |
| M−C5 | 2.313(5)<br>2.323(6) | 2.302(2) | 2.303(2)<br>2.326(2) | 2.312(2) | 2.311(3) | 2.331(2) | 2.346(2)<br>2.346(2) | 2.326(2) | 2.353(2) | 2.484(2) |
| M−C3 | 2.376(5)<br>2.364(6) | 2.375(2) | 2.374(2)<br>2.358(2) | 2.371(2) | 2.412(3) | 2.416(2) | 2.427(2)<br>2.424(2) | 2.422(2) | 2.433(2) | 2.559(2) |
| M−C4 | 2.381(5)<br>2.391(6) | 2.372(2) | 2.366(2)<br>2.374(2) | 2.370(2) | 2.412(3) | 2.432(2) | 2.448(2)<br>2.438(2) | 2.422(2) | 2.445(2) | 2.576(2) |
| $Cp_{(centr.)}$−M | 1.982<br>1.990 | 1.988 | 1.987<br>1.984 | 1.991 | 2.018 | 2.027 | 2.042<br>2.042 | 2.032 | 2.054 | 2.196 |
| M−N | 1.936(4)<br>1.930(4) | 1.942(1) | 1.921(1)<br>1.919(1) | 1.933(1) | 1.944(2) | 1.963(1) | 2.009(2)<br>2.005(2) | 1.956(2) | 1.989(1) | 2.130(1) |
| $Cp_{(centr.)}$−C1−C6 | 155.5<br>154.6 | 154.0 | 153.3<br>153.1 | 153.7 | 153.8 | 156.5 | 155.7<br>155.4 | 155.8 | 155.1 | 158.0 |
| N−M−$Cp_{(centr.)}$ | 96.3<br>96.8 | 96.2 | 96.1<br>95.9 | 96.0 | 97.4 | 93.6 | 94.2<br>93.9 | 93.4 | 93.3 | 89.4 |
| C1−C6−N | 94.7(4)<br>95.5(4) | 96.8(1) | 95.6(1)<br>95.1(1) | 96.4(1) | 98.5(2) | 94.0(1) | 96.7(2)<br>96.3(2) | 94.8(2) | 96.5(1) | 98.2(1) |
| M−O | | | | | | 2.282(1) | 2.320(2)<br>2.302(2) | 2.295(2) | 2.332(1) | 2.320(1) |
| ∑ N angles | 356.3<br>358.4 | 359.0 | 358.3<br>354.2 | 359.0 | 359.5 | 357.6 | 349.4<br>348.7 | 360.0 | 358.7 | 353.0 |
| ∑ O angles | | | | | | 356.7 | 355.0<br>354.2 | 359.5 | 359.2 | 357.8 |

[a] Bond lengths in Å, angles in deg. [b] Values from two independent molecules in the unit cell.

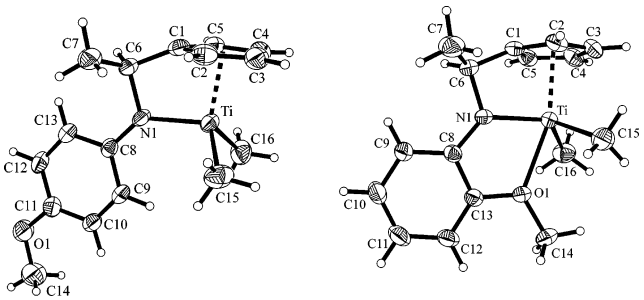



**Figure 4.** Molecular structures of the *p*-/*o*-anisyl-substituted ("CpCN")$TiMe_2$ complexes **18b** (left) and **18a** (right).

Ti−N bond length in the "pentacoordinated" complex **3a** is 1.964(1) Å, which is >0.04 Å longer than the corresponding bond in **3b**. The chelating oxygen forces the phenylene moiety in an orientation closer to the CpCN ligand plane ($\theta$C1−C6−N−C8 159.9(1)°, Ti−N−C8−C13−21.4(2)°).

The pairs of the corresponding $CH(CH_3)$-bridged *p*- and *o*-anisyl-substituted "CpCN"$TiCl_2$ complexes (**4b**, **4a**) show similar structural features (for details see Table 2 and the Supporting Information). Figure 4 shows views of the molecular structures of the corresponding pair of *p*-/*o*-anisyl-substituted ("CpCN")$TiMe_2$ complexes **18b** and **18a**.

In the dimethyl-Ti complexes **18** the Ti−C(Cp) bonds seem to be slightly longer than in the respective $[Ti]Cl_2$ complexes. Aside from that, very similar characteristic differences in the essential bonding features are observed between the examples of this pair of "constrained geometry" complexes. In the chelate complex **18a** the Ti−N bond is >0.04 Å longer than in **18b** (see Table 2), which is probably caused by the competing oxygen coordination. Also the Ti−$CH_3$ $\sigma$-bonds in **18b** [2.090(3) Å (Ti−C16), 2.092(3) Å (Ti−C15)] are shorter than in **18a** [2.130(2) Å (Ti−C16), 2.140(2) Å (Ti−C15)]. Again, the central CpCN framework seems to be more "constrained" in the five-coordinate system **18a**, which features a Cp(centroid)−Ti−N angle (93.3°) that is ca. 4° smaller than the corresponding angle in the tetracoordinated isomer **18b** (see Table 2). The zirconium complex **19a** also features a disturbed tetrahedral coordination geometry of the central complex core that is complemented by a weaker fifth donor coordination of the *o*-anisyl ether oxygen. Again, the metal−oxygen linkage is rather long (2.320(1) Å). The $C_5H_4$ unit of the "CpCN" ligand features the typical slightly disturbed $\eta^5$-coordination with an elongated M−Cp(centroid) value of 2.196 Å. The C1−C6 vector is oriented even more out of the Cp plane [Cp(centroid)−Zr−C6: 158.0°], and the Cp(centroid)−Zr−N angle in **19a** amounts to only 89.4° (see Table 3 and Figure 5).

The Cp(centroid)−metal−nitrogen angle serves as a good qualitative measure to assess and compare the structural "constraints" featured by the respective Cp/amido ligand frameworks in the series of "CpCN"$MX_2$ complexes and their various differently bridged counterparts that were previously published in the literature. The open, nonbridged reference system **25** (see Scheme 8) may mark the extreme, featuring a rather large Cp(centroid)−Ti−N angle of 116.2°. Most of the $Me_2Si$-bridged titanium complexes (**1**) exhibit Cp(centroid)−Ti−N angles around 105° to 107°, similar to the $-C_2H_4$-bridged complex **24** (104°). All the four-coordinate $C_1$-bridged "CpCN" titanium complexes feature far more "constrained" frameworks, featuring Cp(centroid)−Ti−N angles between 97.4° and 95.9°. The corresponding five-coordinate $C_1$-bridged systems that contain a weak internal ether oxygen donor binding to the metal show even slightly smaller Cp(centroid)−Ti−N angles in a range between 93.3° and 94.2° (see Table 2). We must assume that the introduction of the one-carbon $\mu$-CHR bridge between the Cp and the amido unit in the "CpCN" ligand frameworks results in an increase of the steric constraints of the dianionic ligand systems and an increased exposure of the central metal atom to other incoming ligands. This effect becomes even more pronounced on going to the related "CpCN"$ZrX_2$ sys-

**Table 3. Ethene Polymerization Examples Employing the ("CpCN")$MCl_2$ and ("CpCN")$MMe_2$ Complexes with Different Activators[a]**

| entry | compd | activator | $T$ (°C) | $t$ (min) | g(PE) | activity[b] |
|---|---|---|---|---|---|---|
| 1 | **3c** | MAO | 60 | 5 | 3.7 | 380 |
| 2 | **3c** | MAO | 25 | 30 | 5.8 | 100 |
| 3 | **3d** | MAO | 25 | 60 | 5.4 | 43 |
| 4 | **4c** | MAO | 60 | 60 | 0.8 | 6 |
| 5 | **3b** | MAO | 25 | 60 | 1.1 | 10 |
| 6 | **4b** | MAO | 25 | 40 | 0.5 | 5 |
| 7 | **3a** | MAO | 60 | 60 | 1.4 | 12 |
| 8 | **4a** | MAO | 60 | 60 | 4.4 | 37 |
| 9 | **1a** | MAO | 60 | 20 | 37 | 980 |
| 10 | **17d** | MAO | 25 | 30 | 8.5 | 96 |
| 11 | **17a** | $B(C_6F_5)_3$ | 60 | 30 | 0.33 | 6 |
| 12 | **17a** | $[Ph_3C^+]$[c] | 60 | 60 | 5.8 | 48 |
| 13 | **18a** | MAO | 60 | 30 | 1.9 | 27 |
| 14 | **18a** | $B(C_6F_5)_3$ | 60 | 30 | 0.15 | 2 |
| 15 | **18a** | $[Ph_3C^+]$[c] | 60 | 30 | 6.5 | 94 |
| 16 | **19a** | MAO | 60 | 10 | 16.1 | 910 |
| 17 | **19a** | MAO | 90 | 20 | 17.8 | 1006 |
| 18 | **19a** | $B(C_6F_5)_3$ | 60 | 20 | 0 | |
| 19 | **19a** | $[Ph_3C^+]$[c] | 60 | 3 | 9.4 | 3520 |
| 20 | **19a** | $[Ph_3C^+]$[c] | 60 | 3 | 9.0 | 3370 |

[a] In toluene solution, 2 bar ethene pressure, MAO-activated reactions with Al/M ratios of ca. 500. [b] Catalyst activities in g(PE)/[mmol(group 4 metal complex) h bar]$^{-1}$. Catalyst amounts used: 20 mg except entries 6, 7, 10 (25 mg) and 17, 19, 20 (10 mg). [c] $[Ph_3C^+][B(C_6F_5)_3^-]$.

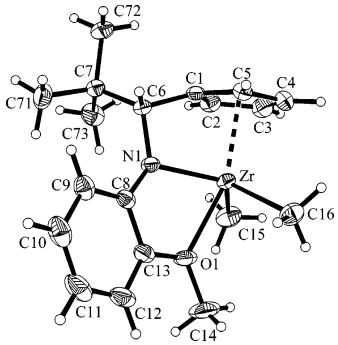
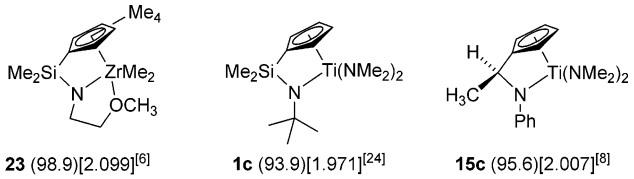
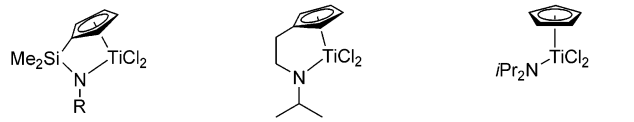



**Figure 5.** View of the molecular structure of the ("CpCN")-$Zr(CH_3)_2$ complex **19a**.

**Scheme 8. Cp(centroid)−M−N (deg) Angles and M−N [Å] Bond Lengths of Some "Constrained Geometry" Group 4 Metal Complexes and Related Systems for Comparison**




**23** (98.9)[2.099][6] **1c** (93.9)[1.971][24] **15c** (95.6)[2.007][8]




**1d** (R=tert-butyl) (107.0)[2.019][24]
**1e** (R=2,6-dimethyl-Ph) (105.1)[2.016][25]
**24** (104.4)[2.088][26]
**25** (116.2)[2.035][27]

tems. The Cp(centroid)−Zr−N angle in complex **19a** is only 89.4°, which is ca. 4° smaller than found in its ("CpCN")$TiMe_2$ analogue **18a** and ca. 7° smaller than found in complex **18b**. We will see whether these very substantial structural changes introduced by the "CpCN" relative to, for example, the commonly employed "CpSiN" ligand will have an influence on some of the chemical properties of these compounds and the active catalysts derived from them.

**Olefin Polymerization Experiments.** Preliminary investigations were carried out to study the behavior of the ("CpCN")$MCl_2$ and ("CpCN")$MMe_2$ (M = Ti, Zr) derived catalyst systems in olefin polymerization. Test reactions on ethene homopolymerization and subsequently on ethene/1-octene copolymerization reactions were performed. The catalytic features were very dependent on the specific activation method applied. The ("CpCN")$TiX_2$-derived systems were often found less active catalysts than their ("CpCN")$ZrX_2$ counterparts, a trend contrary to what had previously been observed in the ("CpSiN")$MX_2$ series.[3]

Some representative data of ethene polymerization reactions are listed in Table 3 (see the Supporting Information for more details and additional polymerization experiments). It reveals that most of the ("CpCN")$TiCl_2$ systems gave rather low activity ethene polymerization catalysts under the applied experimental conditions when activated with excess methylalumoxane (MAO, Al/Ti ratio ≥ 500). The **3c**/MAO catalyst is more active (entries 1 and 2 in Table 3), but even this system is less active than the ("CpSiN")$TiCl_2$ reference **1a**/MAO (Table 3, entry 9).

The method of activation seems to be of importance. Treatment of the ("CpCN")$TiMe_2$ complexex with $B(C_6F_5)_3$, a method widely used in homogeneous metallocene Ziegler−Natta catalyst activation,[28] here led to low activities. In our study, treatment of the ("CpCN")-$ZrMe_2$ complex **19a** with $B(C_6F_5)_3$ did not give an active ethene polymerization catalyst, although **19a** turned out to be a precursor for markedly faster catalysts when other methods of activation were used. MAO activation of ("CpCN")$ZrMe_2$ (**19a**) gave ethene polymerization catalysts of activities (entries 16 and 17) equal to those of the ("CpSiN")$TiCl_2$/MAO reference system (entry 9). The ("CpCN")$ZrMe_2$-derived system even surpassed this reference when the activation was carried out with trityl cation as methyl anion abstractor.[29] The **19a**/$[Ph_3C^+][B(C_6F_5)_4^-]$ catalyst exhibited a more than 3 times higher activity (Table 3, entries 19 and 20) than the already fast **1a**/MAO reference system in ethene polymerization under our reaction conditions.

Some of the ("CpCN")$TiCl_2$/MAO catalysts gave reasonable ethene/1-octene copolymerization activities (see Table 4, entries 1−4). The ethene/1-octene molar ratio

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**Table 4. Ethene/1-Octene Copolymerization with the ("CpCN")$MX_2$ (M = Ti, Zr; X = Cl or Me) Derived Catalysts[a]**

| entry | compd | activator | $T$ (°C) | $t$ (min) | g(copol) | ethene/1-octene[b] | $M_w$[c] | $M_w/M_n$[c] | activity[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **3c** | MAO | 60 | 20 | 19.3 | 3.0 | 7900 | 1.5 | 990 |
| 2 | **3c** | MAO | 90 | 10 | 8.4 | 3.6 | 6100 | 1.5 | 860 |
| 3 | **3d** | MAO | 60 | 10 | 7.2 | 3.4 | 6700 | 1.7 | 670 |
| 4 | **4a** | MAO | 60 | 10 | 1.6 | 3.5 | 5500 | 3.9 | 160 |
| 5 | **1a** | MAO | 60 | 5 | 35.1 | 3.4 | 52000 | 2.1 | 14 900 |
| 6 | **17a** | $[Ph_3C^+]$[d] | 60 | 10 | 1.5 | 5.8 | 21000 | 4.4 | 145 |
| 7 | **18a** | $[Ph_3C^+]$[d] | 60 | 10 | 11.4 | 3.6 | 29000 | 1.7 | 1000 |
| 8 | **19a** | MAO | 60 | 5 | 3.2 | 31 | 2700 | 2.0 | 1420 |
| 9 | **19a** | MAO | 90 | 5 | 5.6 | 21 | 1800 | 1.5 | 2540 |
| 10 | **19a** | $[Ph_3C^+]$[d] | 90 | 5 | 6.2 | 14 | 6700 | 1.7 | 2780 |
| 11 | **19a** | $[Ph_3C^+]$[d] | 90 | 5 | 6.7 | 14 | 7000 | 1.6 | 3040 |

[a] Reactions in 50 mL toluene/30 mL 1-octene at 2 bar ethene pressure. [b] Molar monomer ratio in the copolymer determined by $^{13}C$ NMR spectroscopy. [c] Determined by GPC. [d] In g(copolymer)/[mmol(group 4 metal complex) h bar]$^{-1}$. Catalyst amounts used: 20 mg except entries 5, 8−11 (10 mg). [e] $[Ph_3C^+][B(C_6F_5)_4^-]$.

in the random copolymer (as determined by $^{13}C$ NMR spectroscopy)[30] is similar to that typically observed for the **1a**/MAO reference, but the ("CpCN")$TiCl_2$/MAO systems are less active than the **1a**/MAO system and give lower molecular weights under the here applied reaction conditions. Again the ("CpCN")$ZrMe_2$-derived catalysts are more active also for ethene/1-octene copolymerization than their ("CpCN")$TiX_2$ counterparts, especially when the activation was carried out by treatment of complex **19a** with $[Ph_3C^+][B(C_6F_5)_4^-]$ (Table 4, entries 9−11), but in this case the 1-octene incorporation is markedly reduced (see Table 4).

**Some Conclusions.** It was shown in this study that the ("CpCN") group 4 metal dihalides and a variety of typical organometallic derivates of these complexes can rather easily be prepared. The synthetic routes allow for some variation of the substituents at the "CpCN" complex framework. For the catalytic use of these systems it seems important that ("CpCN")M derivates can now be prepared that feature $\sigma$-bonded hydrocarbyl ligands since this allows the application of a variety of catalyst activation procedures. The small number of variations carried out in the course of this study has already shown that finding the right activation method may be an important feature for generating active and selective CC-coupling catalysts from these "CpCN"M-(IV) precursors. The ("CpCN")$MX_2$-derived catalysts in some cases seem to exhibit properties different from those of the conventional ("CpSiN")$TiX_2$-derived systems. The rather small number of experiments carried out so far may suggest that ion-pairing effects[31] could be significantly determining some of the chemistry of these very open ("CpCN")M(IV) complex derived Ziegler−Natta catalysts systems. Some of the remarkable features of the neutral ("CpCN")$MX_2$ complexes and the (charged) catalyst systems derived thereof probably make it worthwhile to explore these interesting new $C_1$-bridged Cp/amido metal complex systems further.

## Experimental Section

**General Comments.** All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. Elemental analyses were made at a Foss-Heraeus CHN-O-Rapid, and a Nicolet 5DXC FT-IR spectrometer was used for IR spectra. NMR experiments were measured using a Bruker AC 200 P, a Varian Inova 500, or a Varian Unity Plus 600 NMR spectrometer. Most assignments were based on a series of 2D NMR experiments.

**X-ray Crystal Structure Analyses.** Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a 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) and Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000).

**Preparation of the Lithium Compounds. Preparation of (1-Phenylamido-2,2-dimethyl)propylcyclopentadienyldilithium (9c).** Aniline (2.79 g, 30.0 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. n-BuLi (1.69 M in hexane, 17.8 mL, 30.0 mmol) was added dropwise. The solution was stirred at room temperature for 30 min and then cooled to −78 °C. 6-*tert*-Butylfulvene (**7**) (4.02 g, 30.0 mmol) in THF (10 mL) was slowly added. The mixture was warmed slowly to room temperature followed by stirring for 2 h to give a solution whose yellow color faded away. The solution was cooled to −78 °C, and n-BuLi (1.69 M in hexane, 17.8 mL, 30.0 mmol) was added dropwise. The mixture was stirred overnight, while it warmed to room temperature. THF was removed, and the residue was washed with pentane and dried under vacuum to give a white powder of **9c** (9.82 g, 27.4 mmol, 91%). $^1H$ NMR experiment suggested the product contained 1.65 equiv of THF. $^1H$ NMR (200.1 MHz, $d_6$-DMSO, 298 K): $\delta$ 6.89 (m, 2H, *m*-Ph), 6.55 (m, 2H, *o*-Ph), 6.29 (m, 1H, *p*-Ph), 5.28, 5.17 (each m, each 2H, Cp), 3.89 (s, 1H, 6-H), 0.91 (s, 9H, 8-H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $d_6$-DMSO, 298 K): $\delta$ 128.2 (*m*-Ph), 113.6 (*p*-Ph),112.6 (*o*-Ph), 102.6, 101.7 (C-1/C-2/C-3/C-4), 64.8 (C-6), 36.2 (C-7), 27.7 (C-8).

**Preparation of (1-*tert*-Butylamido-2,2-dimethyl)propylcyclopentadienyldilithium (9d).** Lithium *N*-*tert*-butylamide (3.16 g, 40.0 mmol) was dissolved in THF (40 mL) and cooled to −78 °C. 6-*tert*-Butylfulvene (**7**) (5.36 g, 40.0 mmol) in THF (10 mL) was slowly added. The mixture was warmed slowly to room temperature followed by stirring overnight to give a light yellow solution. The solution was cooled to −78 °C, and n-BuLi (1.68 M in hexane, 23.8 mL, 40.0 mmol) was added dropwise. The mixture was stirred overnight while it warmed to room temperature. THF was removed, and the residue was washed with pentane and dried under vacuum to

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(31) Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257−8258. Lanza, G.; Fragalà, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764−12777.

a white powder of **9d** (10.48 g, 38.4 mmol, 96%). $^1$H NMR suggested the product contained 0.75 equiv of THF. $^1$H NMR (200.1 MHz, $d_6$-DMSO, 298 K): $\delta$ 5.13 (ps, 4H, Cp), 3.00 (s, 1H, 6-H), 0.87 (s, 9H, 10-H), 0.78 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (50.3 MHz, $d_6$-DMSO, 298 K): $\delta$ 123.4 (C-5), 101.9, 101.1 (C-1/C-2/C-3/C-4), 62.6 (C-6), 50.1 (C-9), 35.5 (C-7), 30.6 (C-10), 28.0 (C-8).

**Preparation of [1-(*o*-Methoxyphenylamido)-2,2-dimethyl]propylcyclopentadienyldilithium (9a).** By the same method used in the preparation of compound **9c**, from *o*-anisidine (3.69 g, 30.0 mmol) and 6-*tert*-butylfulvene (**7**) (4.02 g, 30.0 mmol), a pale gray powder of **9a** (11.89 g, 28.5 mmol, 95%) was obtained. $^1$H NMR suggested the product contained 2.0 equiv of THF. $^1$H NMR (200.1 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 6.58, 6.37, 5.74 (each m, 4H, Ph), 5.86 (ps, 4H, Cp), 3.98 (s, 1H, 6-H), 3.47 (s, 3H, $OCH_3$), 1.11 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (50.3 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 153.3, 149.3 (*ipso*-Ph), 123.4 (C-5), 125.1, 106.6, 103.5, 100.9, 100.5 (Ph and Cp, the peak at 100.9 ppm shows double intensity), 67.8 ($OCH_3$), 53.5 (C-6), 36.0 (C-7), 28.9 (C-8).

**Preparation of [1-(*p*-Methoxyphenylamido)-2,2-dimethyl]propylcyclopentadienyldilithium (9b).** By the same method used in the preparation of compound **9c**, from *p*-anisidine (3.69 g, 30.0 mmol) and 6-*tert*-butylfulvene (**8**) (4.02 g, 30.0 mmol), a yellow powder of **9b** (8.83 g, 27.3 mmol, 91%) was obtained. $^1$H NMR suggested the product contained 0.75 equiv of THF. $^1$H NMR (200.1 MHz, $d_6$-DMSO, 298 K): $\delta$ 6.58, 6.50 (each d, $^3J_{HH}$ = 9.2 Hz, each 2H, Ph), 5.26, 5.16 (each m, each 2H, Cp), 3.77 (s, 1H, 6-H), 3.58 (s, 3H, $OCH_3$), 0.91 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (50.3 MHz, $d_6$-DMSO, 298 K): $\delta$ 149.5, 145.5 (*ipso*-Ph), 119.1 (C-5), 114.2, 113.6 (Ph), 102.6, 101.7 (C-1/C-2/C-3/C-4), 66.0 ($OCH_3$), 55.5 (C-6), 36.1 (C-7), 27.8 (C-8).

**Preparation of [1-(Phenylamido)ethyl]cyclopentadienyldilithium (14c). Method 1**. MeLi (2.0 M in ether, 4.0 mL, 8.0 mmol) was added dropwise to a solution of (*N*-phenylformimidoyl)cyclopentadienyllithium (**13c**) (1.40 g, 8.0 mmol) in ether (25 mL) at −78 °C. The reaction mixture was warmed slowly to room temperature and stirred for 14 h. Ether was removed under vacuum; the remaining brown powder was washed with pentane and dried under vacuum to get **14c** (9.82 g, 7.26 mmol, 91%). $^1$H NMR suggested the dilithium salt was coordinated with one-third of an equivalent of ether. $^1$H NMR (200.1 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 7.17 (m, 2H, *m*-Ph), 6.64 (m, 2H, *o*-Ph), 6.44 (m, 1H, *p*-Ph), 5.95 (b, 4H, Cp), 4.51 (q, $^3J_{HH}$ = 5.9 Hz, 1H, 6-H), 1.64 (d, $^3J_{HH}$ = 5.9 Hz, 3H, 7-H).

**Method 2.** Lithium anilide (41.3 mmol) was prepared by adding n-BuLi (1.74 M in hexane, 41.3 mL, 41.3 mmol) to a solution of aniline (3.84 g, 41.3 mmol) in THF (20 mL) at −78 °C. The reaction mixture was stirred at room temperature for 1 h. The solution of lithium anilide was added slowly to a solution of 6-(dimethylamino)fulvene (**9**) (5.00 g, 41.3 mmol) in THF (20 mL), and the reaction mixture was stirred overnight. The reaction mixture was concentrated under vacuum to near dryness, and then 50 mL of ether was added. At −78 °C, MeLi (2.04 M in ether, 20.3 mL, 41.3 mmol) was added slowly, and the reaction mixture was stirred overnight. All volatiles were removed under vacuum. The residue was washed with pentane and dried under vacuum to give **14c** (10.96 g, 40.7 mmol, 98%) as a brown powder. The $^1$H NMR spectrum of the product revealed the dilithium salt was coordinated with 1 equiv of THF. $^1$H NMR (200.1 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 7.01 (m, 2H, *m*-Ph), 6.60 (m, 2H, *o*-Ph), 6.22(m, 1H, *p*-Ph), 5.93 (b, 4H, Cp), 4.49 (q, $^3J_{HH}$ = 5.9 Hz, 1H, 6-H), 1.49 (d, $^3J_{HH}$ = 5.9 Hz, 3H, 7-H).

**Preparation of [1-(*p*-Methoxyphenylamido)ethyl]cyclopentadienyldilithium (14b).** By method 2 used in preparation of compound **14c**, from *p*-anisidine (3.69 g, 30.0 mmol) and 6-(dimethylamino)fulvene (**9**) (3.63 g, 30.0 mmol) in THF (20 mL), a brown powder of **14b** (9.73 g, 29.0 mmol, 97%) was obtained. The $^1$H NMR spectrum of the product revealed that the dilithium salt contained 1.5 equiv of THF. $^1$H NMR (200.1 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 6.82, 6.58 (each d, $^3J_{HH}$ = 8.7 Hz, each 2H, Ph), 5.99 (b, 4H, Cp), 4.48 (q, $^3J_{HH}$ = 5.9 Hz, 1H, 6-H), 3.54 (s, 3H, $OCH_3$), 1.63 (d, $^3J_{HH}$ = 5.9 Hz, 3H, 7-H). $^{13}$C{$^1$H} NMR (50.3 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 155.7, 147.4 (*ipso*-Ph), 130.4 (C-5), 116.0, 113.7, 103.2, 102.6 (Ph and Cp), 67.8 ($OCH_3$), 56.5 (C-6), 25.7 (C-7).

**Preparation of [1-(*o*-Methoxyphenylamido)ethyl]cyclopentadienyldilithium (14a).** By the method used in preparation of compound **14b**, from *o*-anisidine (3.69 g, 30.0 mmol) and 6-(dimethylamino)fulvene (**11**) (3.63 g, 30.0 mmol), a brown powder of **14a** (8.31 g 29.0 mmol, 97%) was obtained. The $^1$H NMR spectrum of the product revealed that the dilithium salt contained 0.75 equiv of THF. $^1$H NMR (200.1 MHz, $d_8$-tetrahydrofuran, 298 K): $\delta$ 6.49, 6.33, 6.18, 5.64 (each m, each 1H, Ph), 5.71, 5.57 (each m, each 2H, Cp), 4.29 (q, $^3J_{HH}$ = 6.2 Hz, 1H, 6-H), 3.63 (s, 3H, $OCH_3$), 1.37 (d, $^3J_{HH}$ = 6.2 Hz, 3H, 7-H). $^{13}$C{$^1$H} NMR (50.3 MHz, $d_8$-tetrahydrofuran, 298 K): $\delta$ 152.2, 149.5 (*ipso*-Ph), 130.7 (C-5), 123.8, 107.0, 106.3, 102.5, 101.7 (Ph and Cp, the peak at 101.7 ppm shows double intensity), 68.3 ($OCH_3$), 54.2 (C-6), 26.3 (C-7).

**Synthesis of CpCN-Titanium and -Zirconium Diamides. General Procedure.** The dilithium salt ligand was dissolved in THF (10 mL THF/g lithium salt) and added slowly to a solution of bis(diamido)dichlorotitanium or bis(diamido)-dichlorozirconium (1 equiv) in THF (5 mL THF/g lithium salt) at −78 °C. The mixture was warmed to room temperature and stirred for 2 h. THF was removed, and the residue was extracted with pentane (3 × 20 mL). Removal of pentane gave a dark red oil (sometimes solid). The product was checked by $^1$H NMR and was used for the chlorination reaction without further purification.

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]titanium (10a).** From [1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyldilithium (**9a**) (2.0 THF adduct, 6.26 g, 15.0 mmol) and bis(dimethylamido)dichlorotitanium (3.10 g, 15.0 mmol) a dark red oil of **10a** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 7.60, 6.87, 6.58 (each br, 4H, Ph), 6.28, 6.14, 5.90 (each br, 4H, Cp), 5.55 (br, 1H, 6-H), 3.36 (br, 3H, $OCH_3$), 3.06, 2.86 (each s, each 6H, $(NCH_3)_2$), 1.14 (s, 9H, 8-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*p*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]titanium (10b).** From [1-(*p*-methoxylphenylamido)-2,2-dimethylpropyl]cyclopentadienyldilithium (**9b**) (0.75 THF adduct, 4.85 g, 15.0 mmol) and bis(dimethylamido)dichlorotitanium (3.10 g, 15.0 mmol) a dark red oil of **10b** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 6.97, 6.80 (each m, each 2H, Ph), 6.18, 6.13, 5.85, 5.74 (each m, each 1H, Cp), 4.79 (s, 1H, 6-H), 3.39 (s, 3H, $OCH_3$), 3.03, 2.88 (each s, each 6H, $(NCH_3)_2$), 1.14 (s, 9H, 8-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]titanium (10c).** From [1-(phenylamido)-2,2-dimethylpropyl]cyclopentadienyldilithium (**9c**) (1.65 equiv THF adduct, 4.22 g, 11.8 mmol) and bis(dimethylamido)dichlorotitanium (2.44 g, 11.8 mmol) a dark red oil of **10c** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 7.20 (m, 2H, *m*-Ph), 7.06 (m, 2H, *o*-Ph), 6.78 (m, 1H, *p*-Ph), 6.14, 6.11, 5.80, 5.71 (each m, each 1H, Cp), 4.87 (s, 1H, 6-H), 3.01, 2.84 (each s, each 6H, $N(CH_3)_2$), 1.13 (s, 9H, 8-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*tert*-butylamido)-2,2-dimethylpropyl]cyclopentadien-yl-$\kappa N$]titanium (10d).** From (1-*tert*-butylamido-2,2-dimethyl)propylcyclopentadienyldilithium (**9d**) (0.75 THF adduct, 4.10 g, 15.0 mmol) and bis(dimethylamido)dichlorotitanium (3.10 g, 15.0 mmol) a dark red oil of **10d** was obtained. $^1$H NMR (200.1

MHz, $d_6$-benzene, 298 K): $\delta$ 6.24, 5.71, 5.60, 5.45 (each m, each 1H, Cp), 4.39 (s, 1H, 6-H), 3.08, 2.91 (each s, each 6H, $(NCH_3)_2$), 1.33, 1.24 (each s, each 9H, 8-H/10-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N,O$]titanium (15a).** From [1-(*o*-methoxyphenylamido)ethyl]cyclopentadienyldilithium (**14a**) (0.75 THF adduct, 4.22 g, 15.0 mmol) and bis(dimethylamido)dichlorotitanium (3.10 g, 15.0 mmol), a dark red oil of **15a** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 6.83, 6.65−6.59 (4H, Ph), 6.09, 5.80 (each m, each 1H, Cp), 5.90 (m, 2H, Cp), 5.10 (q, $^3J_{HH}$ = 6.2 Hz, 1H, 6-H), 3.44 (s, 3H, $OCH_3$), 2.88, 2.85 (each s, each 6H, $NCH_3$), 1.35 (d, $^3J_{HH}$ = 6.2 Hz, 3H, 7-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*p*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N$]titanium (15b).** From [1-(*p*-methoxyphenylamido)ethyl]cyclopentadienyldilithium (**14b**) (1.5 THF adduct, 5.03 g, 15.0 mmol) and bis(dimethylamido)dichlorotitanium (3.10 g, 15.0 mmol), a dark red oil of **15b** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 6.92 (ps, 4H, Ph), 6.11, 6.06 (each m, each 1H, Cp), 5.87 (m, 2H, Cp), 4.94 (q, $^3J_{HH}$ = 6.2 Hz, 1H, 6-H), 3.44 (s, 3H, $OCH_3$), 3.03, 2.99 (each s, each 6H, $(NCH_3)_2$), 1.46 (d, $^3J_{HH}$ = 6.2 Hz, 3H, 7-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(phenylamido)ethyl]cyclopentadienyl-$\kappa N$]titanium (15c).** From [1-(phenylamido)ethyl]cyclopentadienyldilithium (**14c**) (1.0 equiv THF adduct, 5.40 g, 20.0 mmol) and bis(dimethylamido)dichlorotitanium (4.12 g, 20.0 mmol), a red powder of **15c** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 7.29 (m, 2H, *m*-Ph), 6.98 (m, 2H, *o*-Ph), 6.81 (m, 1H, *p*-Ph), 6.09, 6.02 (each m, each 1H, Cp), 5.85 (m, 2H, Cp), 4.94 (q, $^3J_{HH}$ = 6.2 Hz, 1H, 6-H), 3.00, 2.96 (each s, each 6H, $NCH_3$), 1.44 (d, $^3J_{HH}$ = 6.2 Hz, 3H, 7-H).

**Preparation of Bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]zirconium (16a).** From [1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyldilithium (**9a**) (2.0 THF adduct, 4.17 g, 10.0 mmol) and bis(dimethylamido)dichlorozirconiumbis(tetrahydrofuran) (**25**) (3.94 g, 10.0 mmol), a brown oil of **16a** was obtained. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 6.97, 6.78, 6.48 (each m, 4H, Ph), 6.28, 6.11, 6.04, 5.77 (each m, each 1H, Cp), 4.80 (s, 1H, 6-H), 3.63 (s, 3H, $OCH_3$), 2.78, 2.41 (each s, each 6H, $N(CH_3)_2$), 1.25 (s, 9H, 8-H).

**Synthesis of CpCN-Titanium or -Zirconium Dichloride Complexes. Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]-dichlorotitanium (3a).** After treatment of bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]-cyclopentadienyl-$\kappa N,O$]titanium (**10a**) [prepared from **9a** (6.26 g, 15.0 mmol) and $TiCl_2(NMe_2)_2$ (3.10 g, 15.0 mmol)] with 18 mL of dichlorodimethylsilane (18.58 g, 144 mmol) in 20 mL of toluene at 50 °C for 2 h, the reaction mixture was slowly cooled to −30 °C. The dark brown precipitated powder was collected by filtration and dried in a vacuum (**3a**: 4.86 g, 11.6 mmol, 77%). Suitable X-ray crystals were obtained by slow diffusion of pentane into a solution of this dichloride in toluene. $^1$H NMR experiment and X-ray crystal structure analysis suggested that complex **3a** contained 0.5 equiv of toluene. Anal. Calcd for $C_{17}H_{21}Cl_2NOTi$ $0.5C_7H_8$ (420.2): C 58.60, H 6.00, N 3.33. Found C 58.43, H 6.01, N 3.10. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 6.77 (m, 1H, 11-H), 6.75 (m, 1H, 3-H), 6.62 (m, 1H, 2-H), 6.58 (m, 1H, 12-H), 6.56 (m, 1H, 13-H), 6.41 (m, 1H, 10-H), 6.25 (m, 1H, 1-H), 5.70 (m, 1H, 4-H), 4.82 (s, 1H, 6-H), 4.35 (s, 3H, 15-H), 0.92 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 153.4 (C-14), 145.0 (C-9), 125.7 (C-3), 124.6 (C-2), 122.2 (C-4), 120.9 (C-12), 120.4 (C-11), 119.0 (C-1), 111.9 (C-5), 109.8 (C-13), 106.0 (C-10), 68.5 (C-6), 59.4 (C-15), 36.9 (C-7), 29.8 (C-8). X-ray crystal structure analysis of **3a**: formula $C_{17}H_{21}NOTiCl_2 \cdot 0.5\ C_7H_8$, $M$ = 420.21, red crystal 0.30 × 0.25 × 0.20 mm, $a$ = 9.118(1) Å, $b$ = 10.196(1) Å, $c$ = 11.842(1) Å, $\alpha$ = 78.07(1)°, $\beta$ = 73.09(1)°, $\gamma$ = 81.50(1)°, $V$ = 1026.0(2) Å$^3$, $\rho_{calc}$ = 1.360 g cm$^{-3}$, $\mu$ = 6.86 cm$^{-1}$, empirical absorption correction (0.821 ≤ $T$ ≤ 0.875), $Z$ = 2, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 9375 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 4830 independent ($R_{int}$ = 0.039) and 4246 observed reflections [$I \geq 2\sigma(I)$], 255 refined parameters, $R$ = 0.035, $R_w^2$ = 0.096, max. residual electron density 0.28 (−0.34) e Å$^{-3}$, toluene refined with geometrical restraints, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (3b).** After treatment of bis(dimethylamido)[$\eta^5$:[1-(methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]titanium (**10b**) [prepared from **9b** (4.85 g, 15.0 mmol) and $TiCl_2(NMe_2)_2$ (3.10 g, 15.0 mmol)] with 18 mL of dichlorodimethylsilane (18.58 g, 144 mmol) in 20 mL of toluene at 50 °C for 1 h, the reaction mixture was filtered, and the filtrate was slowly cooled to −30 °C and stored overnight at this temperature (**3b**: 3.47 g, 9.3 mmol, 62%). The dark brown precipitated powder was collected by filtration and dried under vacuum. Suitable X-ray crystals were obtained by slow diffusion of pentane into a solution of this dichloride in toluene. Anal. Calcd for $C_{17}H_{21}Cl_2NOTi$ (374.1): C 54.58, H 5.66, N 3.74. Found: C 54.33, H 5.66, N 3.36. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 7.15 (m, 2H, 10-H), 6.74 (m, 2H, 11-H), 6.29 (m, 1H, 1-H), 6.26 (m, 1H, 2-H), 6.23 (m, 1H, 3-H), 5.91 (m, 1H, 4-H), 4.98 (s, 1H, 6-H), 3.23 (s, 3H, 13-H), 0.79 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 158.2 (C-12), 147.4 (C-9), 125.2 (C-4), 123.3 (C-1), 120.7 (C-2), 120.1 (C-3), 119.8 (C-10), 114.8 (C-11), 110.8 (C-5), 70.5 (C-6), 54.9 (C-13), 36.6 (C-7), 27.8 (C-8). X-ray crystal structure analysis of **3b**: formula $C_{17}H_{21}NOTiCl_2$, $M$ = 374.15, dark red crystal 0.45 × 0.40 × 0.15 mm, $a$ = 8.950(1) Å, $b$ = 14.276(1) Å, $c$ = 15.915(1) Å, $\alpha$ = 64.89(1)°, $\beta$ = 88.06(1)°, $\gamma$ = 80.45(1)°, $V$ = 1814.3(3) Å$^3$, $\rho_{calc}$ = 1.370 g cm$^{-3}$, $\mu$ = 7.67 cm$^{-1}$, empirical absorption correction (0.724 ≤ $T$ ≤ 0.894), $Z$ = 4, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 19 626 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 8575 independent ($R_{int}$ = 0.039) and 7204 observed reflections [$I \geq 2\sigma(I)$], 405 refined parameters, $R$ = 0.034, $R_w^2$ = 0.092, max. residual electron density 0.34 (−0.36) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(Phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (3c).** After treatment of bis(dimethylamido)[$\eta^5$:[1-(phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]titanium (**10c**) [prepared from **9c** (4.22 g, 11.8 mmol) and $TiCl_2(NMe_2)_2$ (2.44 g, 11.8 mmol)] with 15 mL of dichlorodimethylsilane (15.48 g, 120 mmol) in 20 mL of toluene at 50 °C for 1 h, the reaction mixture was filtered, and the filtrate was cooled to −30 °C and stored overnight at this temperature. The brown precipitated powder was collected by filtration and dried in a vacuum (**3c**: 2.63 g, 7.6 mmol, 65%). Anal. Calcd for $C_{16}H_{19}Cl_2NTi$ (344.1): C 55.85, H 5.57, N 4.07. Found: C 55.33, H 5.66, N 4.02. $^1$H NMR (200.1 MHz, $d_6$-benzene, 298 K): $\delta$ 7.26−7.10 (m, 4H, *o*-Ph/*m*-Ph), 6.82 (m, 1H, *p*-Ph), 6.26 (m, 3H, Cp), 5.88 (m, 1H, Cp), 5.03 (s, 1H, 6-H), 0.77 (s, 9H, 8-H). $^1$H NMR (599.9 MHz, $d_2$-dichloromethane, 298 K): $\delta$ 7.44 (m, 2H, *m*-Ph), 7.24 (m, 2H, *o*-Ph), 7.14 (m, 1H, *p*-Ph), 6.93 (m, 1H, 2-H), 6.92 (m, 1H, 3-H), 6.76 (m, 1H, 1-H), 6.48 (m, 1H, 4-H), 5.57 (s, 1H, 6-H), 1.04 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_2$-dichloromethane, 298 K): $\delta$ 153.6 (*ipso*-Ph), 129.7 (*m*-Ph), 126.7 (C-4), 126.2 (*p*-Ph), 124.6 (C-1), 121.7 (C-2), 121.3 (C-3), 118.6 (*o*-Ph), 111.6 (C-5), 70.9 (C-6), 37.2 (C-7), 28.1 (C-8).

**Preparation of [$\eta^5$:[1-(*tert*-Butylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (3d).** Bis(dimethylamido)[$\eta^5$:[1-(*tert*-butylamido)-2,2-dimethylpropyl]-cyclopentadienyl-$\kappa N$]titanium (**10d**) [prepared from **9d** (4.10 g, 15.0 mmol) and $TiCl_2(NMe_2)_2$ (3.10 g, 15.0 mmol)] was dissolved in 20 mL of toluene. To the solution was added 18 mL of dichlorodimethylsilane (18.58 g, 144 mmol). The mixture

was stirred at 50 °C for 1 h. All volatiles were removed. The residue was extracted with pentane (3 × 30 mL). After filtration, the pentane solution was stored at −30 °C overnight. The precipitated yellow solid were collected by filtration and dried under vacuum (**3d**: 1.89 g, 5.8 mmol, 39%). Suitable X-ray crystals were obtained by slow diffusion of pentane into a solution of this dichloride in toluene. Anal. Calcd for $C_{14}H_{23}Cl_2NTi$ (324.1): C 51.88, H 7.15, N 4.32. Found: C 51.54, H 7.05, N 4.40. $^1$H NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 6.39 (m, 1H, 3-H), 6.25 (m, 1H, 2-H), 6.04 (m, 1H, 1-H), 5.53 (m, 1H, 4-H), 4.38 (s, 1H, 6-H), 1.46 (s, 1H, 10-H), 0.93 (s, 1H, 8-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 125.0 (C-4), 121.9 (C-3), 121.5 (C-2), 121.4 (C-1), 110.5 (C-5), 71.9 (C-6), 62.4 (C-9), 35.7 (C-7), 29.9 (C-10), 29.0 (C-8). X-ray crystal structure analysis of **3d**: formula $C_{14}H_{23}NTiCl_2$, $M$ = 324.13, orange crystal 0.30 × 0.20 × 0.20 mm, $a$ = 15.058(1) Å, $b$ = 18.737(1) Å, $c$ = 12.564(1) Å, $\beta$ = 114.18(1)°, $V$ = 3233.8(4) Å$^3$, $\rho_{calc}$ = 1.332 g cm$^{-3}$, $\mu$ = 8.44 cm$^{-1}$, empirical absorption correction (0.786 ≤ $T$ ≤ 0.849), $Z$ = 8, monoclinic, space group $P2_1/c$ (No. 14), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 30 503 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 7659 independent ($R_{int}$ = 0.059) and 6068 observed reflections [$I \geq 2\sigma(I)$], 337 refined parameters, $R$ = 0.078, $R_w^2$ = 0.196, max. residual electron density 0.51 (−0.43) e Å$^{-3}$, two almost identical molecules in the asymmetric unit, crystals are always of relatively poor quality, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)ethyl]-cyclopentadienyl-$\kappa N,O$]dichlorotitanium (4a).** Bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N,O$]titanium (**15a**) [prepared from **14a** (4.22 g, 15.0 mmol) and $TiCl_2(NMe_2)_2$ (3.10 g, 15.0 mmol)] was dissolved in 50 mL of toluene, and 20 mL of dichlorodimethylsilane (20.64 g, 160 mmol) was added. After it was stirred at 50 °C for 8 h, the mixture was cooled slowly to room temperature and finally stored at −30 °C overnight. The precipitated brown powder was collected by filtration and dried under vacuum (**4a**: 4.48 g, 13.5 mmol, 90%). Suitable X-ray crystals were obtained by slow diffusion of ether to a solution of the dichloride in dichloromethane, THF, and toluene. Anal. Calcd for $C_{14}H_{15}Cl_2NOTi$ (332.1): C 50.64, H 4.55, N 4.22. Found: C 49.76, H 4.04, N 2.98. $^1$H NMR (499.8 MHz, $d_2$-dichloromethane, 298 K): $\delta$ 7.18 (m, 1H, 12-H), 7.07 (m, 1H, 3-H), 7.05 (m, 1H, 2-H), 7.04 (m, 1H, 10-H), 6.97 (m, 1H, 11-H), 6.51 (m, 1H, 9-H), 6.45 (m, 1H, 1-H), 6.27 (m, 1H, 4-H), 5.47 (q, $^3J_{HH}$ = 6.4 Hz, 1H, 6-H), 4.60 (s, 3H, 14-H), 1.71 (d, $^3J_{HH}$ = 6.4 Hz, 3H, 7-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_2$-dichloromethane, 298 K): $\delta$ 153.0 (C-13), 143.0 (C-8), 125.7 (C-3), 125.2 (C-2), 121.9 (C-10), 121.8 (C-11), 121.3 (C-4), 118.2 (C-1), 114.6 (C-1), 109.9 (C-12), 105.0 (C-9), 59.3 (C-14), 54.3 (C-6), 16.4 (C-7). X-ray crystal structure analysis of **4a**: formula $C_{14}H_{15}NOTiCl_2$, $M$ = 332.07, red crystal 0.30 × 0.20 × 0.05 mm, $a$ = 18.280(1) Å, $b$ = 8.406(1) Å, $c$ = 9.450(1) Å, $V$ = 1452.1(2) Å$^3$, $\rho_{calc}$ = 1.519 g cm$^{-3}$, $\mu$ = 9.47 cm$^{-1}$, empirical absorption correction (0.764 ≤ $T$ ≤ 0.954), $Z$ = 4, orthorhombic, space group $Pca2_1$ (No. 29), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 11 076 reflections collected ($\pm h$, $\pm k$, $\pm l$)), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 3375 independent ($R_{int}$ = 0.061) and 3131 observed reflections [$I \geq 2\sigma(I)$], 174 refined parameters, $R$ = 0.031, $R_w^2$ = 0.079, Flack parameter −0.01(3), max. residual electron density 0.21 (−0.42) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)ethyl]-cyclopentadienyl-$\kappa N$]dichlorotitanium (4b).** After treatment of bis(dimethylamido)[$\eta^5$:[1-(*p*-methoxyphenylamido)-ethyl]cyclopentadienyl-$\kappa N$]titanium (**15b**) [prepared from **14b** (5.03 g, 15.0 mmol) and $TiCl_2(NMe_2)_2$ (3.10 g, 15.0 mmol)] with 18 mL of dichlorodimethylsilane (18.58 g, 144 mmol) in 20 mL of toluene at 50 °C for 4 h, the mixture was cooled slowly to room temperature. Then 20 mL of pentane was added. The dark red solution was stored at −30 °C overnight. The precipitated dark brown powder was collected by filtration and dried under vacuum (**4b**: 4.30 g, 11.4 mmol, 76%). Suitable X-ray crystals were obtained by slow diffusion of pentane into a solution of this dichloride in toluene. $^1$H NMR and X-ray crystal structure analysis suggested that complex **4b** contained 0.5 equiv of toluene. Anal. Calcd for $C_{14}H_{15}Cl_2NOTi\ 0.5C_7H_8$ (378.1): C 55.59, H 5.06, N 3.70. Found: C 55.66, H 5.05, N 3.59. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 7.31 (m, 2H, 9-H), 6.72 (m, 2H, 10-H), 6.24 (m, 1H, 2-H), 6.20 (m, 1H, 3-H), 6.05 (m, 1H, 1-H), 5.86 (m, 1H, 4-H), 5.01 (q, $^3J_{HH}$ = 6.4 Hz, 1H, 6-H), 3.25 (s, 3H, 12-H), 1.01 (d, $^3J_{HH}$ = 6.4 Hz, 3H, 7-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 157.7 (C-11), 147.4 (C-8), 123.5 (C-4), 121.4 (C-1), 120.5 (C-3), 120.1 (C-2), 115.8 (C-9), 114.1 (C-10), 112.1 (C-5), 55.0 (C-12), 54.8 (C-6), 15.3 (C-7). X-ray crystal structure analysis of **4b**: formula $C_{14}H_{15}NOTiCl_2 \cdot 0.5\ C_7H_8$, $M$ = 378.14, red crystal 0.35 × 0.30 × 0.10 mm, $a$ = 8.739(1) Å, $b$ = 9.758(1) Å, $c$ = 11.401(1) Å, α = 91.13(1)°, $\beta$ = 95.52(1)°, $\gamma$ = 112.59(1)°, $V$ = 891.8(2) Å$^3$, $\rho_{calc}$ = 1.408 g cm$^{-3}$, $\mu$ = 7.81 cm$^{-1}$, empirical absorption correction (0.772 ≤ $T$ ≤ 0.926), $Z$ = 2, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 9961 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.67 Å$^{-1}$, 4219 independent ($R_{int}$ = 0.035) and 3787 observed reflections [$I \geq 2\sigma(I)$], 214 refined parameters, $R$ = 0.035, $R_w^2$ = 0.094, max. residual electron density 0.29 (−0.30) e Å$^{-3}$, toluene refined with split positions, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(Phenylamido)ethyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (4c).** Bis(dimethylamido)[$\eta^5$:[1-(*N*-phenylamido)ethyl]cyclopentadienyl-$\kappa N$]titanium (**15c**) [prepared from **14c** (5.40 g, 20.0 mmol) and $TiCl_2(NMe_2)_2$ (4.12 g, 20.0 mmol)] was dissolved in 50 mL of toluene, and 10 mL of dichlorodimethylsilane (10.32 g, 80 mmol) was added. The mixture was stirred at 50 °C for 3 h. Then most of the dichlorodimethylsilane was removed under reduced pressure. The remaining solution was filtered through Celite. The filtrate was concentrated to about 30 mL, and 15 mL of pentane was slowly added. The mixture was stored overnight at −30 °C. The precipitated dark red crystals were collected by filtration and dried under vacuum (**4c**: 6 g, 0.1 mmol, 80%). Anal. Calcd for $C_{13}H_{13}Cl_2NTi$ (302.0): C 51.69, H 4.34, N 4.64. Found: C 51.45, H 4.42, N 4.67. $^1$H NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 7.33 (m, 2H, *o*-Ph), 7.14 (m, 2H, *m*-Ph), 6.80 (m, 1H, *p*-Ph), 6.21 (m, 1H, 2-H), 6.16 (m, 1H, 3-H), 6.01 (m, 1H, 1-H), 5.81 (m, 1H, 4-H), 4.97 (q, $^3J_{HH}$ = 6.6 Hz, 1H, 6-H), 0.99 (d, $^3J_{HH}$ = 6.6 Hz, 3H, 7-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 151.8 (*ipso*-Ph), 129.0 (*m*-Ph), 125.3 (*p*-Ph), 123.8 (C-4), 121.6 (C-1), 120.8 (C-3), 120.4 (C-2), 114.2 (*o*-Ph), 112.3 (C-5), 54.6 (C-6), 15.2 (C-7). X-ray crystal structure analysis of **4c**: formula $C_{13}H_{13}NTiCl_2$, $M$ = 302.04, red crystal 0.25 × 0.15 × 0.10 mm, $a$ = 12.527(1) Å, $b$ = 13.747(1) Å, $c$ = 15.721(1) Å, $V$ = 2707.3(3) Å$^3$, $\rho_{calc}$ = 1.482 g cm$^{-3}$, $\mu$ = 10.03 cm$^{-1}$, empirical absorption correction (0.788 ≤ $T$ ≤ 0.906), $Z$ = 8, orthorhombic, space group $Pbca$ (No. 61), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 20 694 reflections collected ($\pm h$, $\pm k$, $\pm l$)), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 3220 independent ($R_{int}$ = 0.042) and 2649 observed reflections [$I \geq 2\sigma(I)$], 155 refined parameters, $R$ = 0.031, $R_w^2$ = 0.080, max. residual electron density 0.24 (−0.50) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]dichlorozirconium (5a).** Bis(dimethylamido)[$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]zirconium (**16a**) [prepared from **9a** (4.17 g, 10.0 mmol) and $ZrCl_2(NMe_2)_2$ (3.94 g, 10.0 mmol)] was dissolved in 40 mL of toluene. Then 10 mL of dichlorodimethylsilane (10.32 g, 80 mmol) was added at −20 °C. The mixture was warmed to room temperature and stirred for 1 h. The precipitated yellow powder was collected by filtration and dried under vacuum (**5a**: 3.46 g, 8.3 mmol, 83%). The zirconium complex does not dissolve in any selected

solvents (such as toluene, benzene, chloroform, dichloromethane) without tetrahydrofuran. It could be that the zirconium dichloride complex is a polymer with the chorines as bridges between individual molecules. Anal. Calcd for $C_{17}H_{21}Cl_2NOZr$ (417.5): C 48.91, H 5.07, N 3.36. Found: C 48.95, H 4.76, N 3.02. $^1$H NMR (499.8 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 6.90 (m, 1H, 11-H), 6.69 (m, 1H, 1-H), 6.67 (m, 1H, 10-H), 6.59 (m, 1H, 13-H), 6.54 (m, 1H, 12-H), 6.34 (m, 1H, 4-H), 6.25 (m, 1H, 2-H), 6.21 (m, 1H, 3-H), 4.78 (s, 1H, 6-H), 4.00 (s, 3H, 15-H), 1.17 (s, 9H, 8-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene/$d_8$-tetrahydrofuran, 10:1, 298 K): $\delta$ 151.1 (C-14), 143.2 (C-9), 122.8 (C-11), 120.0 (C-4), 116.9 (C-12), 115.9 (C-1), 115.5 (C-5), 115.4 (C-3), 114.0 (C-2), 110.4 (C-10), 110.2 (C-13), 66.1 (C-6), 58.2 (C-15), 37.3 (C-7), 30.1 (C-8).

**Synthesis of CpCN-Titanium or -Zirconium Dimethyl Complexes. General Procedure.** The CpCN titanium or CpCN zirconium dichloride was dissolved in toluene (ca. 10 mL toluene/mmol dichloride) and cooled to −78 °C. MeMgCl (3.0 M in THF, 2 molar equiv) was added. The mixture was warmed slowly to room temperature. All volatiles were removed under vacuum, and the residue was extracted with pentane (20 mL), followed by filtration. After evaporation of the solvent, normally a dark yellow oil or a brown solid was obtained.

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]dimethyltitanium (17a).** From [$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]dichlorotitanium (**3a**) (630 mg, 1.5 mmol) and MeMgCl (3.0 M in THF, 1.0 mL, 3.0 mmol), a yellow to brown powder of **17a** (403 mg 1.2 mmol, 81%) was obtained. Suitable X-ray crystals were obtained by slow diffusion of pentane into a toluene solution of the dimethyl complex at −30 °C. Anal. Calcd for $C_{19}H_{27}NOTi$ (333.3): C 68.47, H 8.17, N 4.20. Found: C 68.28, H 7.88, N 4.13. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 6.91 (m, 1H, 11-H), 6.74 (m, 1H, 3-H), 6.71 (m, 1H, 13-H), 6.60 (m, 2H, 10-H/12-H), 6.50 (m, 1H, 2-H), 5.88 (m, 1H, 1-H), 5.38 (m, 1H, 4-H), 4.32 (s, 1H, 6-H), 4.03 (s, 3H, 15-H), 1.03 (s, 9H, 8-H), 0.46 (s, 3H, 16-H), 0.03 (s, 3H, 17-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 152.2 (C-14), 144.2 (C-9), 122.1 (C-11), 119.4 (C-3), 117.3 (C-4), 117.2 (C-2), 115.7 (C-12), 113.6 (C-1), 109.3 (C-13), 108.6 (C-10), 107.1 (C-5), 65.7 (C-6), 57.2 (C-15), 48.7 (C-17), 44.8 (C-16), 36.6 (C-7), 29.5 (C-8). X-ray crystal structure analysis of **17a**: formula $C_{19}H_{27}NOTi$, $M$ = 333.32, yellow crystal 0.20 × 0.15 × 0.05 mm, $a$ = 9.197(1) Å, $b$ = 11.255(1) Å, $c$ = 17.432(1) Å, α = 79.97(1)°, $\beta$ = 87.83(1)°, $\gamma$ = 86.50(1)°, $V$ = 1772.9(3) Å$^3$, $\rho_{calc}$ = 1.249 g cm$^{-3}$, $\mu$ = 4.85 cm$^{-1}$, empirical absorption correction ($0.909 \le T \le 0.976$), $Z$ = 4, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 18 724 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 8441 independent ($R_{int}$ = 0.055) and 5678 observed reflections [$I \ge 2\sigma(I)$], 409 refined parameters, $R$ = 0.051, $R_w^2$ = 0.119, max. residual electron density 0.31 (−0.38) e Å$^{-3}$, two almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dimethyltitanium (17b).** From [$\eta^5$:[1-(*p*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**3b**) (374 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a yellow to red oil of **17b** (236 mg 0.71 mmol, 71%) was obtained. Anal. $C_{19}H_{27}NOTi$ (333.3): C 68.47, H 8.17, N 4.20. Found: C 68.49, H 8.08, N 3.88. $^1$H NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 7.11 (m, 2H, 10-H), 6.84 (m, 2H, 11-H), 6.39 (m, 1H, 3-H), 6.36 (m, 1H, 2-H), 5.86 (m, 1H, 1-H), 5.60 (m, 1H, 4-H), 4.55 (s, 1H, 6-H), 3.31 (s, 3H, 13-H), 0.87 (s, 9H, 8-H), 0.86 (s, 3H, 14-H), 0.25 (s, 3H, 15-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 156.3 (C-12), 145.5 (C-9), 121.8 (C-4), 120.0 (C-10), 119.4 (C-1), 115.3 (C-11), 115.2 (C-2), 115.0 (C-3), 104.5 (C-5), 68.0 (C-6), 56.0 (C-15), 54.9 (C-13), 46.0 (C-14), 36.9 (C-7), 27.9 (C-8).

**Preparation of [$\eta^5$:[1-(Phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dimethyltitanium (17c).** From [$\eta^5$:[1-(phenylamido)-2,2-dimethylpropyl)]cyclopentadienyl-$\kappa N$]-dichlorotitanium (**3c**) (344 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a dark yellow oil was obtained (**17c**: 218 mg, 0.72 mmol, 72%). Anal. Calcd for $C_{18}H_{25}NTi$ (303.3): C 71.29, H 8.31, N 4.62. Found: C 71.46, H 8.16, N 4.05. $^1$H NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 7.28 (m, 2H, *o*-Ph), 7.26 (m, 2H, *m*-Ph), 6.90 (m, 1H, *p*-Ph), 6.39 (m, 1H, 3-H), 6.37 (m, 1H, 2-H), 5.88 (m, 1H, 1-H), 5.59 (m, 1H, 4-H), 4.63 (s, 1H, 6-H), 0.92 (s, 3H, 9-H), 0.89 (s, 9H, 8-H), 0.29 (s, 3H, 10-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 151.9 (*ipso*-Ph), 130.0 (*m*-Ph), 122.7 (*p*-Ph), 121.8 (C-4), 119.5 (C-1), 118.2 (*o*-Ph), 115.6 (C-2), 115.4 (C-3), 104.4 (C-5), 67.0 (C-6), 57.8 (C-10), 47.5 (C-9), 37.1 (C-7), 28.0 (C-8).

**Preparation of [$\eta^5$:[1-(*tert*-Butylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dimethyltitanium (17d).** From [$\eta^5$:[1-(*tert*-butylamido)-2,2-dimethylpropyl)]cyclopentadienyl-$\kappa N$]dichlorotitanium (**3d**) (324 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a dark yellow oil was obtained (**17d**: 229 mg, 0.81 mmol, 81%). Anal. Calcd for $C_{16}H_{29}NTi$ (283.3): C 67.84, H 10.32, N 4.94. Found: C 67.14, H 9.98, N 4.80. $^1$H NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 6.47 (m, 1H, 3-H), 6.43 (m, 1H, 2-H), 5.61 (m, 1H, 1-H), 5.31 (m, 1H, 4-H), 4.04 (s, 1H, 6-H), 1.59 (s, 9H, 10-H), 1.02 (s, 9H, 8-H), 0.60 (s, 3H, 11-H), 0.27 (s, 3H, 12-H). $^{13}$C{$^1$H} NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 121.1 (C-4), 117.3 (C-1), 116.4 (C-3), 116.2 (C-2), 105.5 (C-5), 69.1 (C-6), 57.7 (C-9), 47.3 (C-12), 43.5 (C-11), 35.1 (C-7), 31.2 (C-10), 29.4 (C-8).

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)ethyl]-cyclopentadienyl-$\kappa N,O$]dimethyltitanium (18a).** From [$\eta^5$:[1-(*o*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N,O$]dichlorotitanium (**4a**) (498 mg, 1.5 mmol) and MeMgCl (3.0 M in THF, 1.0 mL, 3.0 mmol), a yellow to brown powder of **18a** (297 mg 1.0 mmol, 68%) was obtained. Suitable X-ray crystals were obtained by slow diffusion of pentane into a toluene solution of the dimethyl complex at −30 °C. Anal. Calcd for $C_{16}H_{21}NOTi$ (291.2): C 65.99, H 7.27, N 4.81. Found: C 65.74, H 6.96, N 4.47. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 6.96 (m, 1H, 10-H), 6.74 (m, 1H, 12-H), 6.71 (m, 1H, 3-H), 6.67 (m, 1-H, 11-H), 6.63 (m, 1H, 2-H), 5.71 (m, 1H, 1-H), 5.45 (m, 1H, 4-H), 4.34 (q, $^3J_{H-H}$ = 6.4 Hz, 1H, 6-H), 4.00 (s, 3H, 14-H), 1.17 (d, $^3J_{H-H}$ = 6.4 Hz, 3H, 7-H), 0.29 (s, 3H, 15-H), 0.11 (s, 3H, 16-H). $^{13}$C{$^1$H} NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 151.7 (C-13), 142.4 (C-8), 122.3 (C-10), 118.3 (C-3), 117.2 (C-2), 115.8 (C-11), 115.4 (C-4), 112.1 (C-1), 108.9 (C-5), 108.8 (C-12), 106.2 (C-9), 57.2 (C-14), 51.1 (C-6), 46.4 (C-16), 44.3 (C-15), 16.4 (C-7). X-ray crystal structure analysis of **18a**: formula $C_{16}H_{21}NOTi$, $M$ = 291.24, yellow crystal 0.35 × 0.25 × 0.15 mm, $a$ = 8.889(1) Å, $b$ = 8.988(1) Å, $c$ = 10.515(1) Å, α = 111.86(1)°, $\beta$ = 94.71(1)°, $\gamma$ = 104.14(1)°, $V$ = 742.0(1) Å$^3$, $\rho_{calc}$ = 1.304 g cm$^{-3}$, $\mu$ = 5.69 cm$^{-1}$, empirical absorption correction ($0.826 \le T \le 0.920$), $Z$ = 2, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 7546 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 3506 independent ($R_{int}$ = 0.044) and 3092 observed reflections [$I \ge 2\sigma(I)$], 176 refined parameters, $R$ = 0.038, $R_w^2$ = 0.104, max. residual electron density 0.30 (−0.36) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)ethyl]-cyclopentadienyl-$\kappa N$]dimethyltitanium (18b).** From [$\eta^5$:[1-(*p*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**4b**) (0.5 equiv toluene adduct, 378 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a red powder of **18b** (186 mg 0.64 mmol, 64%) was obtained. Suitable X-ray crystals could be obtained by slow diffusion of pentane into a solution of the dimethyl complex in toluene at −30 °C. Anal. Calcd for $C_{16}H_{21}NOTi$ (291.2): C 65.99, H 7.27, N 4.81. Found: C 65.46, H 7.30, N 4.78. $^1$H NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 7.25 (m, 2H, 9-H), 6.87 (m, 2H, 10-H), 6.36 (m, 2H, 2-H/3-H), 5.77 (m, 1H, 1-H), 5.63 (m, 1H, 4-H),

4.69 (q, $^3J_{HH}$ = 6.5 Hz, 1H, 6-H), 3.37 (s, 3H, 12-H), 1.13 (d, $^3J_{HH}$ = 6.5 Hz, 3H, 7-H), 0.84 (13-H), 0.58 (14-H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 154.9 (C-11), 145.0 (C-8), 120.0 (C-4), 117.5 (C-1), 115.2 (C-3), 115.1 (C-9), 114.8 (C-10), 114.7 (C-2), 106.3 (C-5), 57.4 (C-14), 54.9 (C-12), 52.0 (C-6), 49.7 (C-13), 15.6 (C-7). X-ray crystal structure analysis of **18b**: formula $C_{16}H_{21}NOTi$, $M$ = 291.24, red crystal 0.20 × 0.20 × 0.15 mm, $a$ = 7.820(1) Å, $b$ = 11.577(1) Å, $c$ = 16.910(1) Å, $V$ = 1530.9(3) Å$^3$, $\rho_{calc}$ = 1.264 g cm$^{-3}$, $\mu$ = 5.51 cm$^{-1}$, empirical absorption correction ($0.898 \le T \le 0.922$), $Z$ = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 12 189 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.66 Å$^{-1}$, 3623 independent ($R_{int}$ = 0.063) and 2836 observed reflections [$I \ge 2\sigma(I)$], 176 refined parameters, $R$ = 0.042, $R_w^2$ = 0.099, Flack parameter 0.04(3), max. residual electron density 0.31 (−0.31) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Preparation of [$\eta^5$:[1-(Phenylamido)ethyl]cyclopentadienyl-$\kappa N$]dimethyltitanium (18c).** From [$\eta^5$:1-(*N*-phenylamido)ethylcyclopentadienyl-$\kappa N$]dichlorotitanium (**4c**) (302 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a dark yellow oil was obtained (**18c**: 177 mg, 0.68 mmol, 68%). Anal. Calcd for $C_{15}H_{19}NTi$ (261.2): C 68.98, H 7.33, N 5.36. Found: C 70.29, H 6.56, N 4.48. $^1H$ NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 7.34 (m, 2H, *o*-Ph), 7.29 (m, 2H, *m*-Ph), 6.86 (m, 1H, *p*-Ph), 6.35 (m, 2H, 2-H/3-H), 5.77 (m, 1H, 1-H), 5.60 (m, 1H, 4-H), 4.66 (q, $^3J_{HH}$ = 6.6 Hz, 1H, 6-H), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 3H, 7-H), 0.87 (s, 3H, 8-H), 0.62 (s, 3H, 9-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 150.6 (*ipso*-Ph), 129.7 (*m*-Ph), 121.4 (*p*-Ph), 120.4 (C-4), 117.9 (C-1), 115.7 (C-3), 115.1 (C-2), 114.0 (*o*-Ph), 106.7 (C-5), 59.4 (C-9), 51.8 (C-6/C-8), 16.1 (C-7).

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dimethylzirconium (19a).** From [$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]dichlorozirconium (**5a**) (417 mg, 1.0 mmol) and MeMgCl (3.0 M in THF, 0.67 mL, 2.0 mmol), a yellow powder of **19a** (304 mg 0.81 mmol, 81%) was obtained. Suitable X-ray crystals were obtained by slow diffusion of pentane to a toluene solution of the dimethyl complex at −30 °C. Anal. Calcd for $C_{19}H_{27}NOZr$ (376.7): C 60.59, H 7.23, N 3.72. Found: C 60.03, H 6.66, N 3.99. $^1H$ NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 6.93 (m, 1H, 11-H), 6.72 (m, 1H, 10-H), 6.49 (m, 2H, 12-H/13-H), 6.41 (m, 1H, 3-H), 6.21 (m, 1H, 2-H), 6.13 (m, 1H, 1-H), 5.55 (m, 1H, 4-H), 4.49 (s, 1H, 6-H), 3.81 (s, 3H, 15-H), 1.10 (s, 9H, 8-H), 0.09 (s, 3H,16-H), −0.30 (s, 3H, 17-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ = 150.1 (C-14), 142.3 (C-9), 123.5 (C-11), 114.6 (C-3), 114.4 (C-4), 114.2 (C-12), 111.8 (C-2), 111.0 (C-10), 110.4 (C-1), 109.3 (C-13), 109.1 (C-5), 65.3 (C-6), 57.8 (C-15), 36.9 (C-7), 32.3 (C-17), 30.3 (C-16), 29.6 (C-8). X-ray crystal structure analysis of **19a**: formula $C_{19}H_{27}NOZr$, $M$ = 376.64, light yellow crystal 0.25 × 0.20 × 0.10 mm, $a$ = 9.409(1) Å, $b$ = 9.442(1) Å, $c$ = 11.747(1) Å, α = 76.51(1)°, $\beta$ = 73.70(1)°, $\gamma$ = 65.31(1)°, $V$ = 902.0(2) Å$^3$, $\rho_{calc}$ = 1.387 g cm$^{-3}$, $\mu$ = 6.11 cm$^{-1}$, empirical absorption correction ($0.862 \le T \le 0.941$), $Z$ = 2, triclinic, space group $P\bar{1}$ (No. 2), $\lambda$ = 0.71073 Å, $T$ = 198 K, $\omega$ and $\varphi$ scans, 9955 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta$)/$\lambda$] = 0.67 Å$^{-1}$, 4380 independent ($R_{int}$ = 0.036) and 4158 observed reflections [$I \ge 2\sigma(I)$], 205 refined parameters, $R$ = 0.024, $R_w^2$ = 0.067, max. residual electron density 0.37 (−0.55) e Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

**Synthesis of CpCN-Titanium Butadiene Complexes. General Procedure.** The CpCN titanium or CpCN zirconium dichloride and 1.1 equiv of butadiene magnesium THF complex ($C_4H_6Mg$·2THF) were combined and cooled at −78 °C. Precooled toluene (10 mL of toluene/mmol dichloride) was added. The mixture was warmed slowly to room temperature. Toluene was removed, and the residue was taken up with pentane (20 mL of pentane/mmol dichloride). After filtration of lithium chloride, pentane was removed and the remaining dark brown oily product was dried in a vacuum (atom numbering of the butadiene ligand used: 11−14 in complexes **21**, 8−11 in the complexes **22**).

**Preparation of [$\eta^5$:[1-(*o*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$](butadiene)titanium (21a).** From [$\eta^5$:[1-(*o*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N,O$]dichlorotitanium (**3a**) (with 0.5 equiv toluene, 210 mg, 0.5 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (122 mg, 0.55 mmol), a dark green to yellow oil of **21a** (192 mg 0.61 mmol, 61%) was dried in a vacuum. Anal. Calcd for $C_{21}H_{27}NOTi$ (357.3): C 70.59, H 7.62, N 3.92. Found: C 71.53, H 7.65, N 3.73. $^1H$ NMR (499.8 MHz, $d_8$-toluene, 298 K): $\delta$ 6.90 (ps, 1H, 1-H), 6.66 (m, 1H, 16-H), 6.60 (m, 1H, 4-H), 6.58 (m, 1H, 15-H), 6.34 (br, 1H, 14-H), 6.21 (m, 1H, 17-H), 5.76 (m, 1H, 10-H), 5.46 (ps, 1H, 2-H), 5.34 (ps, 1H, 3-H), 5.05 (s, 1H, 6-H), 4.95 (m, 1H, 11-H), 3.29 (m, 1H, $9_{syn}$-H), 3.07 (s, 3H, 19-H), 3.05 (m, 1H, $12_{syn}$-H), 1.00 (s, 9H, 8-H), 0.51 (m, 1H, $9_{anti}$-H), 0.36 (br, 1H, $12_{anti}$-H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $d_8$-toluene, 298 K): $\delta$ 151.0 (C-18), 142.5 (C-13), 126.4 (C-11), 124.0 (C-10), 123.3 (C-16), 120.6 (C-15), 113.8 (C-4), 111.0 (C-5), 110.2 (C-1/C-17), 109.5 (C-3), 108.3 (C-2), 73.5 (C-6), 64.2 (C-12), 63.6 (C-9), 55.0 (C-19), 36.4 (C-7), 28.0 (C-8).

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$](butadiene)titanium (21b).** From [$\eta^5$:[1-(*p*-methoxyphenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**3b**) (374 mg, 1.0 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (244 mg, 1.1 mmol), a dark green to yellow oil of **21b** (239 mg 0.67 mmol, 67%) was obtained. Anal. Calcd for $C_{21}H_{27}NOTi$ (357.3): C 70.59, H 7.62, N 3.92. Found: C 70.55, H 7.66, N 3.90. $^1H$ NMR (599.9 MHz, $d_8$-toluene, 193 K): $\delta$ 6.99 (m, 1H, 1-H), 6.72 (m, 1H, 4-H), 6.54, 6.40 (each d, each $^3J_{HH}$ = 8.0 Hz, each 1H, 14-H/18-H), 6.29 (m, 1H, 10-H), 6.11, 5.81 (each d, each $^3J_{HH}$ = 8.0 Hz, each 1H, 15-H/17-H), 5.26 (m, 1H, 2-H), 5.15 (m, 1H, 11-H), 5.09 (ps, 1H, 3-H), 4.68 (s, 1H, 6-H), 3.67 (m, 1H, $9_{syn}$-H), 3.24 (m, 1H, $12_{syn}$-H), 3.17 (s, 3H, 19-H), 0.99 (s, 9H, 8-H), 0.43 (m, 1H, $9_{anti}$-H), −0.07 (m, 1H, $12_{anti}$-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, $d_8$-toluene, 193 K): $\delta$ 154.9 (C-16), 147.7 (C-13), 125.3, 117.8 (C-15/C-17), 124.9 (C-11), 124.1 (C-10), 113.4, 112.3 (C-14/C-18), 112.3 (C-4), 111.1 (C-1), 110.1 (C-5), 109.5 (C-3), 109.3 (C-2), 72.9 (C-6), 65.7 (C-12), 63.3 (C-9), 54.2 (C-19), 36.7 (C-7), 27.9 (C-8).

**Preparation of [$\eta^5$:[1-(Phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]-(butadiene)titanium (21c).** From [$\eta^5$:[1-(*N*-phenylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**3c**) (344 mg, 1.0 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (244 mg, 1.1 mmol), a dark brown oily product of **21c** (214 mg 0.65 mmol, 65%) was obtained. Anal. Calcd for $C_{20}H_{25}NTi$ (327.3): C 73.40, H 7.70, N 4.28. Found: C 73.76, H 7.84, N 3.73. $^1H$ NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 6.98 (m, 1H, 1-H), 6.90 (m, 2H, *m*-Ph), 6.72 (m, 1H, *p*-Ph), 6.67 (m, 1H, 4-H), 6.20 (m, 2H, *o*-Ph), 6.16 (m, 1H, 10-H), 5.39 (m, 1H, 2-H), 5.23 (m, 1H, 3-H), 4.98 (m, 1H, 11-H), 4.94 (s, 1H, 6-H), 3.57 (m, 1H, $9_{syn}$-H), 3.13 (m, 1H, $12_{syn}$-H), 0.96 (s, 9H, 8-H), 0.47 (m, 1H, $9_{anti}$-H), −0.03 (m, 1H, $12_{anti}$-H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 154.7 (*ipso*-Ph), 128.1 (*m*-Ph), 125.9 (C-11), 125.1 (C-10), 122.5 (*p*-Ph), 121.4 (*o*-Ph), 122.2 (C-4), 111.2 (C-1), 110.6 (C-5), 109.7 (C-2/C-3), 73.8 (C-6), 66.4 (C-12), 64.2 (C-9), 37.1 (C-7), 28.2 (C-8).

**Preparation of [$\eta^5$:[1-(*tert*-Butylamido)-2,2-dimethylpropyl]cyclopentadienyl-$\kappa N$](butadiene)titanium (21d).** From [$\eta^5$:[1-(*tert*-butylamido)-2,2-dimethylpropyl)]cyclopentadienyl-$\kappa N$]dichlorotitanium (**3d**) (324 mg, 1.0 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (244 mg, 1.1 mmol), a dark brown oily product of **21d** (167 mg 0.54 mmol, 54%) was obtained. Anal. Calcd for $C_{18}H_{29}NTi$ (307.3): C 70.35, H 9.51, N 4.56. Found: C 69.73, H 9.40, N 4.26. $^1H$ NMR (599.9 MHz, $d_6$-benzene, 298 K): $\delta$ 6.51 (m, 1H, 4-H), 6.41 (m, 1H, 1-H), 6.31 (m, 1H, 13-H), 5.88 (m, 1H, 12-H), 5.78

(m, 1H, 3-H), 4.95 (s, 1H, 6-H), 4.12 (m, 1H, 2-H), 3.67 (m, 1H, $14_{syn}$-H), 3.20 (m, 1H, $11_{syn}$-H), 1.15 (s, 9H, 8-H), 0.61 (s, 9H, 10-H), 0.28 (m,1H, $11_{anti}$-H), −0.20 (m, 1H, $14_{anti}$-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, $d_6$-benzene, 298 K): $\delta$ 129.9 (C-13), 116.6 (C-12), 122.5 (C-5), 110.7 (C-4), 109.4 (C-3), 108.2 (C-2), 105.5 (C-1), 70.6 (C-6), 66.2 (C-14), 64.2 (C-11), 62.5 (C-9), 35.2 (C-7), 31.2 (C-10), 30.2 (C-8).

**Preparation of [$\eta^5$:[1-(*p*-Methoxyphenylamido)ethyl]-cyclopentadienyl-$\kappa N$](butadiene)titanium (22b).** From [$\eta^5$:[1-(*p*-methoxyphenylamido)ethyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**4b**) (0.5 equiv toluene adduct, 378 mg, 1.0 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (244 mg, 1.1 mmol), a dark green to yellow oil of **22b** (198 mg 0.63 mmol, 63%) was obtained. Anal. Calcd for $C_{18}H_{21}NOTi$ (315.2): C 68.58, H 6.71, N 4.44. Found: C 68.52, H 6.72, N 4.29. $^1H$ NMR (599.9 MHz, $d_8$-toluene, 298 K): $\delta$ 6.86 (m, 1H, 1-H), 6.67 (m, 1H, 4-H), 6.49 (m, 2H, 13-H), 6.20 (m, 1H, 9-H), 6.04 (m, 2H, 14-H), 5.56 (m, 1H, 2-H), 5.37 (m, 1H, 10-H), 5.25 (m, 1H, 3-H), 4.92 (q, $^3J_{HH}$ = 6.5 Hz, 1H, 6-H), 3.48 (m, 1H, $8_{syn}$-H), 3.28 (s, 3H, 16-H), 3.11 (m, 1H, $11_{syn}$-H), 1.19 (d, $^3J_{HH}$ = 6.5 Hz, 3H, 7-H), 0.32 (m, 1H, $8_{anti}$-H), 0.07 (m, 1H, $11_{anti}$-H). $^{13}C\{^1H\}$ NMR (150.8 MHz, $d_8$-toluene, 298 K): $\delta$ 155.4 (C-15), 147.5 (C-12), 124.8 (C-9/C-10), 121.1 (C-14), 113.5 (C-13), 112.2 (C-5), 109.9 (C-4), 109.6 (C-3), 109.1 (C-1), 108.9 (C-2), 65.2 (C-11), 64.0 (C-8), 58.6 (C-6), 54.6 (C-16), 17.0 (C-7).

**Preparation of [$\eta^5$:[1-(Phenylamido)ethyl]cyclopentadienyl-$\kappa$N](butadiene)titanium (22c).** From [$\eta^5$:[1-(*N*-phenylamido)ethyl]cyclopentadienyl-$\kappa N$]dichlorotitanium (**4c**) (302 mg, 1.0 mmol) and butadiene magnesium THF complex ($C_4H_6Mg$·2THF) (244 mg, 1.1 mmol), a gray oily product of **22c** (192 mg 0.67 mmol, 67%) was obtained. Anal. Calcd for $C_{17}H_{19}NTi$ (285.2): C 71.59, H 6.71, N 4.91. Found: C 71.34, H 7.07, N 4.41. $^1H$ NMR (499.8 MHz, $d_6$-benzene, 298 K): $\delta$ 6.97 (m, 2H, *m*-Ph), 6.91 (m, 1H, 1-H), 6.75 (m, 1H, *p*-Ph), 6.66 (m, 1H, 4-H), 6.34 (m, 1H, 9-H), 6.22 (m, 2H, *o*-Ph), 5.55 (m, 1H, 2-H), 5.44 (m, 1H, 10-H), 5.13 (m, 1H, 3-H), 5.09 (q, $^3J_{HH}$ = 6.3 Hz, 1H, 6-H), 3.58 (m, 1H, $8_{syn}$-H), 3.12 (m, 1H, $11_{syn}$-H), 1.28 (d, $^3J_{HH}$ = 6.3 Hz, 3H, 7-H), 0.35 (m, 1H, $8_{anti}$-H), 0.13 (m, 1H, $11_{anti}$-H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $d_6$-benzene, 298 K): $\delta$ 153.5 (*ipso*-Ph), 128.5 (*m*-Ph), 125.7 (C-9), 125.4 (C-10), 121.6 (*p*-Ph), 119.6 (*o*-Ph), 112.5 (C-5), 110.3 (C-3), 109.7 (C-4), 109.5 (C-1/C-2), 66.6 (C-11), 65.6 (C-8), 57.6 (C-6), 17.2 (C-7).

**Catalytic Ethylene Polymerization.** A 1 L Büchi glass autoclave with a catalyst reservoir and magnetic stirrer was evacuated and filled with argon three times before it was charged with 200 mL of toluene and 20 mL of 10% methylalumoxane in toluene. A precise amount of catalyst was dissolved in 7 mL of toluene and then loaded into the catalyst reservoir. The stirrer was started (600 rpm) and the autoclave was thermostated at a certain temperature while the solution was saturated with ethylene at 2 bar, which was controlled by bpc 1202 (Büchi pressflow gas controller with program 'bls2'). After the solution was saturated with ethylene (the line of consumption volume went flat), the catalyst solution in the reservoir was introduced directly into the autoclave.

When $Ph_3C^+B(C_6F_5)_4^-$ or $B(C_6F_5)_3$ was used instead of MAO as activator, 200 mL of toluene and 0.5 mL of triisobutylaluminum (used as scavenger) were introduced into the autoclave before catalysts (prepared by adding a solution of 1 equiv of activator in 5 mL of 1,2-dichlorobenzene to a solution of dimethyl complexes in 2 mL of 1,2-dichlorobenzene) were loaded into the reservoir.

The polymerization reaction was stopped by terminating the transfer of ethylene with the bpc controller and quenching with 20 mL of aqueous HCl in methanol (1:1 v/v). The precipitated polyethylene was collected by filtration, washed subsequently with HCl, water, and methanol, and dried at 80 °C in a vacuum overnight to constant weight.

**Catalytic Ethylene/1-Octene Copolymerization.** A 1 L Büchi glass autoclave with a catalyst reservoir and magnetic stirrer was evacuated and filled with argon three times before it was charged with 30 mL of toluene, 50 mL of 1-octene, and 20 mL of 10% methylalumoxane in toluene. A precise amount of catalyst was dissolved in 7 mL of toluene and then loaded into the reservoir. The stirrer was started (600 rpm), and the autoclave was thermostated at a certain temperature while the solution was saturated with ethylene at 1 bar, which was controlled by a bpc 1202 (Büchi pressflow gas controller with program 'bls2'). After the solution was saturated with ethylene (the line of consumption volume went flat), the catalyst solution in the reservoir was introduced directly into the autoclave.

When $[Ph_3C^+][B(C_6F_5)_4^-]$ was used instead of MAO as activator, 50 mL of toluene, 50 mL of 1-octene, and 0.5 mL of triisobutylaluminum (used as scavenger) were introduced into the autoclave before catalysts (prepared by adding a solution of 1 equiv of activator in 5 mL of 1,2-dichlorobenzene to a solution of dimethyl complexes in 2 mL of 1,2-dichlorobenzene) were loaded into the reservoir.

The polymerization reaction was stopped by terminating the transfer of ethylene with the bpc controller and quenching with 20 mL of aqueous HCl in methanol (1:1 v/v). The reaction mixture was separated. The organic phase was washed with aqueous HCl and water. The toluene solution was concentrated by using a rotating evaporator, and then the residue was dried at 80 °C in a vacuum overnight to constant weight.

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**Supporting Information Available:** A more detailed Experimental Section is provided, including further spectroscopic data of the organometallic compounds and additional information about the polymerization experiments and additional information about the X-ray crystal structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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