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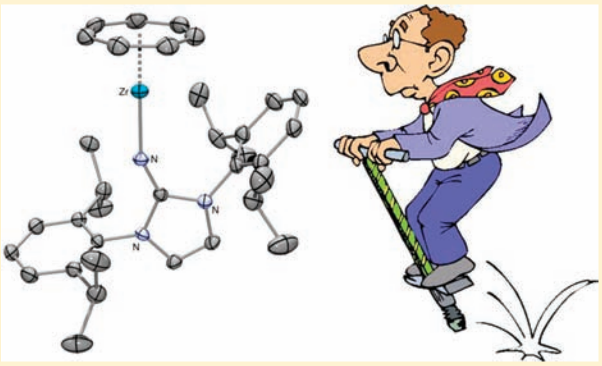
From a Cycloheptatrienylzirconium Allyl Complex to a Cycloheptatrienylzirconium Imidazolin-2-iminato "Pogo Stick" Complex with Imido-Type Reactivity

Andreas Glöckner, Thomas Bannenberg, Constantin G. Daniliuc, Peter G. Jones, and Matthias Tamm*

Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, 38106 Braunschweig, Germany

Supporting Information

ABSTRACT: The reaction of the cycloheptatrienylzirconium half-sandwich complex [(η^7-C_7H_7)ZrCl(tmeda)] (**1**) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with Li(Im^{Dipp}N), generated from bis(2,6-diisopropylphenyl)imidazolin-2-imine (Im^{Dipp}NH) with methyllithium, yields the imidazolin-2-iminato complex [(η^7-C_7H_7)Zr(Im^{Dipp}N)(tmeda)] (**2**). The corresponding tmeda-free complex [(η^7-C_7H_7)Zr(Im^{Dipp}N)] (**5**) can be synthesized via the 1,3-bis(trimethylsilyl)allyl complex [(η^7-C_7H_7)Zr{η^3-$C_3H_3(TMS)_2$}(THF)] (**3**; TMS = $SiMe_3$), which undergoes an acid−base reaction with Im^{Dipp}NH to form **5** and 1,3-bis(trimethylsilyl)propene. **5** exhibits an unusual one-legged piano stool ("pogo stick") geometry with a particularly short Zr−N bond of 1.997(2) Å. Addition of 2,6-dimethylphenyl or *tert*-butyl isocyanide affords the complexes [(η^7-C_7H_7)Zr(Im^{Dipp}N)(CNR)] (R = *o*-Xy, **6**; R = *t*-Bu, **7**), while the reaction with 2,6-dimethylphenyl isocyanate results in a [2 + 2] cycloaddition to form the ureato(1−) complex [(η^7-C_7H_7)Zr{Im^{Dipp}N(C═O)N-*o*-Xy}] (**8**). **5** can also act as an initiator for the ring-opening polymerization of *ε*-caprolactone. These reactivity patterns together with density functional theory calculations reveal a marked similarity of the bonding in imidazolin-2-iminato and conventional imido transition-metal complexes.

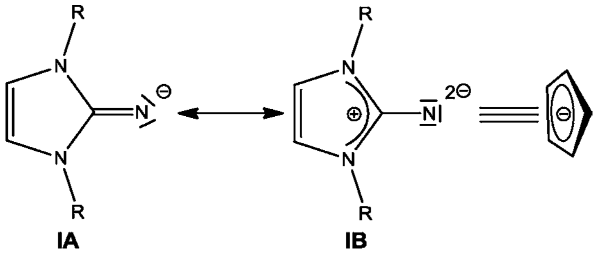


■ INTRODUCTION

In the past few decades, much research has been devoted to organometallic chemistry involving imido ligands.[1] This interest stems in particular from the ability of these ligands not only to act as ancillary spectator ligands in catalytic processes such as olefin polymerization or alkene metathesis,[2] but also to participate in many metathesis, cycloaddition, C−H bond activation, and hydroamination reactions.[3] Furthermore, they are ideal candidates for the stabilization of high oxidation state metal complexes, since extensive electron donation of an $(NR)^{2-}$ ligand to the metal is possible by one σ and either one or two π bonds.[4]

Despite their monanionic nature, a similar bonding picture can be found for imidazolin-2-iminato ligands (Im^{R}N$^-$), which can be described by the two limiting resonance structures **IA** and **IB** (Scheme 1). As a result of efficient stabilization and delocalization of a positive charge within the imidazoline ring in **IB**, these ligands are highly basic and can also act as $2\sigma,4\pi$-electron donors.[5] Thus, imidazolin-2-iminato ligands are related to phosphoraneiminato ligands and can be regarded as monoanionic imido-type ligands or as monodentate analogues of the ubiquitous cyclopentadienyl ligand.[6,7] These ligands have been used extensively by us and others for the complexation of early transition metals,[8] with some of the resulting complexes displaying high activity in ethylene (co)polymerization and alkyne metathesis.[9,10] In addition, these ligands proved useful for supporting rare-earth-metal complexes with exceptionally short metal−nitrogen bonds.[11] Among the latter is a series of [(η^8-C_8H_8)M(Im^{Dipp}N)] complexes (M = Sc, Y, Lu, Gd; Im^{Dipp}N = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-iminato),[11a,b] which are isolobal to a series of cyclooctatetraenyltitanium imido complexes reported by Mountford.[12] Depending on the substituents, these unique [(η^8-C_8H_8)Ti(NR)] complexes exhibit a rare one-legged piano stool ("pogo stick")

Scheme 1. Mesomeric Structures for Imidazolin-2-iminato Ligands (Im^{R}N$^-$) and Isolobal Relationship with the Cyclopentadienyl Anion



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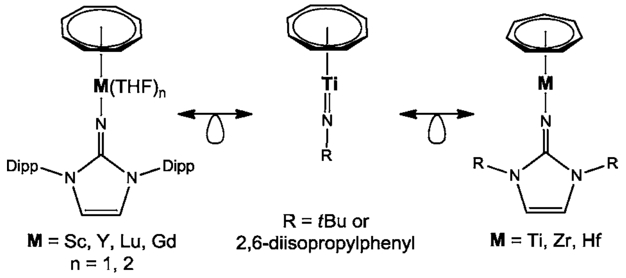
geometry, whereas for the heavier zirconium congeners only dimeric, imido-bridged complexes could be isolated to date.[13] Similarly, group 4 transition-metal complexes with imidazolin-2-iminato ligands can be envisaged, which in turn require a trianionic cyclic ligand as a result of the substitution of the dianionic imido by a monoanionic $\text{Im}^{\text{R}}\text{N}^{-}$ ligand (Scheme 2).

Scheme 2. Isolobal Complexes with Pogo Stick Geometry



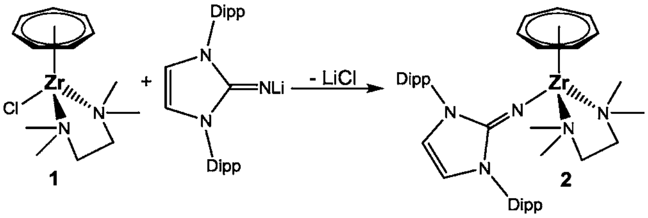
This leads to complexes of the type $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{Im}^{\text{R}}\text{N})]$ (M = Ti, Zr, Hf) bearing a formally trianionic cycloheptatrienyl (Cht) system.[14]

For titanium, the modification of cycloheptatrienyl complexes is thus far limited to $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_5)]$ ("troticene") by a combination of lithiation and subsequent reaction with electrophiles;[15] approaches to complexes bearing non-Cp ligands are not known.[16] For zirconium, in contrast, we have recently found that the complex $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl(tmeda)}]$ (**1**) (tmeda = *N,N,N',N'*-tetramethylethylenediamine), first published in 1991,[17] allows for the straightforward incorporation of pentadienyl,[18] cyclopentadienyl,[19] and also phospholyl ligands by salt metathesis reactions.[20] Consequently, **1** offers an efficient and versatile access to the preparation of various cyloheptatrienylzirconium complexes and should also be the starting material of choice for the generation of cycloheptatrienylzirconium imidazolin-2-iminato complexes with pogo stick geometry (Scheme 2). Herein, we present our attempts leading to $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{R}}\text{N})]$, with the concomitant preparation and characterization of novel cycloheptatrienylzirconium allyl species.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-iminato ligand ($\text{Im}^{\text{Dipp}}\text{N}$) was chosen for our studies, since the steric bulk of the substituents on the nitrogen atoms can be expected to stabilize the resulting monomeric $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{Dipp}}\text{N})]$ complex and to prevent its dimerization. Thus, the reaction of $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl(tmeda)}]$ (**1**) with $\text{Li}(\text{Im}^{\text{Dipp}}\text{N})$, obtained from $\text{Im}^{\text{Dipp}}\text{NH}$ and MeLi,[5b,10a] in THF/toluene affords after workup a brown solid in 79% yield. The ^{1}H NMR spectrum shows a characteristic singlet at 4.82 ppm for the C_7H_7 ligand and two distinct doublets as expected for the diastereotopic isopropyl methyl groups of two magnetically equivalent Dipp substitutents. Among the four remaining resonances, two of them can be assigned to the presence of tmeda (1.96/1.55 ppm), which is in agreement with ^{13}C NMR spectroscopy (58.3/49.3 ppm). It may thus be inferred that $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{Dipp}}\text{N})(\text{tmeda})]$ (**2**) was formed during the reaction (Scheme 3), and this is confirmed by an X-ray diffraction study on crystals grown from a concentrated toluene solution at −20 °C (Figure 1); selected bonding parameters may be found in Table 1.

Scheme 3. Reaction of 1 with $\text{Li}(\text{Im}^{\text{Dipp}}\text{N})$



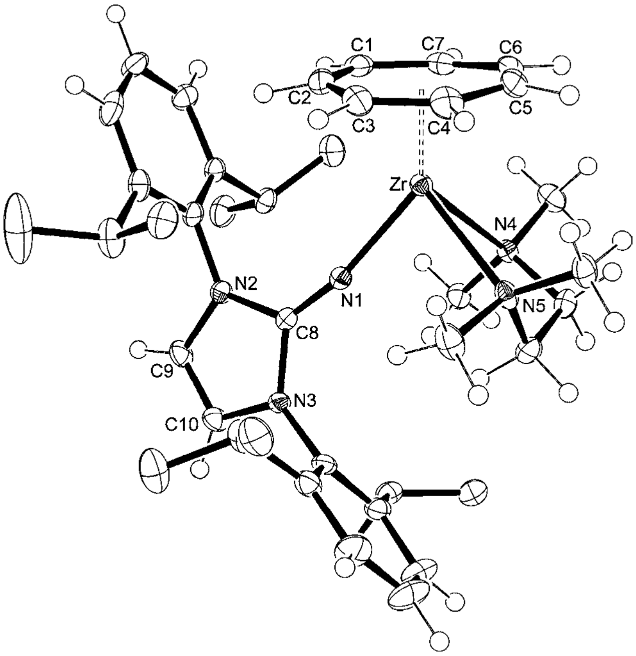


Figure 1. ORTEP diagram of **2** with thermal displacement parameters drawn at 50% probability. The hydrogen atoms of the isopropyl groups are omitted for clarity.

The reaction clearly proves the ability of the $\text{Im}^{\text{Dipp}}\text{N}$ ligand to coordinate to the cycloheptatrienylzirconium complex fragment, but it did not deliver the desired pogo stick complex $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{Dipp}}\text{N})]$. Instead, the tmeda remains coordinated to satisfy the electronic demands of the metal, albeit with slightly longer Zr−N bonds of 2.5136(14) and 2.5737(13) Å in comparison to those of the starting material **1** (2.477(2)/2.519(2) Å).[18a]

In addition to conventional transmetalation reactions, it has been shown that the acid−base reaction between the imine $\text{Im}^{\text{Dipp}}\text{NH}$ and rare-earth-metal neosilyl complexes represents a convenient method for the introduction of the corresponding imidazolin-2-iminato ligand.[11b] However, the corresponding trial reaction of in situ formed $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{CH}_2\text{TMS})(\text{tmeda})]$ with $\text{Im}^{\text{Dipp}}\text{NH}$ indicated the generation of **2**. Clearly a tmeda-free starting material is called for.

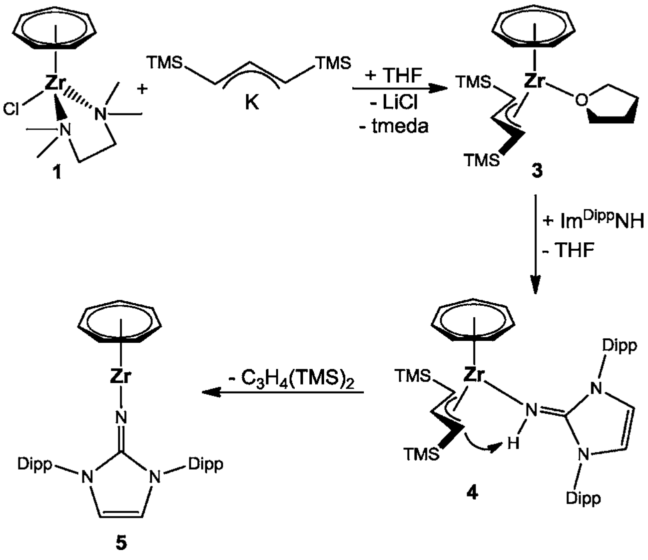
To meet this condition, and as part of our general interest in transition-metal allyl complexes,[21] we have synthesized $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\eta^3\text{-C}_3\text{H}_3(\text{TMS})_2\}(\text{THF})]$ (**3**; TMS = SiMe_3) in 72% yield as a brown solid from **1** and $\text{K}[\text{C}_3\text{H}_3(\text{TMS})_2]$ in THF (Scheme 4),[22] while an analogous reaction with $(\text{C}_3\text{H}_5)\text{MgBr}$ did not result in the formation of any traceable products. This is not surprising, since the exceptional steric demand of the 1,3-bis(trimethylsilyl)allyl ligand,[23] which has been calculated to have 4 times the volume of the parent C_3H_5 ligand,[23b] has recently allowed the stabilization of a number of unusual

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2 and 4−8

	2	4	5^a		6	7	8
Zr−C_{Cht}	2.3599(17)−2.4582(16)	2.3164(17)−2.4091(17)	2.316(3)−2.345(3)	2.326(3)−2.346(3)	2.323(2)−2.4588(18)	2.326(4)−2.376(4)	2.316(2)−2.366(2)
Zr−Cht_{cent}	1.752	1.718	1.661	1.661	1.729	1.725	1.670
Zr−N1	2.0948(12)	2.3243(13)	1.997(2)	2.003(2)	1.9977(14)	2.005(2)	2.3177(15)
N1−C8	1.2699(19)	1.3099(19)	1.286(4)	1.290(4)	1.274(2)	1.272(4)	1.342(2)
Zr−L	2.5136(14)/2.5737(13)				2.3852(18)	2.420(4)	2.2059(16)
Cht_{cent}−Zr−N1	140.0	124.9	179.0	178.5	152.1	154.6	158.2
Zr−N1−C8	163.99(11)	144.42(10)	152.2(3)	149.9(3)	173.57(13)	165.0(2)	149.56(13)

[a] Two independent molecules per asymmetric unit.

Scheme 4. Preparation of 3 and Subsequent Reaction with $Im^{Dipp}NH$ Leading to 5



molecules.[24] Despite the very high solubility of 3 in hydrocarbon solvents such as pentane, its structure could be established by X-ray diffraction analysis (Figure 2); the molecule displays crystallographic mirror symmetry, with atoms Zr, O, C1, and C5 lying in the mirror plane. As also shown by ^{1}H and ^{13}C spectroscopy (see the Experimental Section for details), one THF molecule is coordinated to the metal atom at the open edge of the allyl ligand (*exo*-conformation)[25] with a Zr−O bond length of 2.312(7) Å. The silyl substituents reside in a *syn*−*syn* orientation with respect to the inner hydrogen atom, since otherwise steric interactions with the THF ligand would result. Unsurprisingly, the zirconium bonds to the terminal carbon atoms are at 2.514(6) Å slightly longer than that to the central carbon atom (2.466(8) Å), matching the values found for $[(\eta^5\text{-}C_5Me_5)Zr(\eta^3\text{-}1,2,3\text{-}Me_3C_3H_2)Br_2]$ (2.456(11) vs 2.513(15) Å).[26]

As recently emphasized in two review papers,[23] group 4 silylallyl complexes are rare, and the only other structurally characterized complexes are the two trivalent species $[\{1,3\text{-}(t\text{-}BuMe_2Si)_2C_3H_3\}_2M(\mu\text{-}Cl)_2Li(tmeda)]$ (M = Ti, Zr),[27] while homoleptic *ansa*-bis(silylallyl)zirconium and -hafnium complexes represent the only previously isolated tetravalent examples.[28] Although similar complexes involving less encumbered allyl ligands have been known for quite some time,[26,29] 3 constitutes the only structurally characterized bis(trimethylsilyl)allyl complex of a group 4 metal to date.[23]

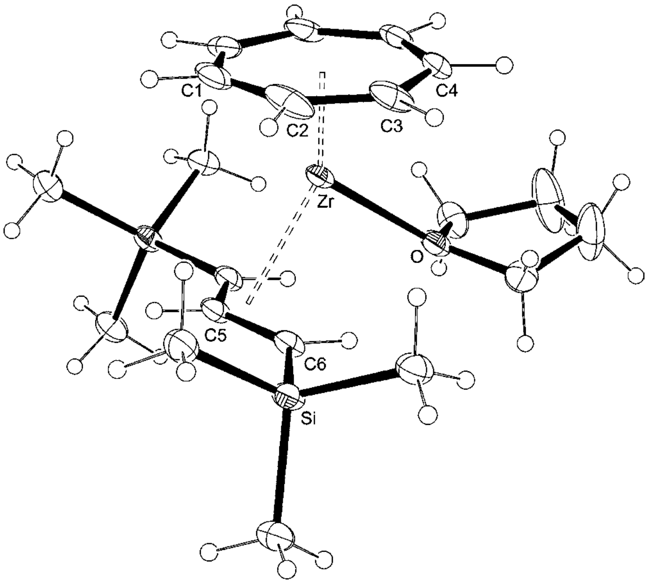


Figure 2. ORTEP diagram of 3 with thermal displacement parameters drawn at 30% probability. The molecule possesses crystallographic mirror symmetry. Selected bond lengths (Å) and angles (deg): Zr−Cht_{cent} = 1.706, Zr−C1 = 2.365(12), Zr−C2 = 2.329, Zr−C3 = 2.358(7), Zr−C4 = 2.386(6), Zr−$allyl_{cent}$ = 2.262, Zr−C5 = 2.466(8), Zr−C6 = 2.514(6), Zr−O = 2.312(7), C6−C5−C6 = 123.7(9).

While 3 is in itself already remarkable, the subsequent reaction with the imidazolin-2-imine $Im^{Dipp}NH$ also represents, to the best of our knowledge, a new reaction pattern for silylallyl ligands: Treatment of complex 3 with 1 equiv of $Im^{Dipp}NH$ in toluene results in the formation of a brown suspension, which gradually changes to a red solution upon stirring for three days at room temperature; heating to 45 °C reduces the reaction time to 22 h. After solvent evaporation and washing with pentane, $[(\eta^7\text{-}C_7H_7)Zr(Im^{Dipp}N)]$ (5) can be isolated as an orange solid in up to 79% yield. The ^{1}H NMR spectrum only shows the expected singlet for the seven-membered ring (5.07 ppm) and the resonances required for the $Im^{Dipp}N$ ligand, specifically two doublets (1.11/1.34 ppm), a virtual septet at 2.86 ppm, and a singlet for the backbone hydrogen atoms of the imidazoline ring (5.76 ppm). No further resonances are detected, clearly showing that the $C_3H_3(TMS)_2$ ligand is lost in the course of the reaction. The intermediate during the formation of 5 appears to result from the replacement of THF in 3 by $Im^{Dipp}NH$ (Scheme 4), because we were able to obtain crystals suitable for X-ray diffraction analysis of $[(\eta^7\text{-}C_7H_7)Zr\{\eta^3\text{-}C_3H_3(TMS)_2\}(Im^{Dipp}NH)]$ (4) by slow diffusion of pentane into a THF solution of a 1:1 mixture of 3 and $Im^{Dipp}NH$ (Figure 3, Table 1). Coordination of

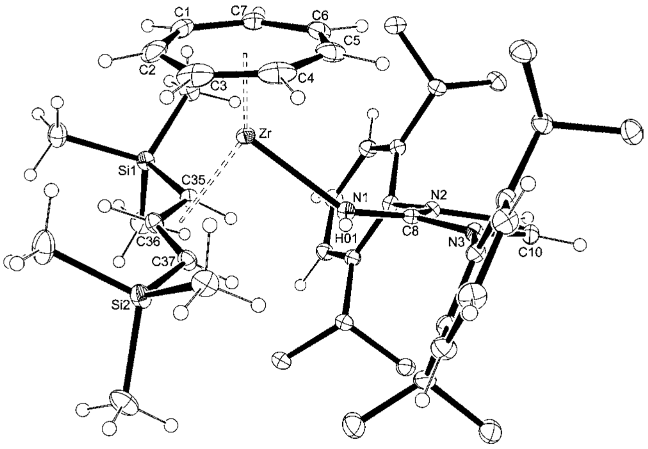


Figure 3. ORTEP diagram of **4** with thermal displacement parameters drawn at 30% probability. Hydrogen atoms of the isopropyl groups are omitted for clarity.

$Im^{Dipp}NH$ brings the hydrogen NH atom into proximity to the allyl ligand (H···C37 = 3.0 Å), suitably oriented for a presumably intramolecular deprotonation, which subsequently gives the monoanionic imidazolin-2-iminato ligand by loss of $C_3H_4(TMS)_2$. Indeed, if a 1:1 mixture of **3** and $Im^{Dipp}NH$ is heated in a sealed NMR tube in d_8-THF, clean formation of **5** along with 1,3-bis(trimethylsilyl)propene is observed.[30]

Of major interest is the nuclearity of **5**, which we were able to determine by X-ray diffraction analysis of single crystals grown from a toluene/pentane solution at −20 °C. The asymmetric unit contains two independent molecules; the geometries of both molecules are tolerably similar, since a least-squares fit gives an rms deviation of 0.4 Å (associated with slightly different orientations of the $Im^{Dipp}N$ ligands). The molecule depicted in Figure 4 shows nicely the monomeric nature and the one-legged piano stool geometry (pogo stick) of the complex. This is in contrast to earlier studies of $[(\eta^8\text{-}C_8H_8)Zr(NR)]$ complexes, where an inherent instability of monomeric species was proposed to explain the exclusive formation of dimeric species.[13] In the present case, dimerization is probably prevented by the bulk of the Dipp substituents and by the large cone angle of the cycloheptatrienyl ring.[16] Consequently, **5** is a rare example of a molecule adopting a pogo stick geometry, and there are to the best of our knowledge only a few other crystallographically characterized complexes with this unusual structural motif.[12,31] The capability of the imidazolin-2-iminato ligand to form particularly strong metal−nitrogen bonds as a $2\sigma,4\pi$-electron donor leads to a remarkably short Zr−N distance of only 1.997(2) Å (2.003(2) Å for the second independent molecule), which is among the shortest 2% ever reported for Zr−N bonds;[32] it is noteworthy that the shortest bonds are found in a series of arylimido complexes.[33] In comparison, the Zr−N distance in **2** is longer at 2.0948(12) Å, because the additional coordination of the chelating tmeda ligand helps to satisfy the electronic demands of the metal. Furthermore, the Cht_{cent}−Zr−N1 axes in **5** are at 179.0°/178.5° close to linearity, while the imidazolin-2-iminato moiety deviates markedly from a linear arrangement with Zr−N1−C8 angles of 152.2(3)° and 149.9(3)° (Table 1). The bending at N1 is essentially parallel to the plane of the imidazole ring, with deviations from the plane of 0.06/0.01 Å for the nitrogen atoms N1 and 0.34/0.02 Å for the Zr atoms.

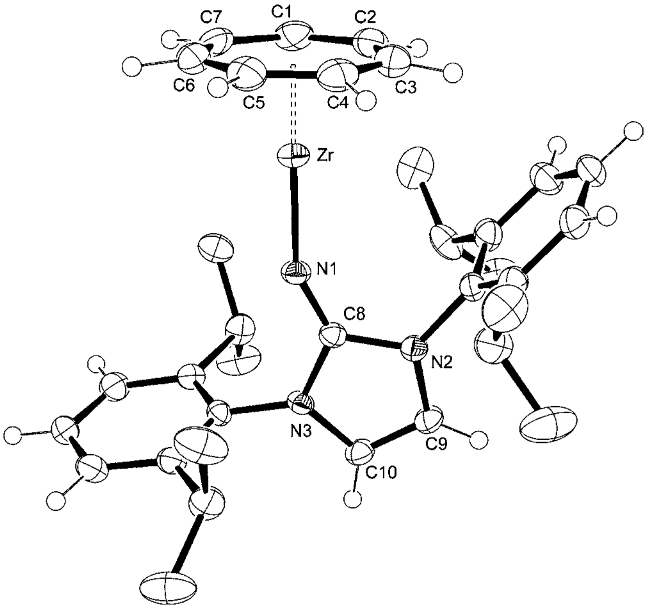


Figure 4. ORTEP diagram of one of the two independent molecules of **5** with thermal displacement parameters drawn at 50% probability. Hydrogen atoms of the isopropyl groups are omitted for clarity.

DFT Studies. To assess further the bonding between zirconium and the imidazolin-2-iminato ligand, the molecular structure of $[(\eta^7\text{-}C_7H_7)Zr(Im^{Dipp}N)]$ (**5**) was optimized by density functional theory (DFT) using the conventional B3LYP functional and also the B97-D functional, which better describes noncovalent and long-term dispersion interactions.[34] The calculated structures (see the Supporting Information) agree well with the experimental results, reproducing very short Zr−N1 bonds of 2.002 and 2.035 Å for the B3LYP and B97-D calculations, respectively. However, both calculations differ significantly with regard to the orientation of the $Im^{Dipp}N$ ligand. While the B3LYP functional affords a perfectly linear structure (Cht_{cent}−Zr−N1 = 179.9°, Zr−N1−C8 = 179.8°), the B97-D structure better correlates with the experimentally observed tilting of the imidazoline ring (Cht_{cent}−Zr−N1 = 170.3°, Zr−N1−C8 = 144.4°). Similar to phosphoraneiminato transition-metal complexes,[6c] however, a comparably flat potential energy surface (PES) should be expected for bending along the Zr−N1−C8 axis, which was confirmed by a relaxed PES scan, affording an energy difference of only 2.1 kcal mol^{-1} between the optimized structures of the bent (144.4°) and linear (180°) molecules (see the Supporting Information). In contrast, bending along the Cht_{cent}−Zr−N1 axis would result in an undesired decrease of orbital overlap and consequently in Zr−N bond destabilization.

Both functionals produce essentially the same results for the metal and ligand fragment contributions to the occupied frontier orbitals of **5** (Table 2). The corresponding contour plots derived from the B3LYP calculation are shown in Figure 5, nicely illustrating the symmetry of the metal−ligand interactions. The lowest unoccupied molecular orbital (LUMO) is principally metal-localized and exhibits predominant d_{z^2} character with a zirconium contribution of 92%. In contrast, the B97-D calculation affords a LUMO which is mainly localized on the phenyl ring, whereas a large contribution (61%) from the d_{z^2} orbital is revealed for the LUMO + 2, resulting from significant mixing of metal and phenyl orbital character (see the Supporting Information for

Table 2. Comparison of Eigenvalues and Composition of Frontier Orbitals

	energy (eV)		Zr contribution (%)		Cht contribution (%)		Im$^{\mathrm{Dipp}}$N contribution (%)	
orbital	B3LYP	B97-D	B3LYP	B97-D	B3LYP	B97-D	B3LYP	B97-D
LUMO[a]	−0.94	−1.50	92	5	1	1	6	94
HOMO	−4.40	−3.66	32	31	67	67	1	3
HOMO − 1	−4.41	−3.66	33	31	67	67	0	2
HOMO − 2	−5.36	−4.56	6	6	2	2	92	92
HOMO − 3	−6.17	−5.26	10	12	6	3	84	85

[a] LUMO + 2 for B97-D: −1.18 eV; Zr, 61%; Cht, 5%; Im$^{\mathrm{Dipp}}$N, 35%.

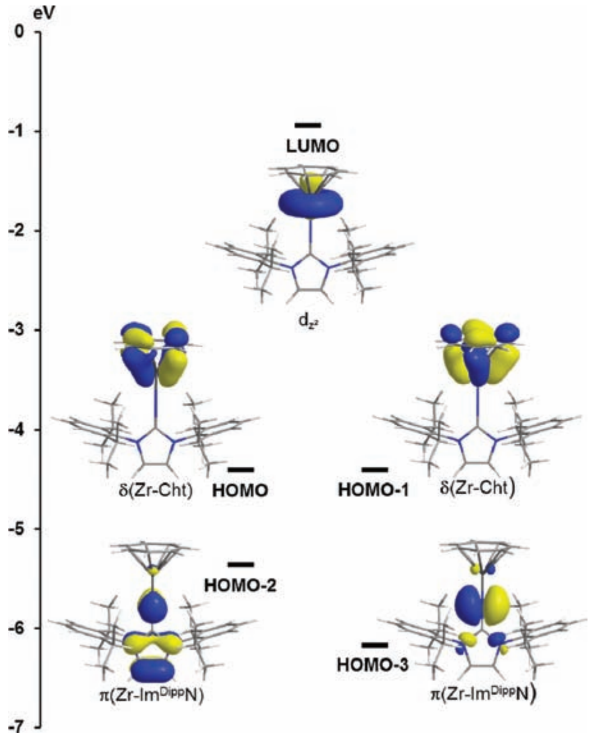


Figure 5. Contour plots of the frontier orbitals in **5** based on the B3LYP calculation.

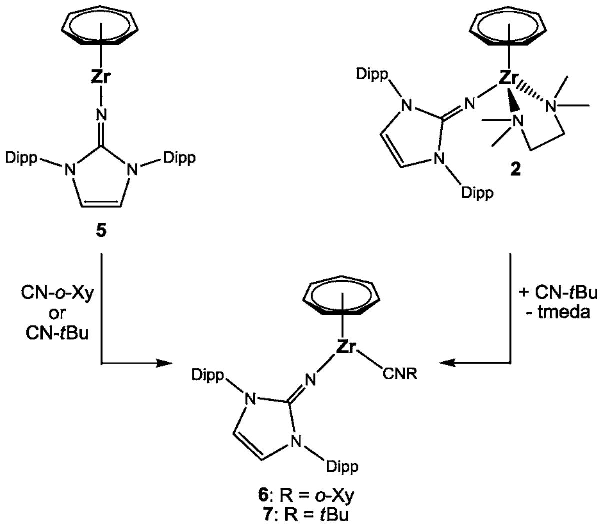
representations). Similarly to recent results for [(η^7-C_7H_7)M(η^5-C_5H_5)] complexes (M = Ti, Zr, Hf),[14,35] the two following quasi-degenerated orbitals, HOMO and HOMO − 1, represent the δ interaction with the seven-membered ring. Here, significant mixing of metal and ligand orbital character can be identified, which implies a strongly covalent interaction. Consistent with the assignment of a formal −3 charge to the cycloheptatrienyl ring, the electrons in HOMO and HOMO − 1 are significantly more ligand- than metal-localized; the respective fragment contributions are 67% and 33%. The next two energy levels consist of two orthogonal orbitals, HOMO − 2 and HOMO − 3, which display the largely ionic π interaction of the imidazolin-2-iminato ligand (92%, 84%) with zirconium (6%, 10%), affording a highly polarized Zr−N bond. In contrast to HOMO and HOMO − 1, the degeneracy is lifted because of an unfavorable antibonding interaction between the p orbital of the terminal nitrogen atom and the π system of the imidazoline ring; a similar conclusion was drawn for arylimido ligands.[12b]

It is noteworthy that the bonding situation found for [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)] (**5**) resembles that established for the related pogo stick complexes of the type [(η^8-C_8H_8)Ti(NR)].[12] This clearly demonstrates their isolobal relationship. Consequently, the imidazolin-2-iminato ligand can be considered as a monoanionic "imido-type" ligand, which should permit the observation of reactivity typically associated with imido ligands.[3]

Reactivity. Shortly after Mountford and co-workers published their series of unique cyclooctatetraenyltitanium imido complexes,[12] they followed up with a number of reactivity studies toward various unsaturated organic molecules such as CO_2, CS_2, isocyanides, isocyanates, isothiocyanates, or phosphaalkynes.[13a,36] Depending on the substrate and the substitution pattern of the metal complex, simple coordination, cycloaddition, or cycloaddition−elimination was observed in some cases, whereas others led to unidentified reaction mixtures. Encouraged by these findings and in view of the similar reactivity observed for the isolobal complex [(η^8-C_8H_8)Sc(Im$^{\mathrm{Dipp}}$N)],[11b] we set out to investigate analogous reactions for [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)] (**5**).

The 16-electron complex [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)] (**5**) has an empty orbital (vide supra), which can potentially allow substrate activation upon coordination followed by reaction along the Zr−N bond. Initially, we have studied the reactivity toward isocyanides, which gave intriguing results, such as single or multiple coupling products with group 4 imido complexes.[37] Therefore, one equiv of 2,6-dimethylphenyl isocyanide (CN-*o*-Xy) was added to **5** (Scheme 5), which resulted in an immediate color change to dark red. After workup, a red product was isolated in good yield, and ^{1}H and ^{13}C NMR spectroscopies suggest the clean formation of a single product, since only one set of resonances is observed; however, on the basis of the NMR data, no final decision of coordination vs insertion can be made. The IR spectrum displays a C−N

Scheme 5. Formation of the Isocyanide Adducts 6 and 7



stretch at 2131 cm^{-1}, similar to that observed for [(η^7-C_7H_7)Zr(η^5-C_5H_5)(CN-*o*-Xy)],[38] indicating the presence of a terminally bound isocyanide, since otherwise a shift to lower values has to be expected.[31b] Furthermore, the observed C−N stretch is close to the value found for the uncoordinated isocyanide (2123 cm^{-1}), which is in agreement with the general observation in group 4 cycloheptatrienyl complexes that metal-to-ligand π back-bonding is usually weak.[14]

These findings are corroborated by an X-ray diffraction study, which proves the formation of [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)(CN-*o*-Xy)] (**6**) (Figure 6). To accommodate the isocyanide, the imidazolin-2-iminato ligand tilts out of the formerly linear arrangement (Cht$_{\mathrm{cent}}$−Zr−N1 = 152.1°), but retains a short Zr−N bond of 1.9977(14) Å. Isocyanide coordination to the zirconium atom affords a Zr−C35 bond length of 2.3852(18) Å, which is almost identical to that found for [(η^7-C_7H_7)Zr(η^5-C_5H_5)(CN-*o*-Xy)] (2.367(2) Å);[19a] the short C35−N4 bond and the C35−N4−C36 angle in **6**, however, remain essentially unperturbed in comparison with the structure of free 2,6-dimethylphenyl isocyanide (1.164(2) vs 1.161(2) Å and 178.1(2)° vs 178.9(2)°).[39]

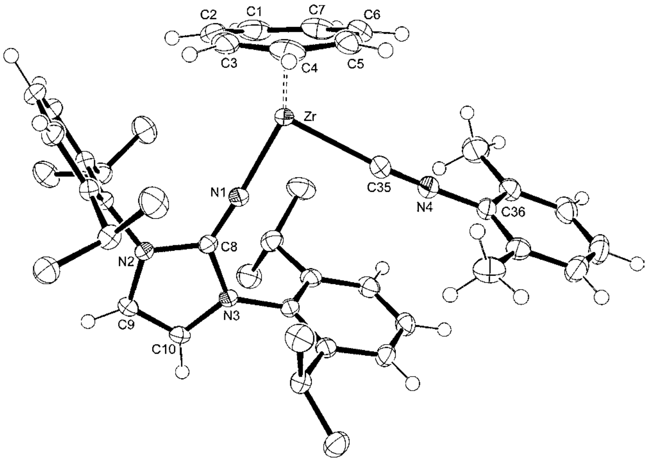


Figure 6. ORTEP diagram of **6** with thermal displacement parameters drawn at 50% probability. Hydrogen atoms of the isopropyl groups are omitted for clarity.

Similarly, an NMR tube experiment suggested the formation of [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)(CN-*t*-Bu)] (**7**) upon reaction of **5** with *tert*-butyl isocyanide (CN-*t*-Bu). Alternatively, replacement of tmeda in [(η^7-C_7H_7)Zr(Im$^{\mathrm{Dipp}}$N)(tmeda)] (**2**) also affords **7**, and this method was used for the synthesis on a preparative scale. The ν(C≡N) stretch appears at 2149 cm^{-1} in the IR spectrum, and simple coordination of CN-*t*-Bu is confirmed by X-ray diffraction analysis (Figure 7). The isocyanide approaches the metal in **7** in a perpendicular fashion with respect to the imidazoline ring, which differs from the orientation found in **6** (vide supra), while most other structural parameters are very similar (Table 1); the corresponding angles between the imidazoline and the N1−Zr−C35 planes are 10.0° and 78.2° in **6** and **7**, respectively.

In contrast to some isocyanide adducts of [(η^8-C_8H_8)Ti(NR)], which were unstable with respect to decomposition or carbodiimide formation,[13a] compounds **6** and **7** are indefinitely stable at room temperature in C_6D_6, and even heating to 50 °C for 24 h and an additional 48 h at 70 °C did not lead to any noticeable changes in their ^{1}H NMR spectra.

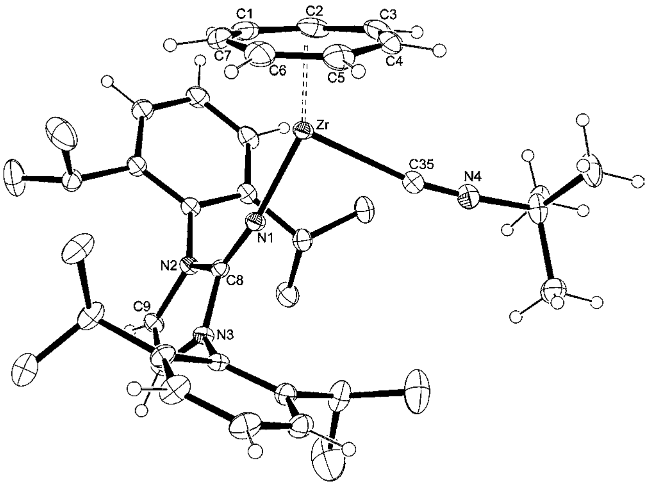


Figure 7. ORTEP diagram of **7** with thermal displacement parameters drawn at 50% probability. Hydrogen atoms of the isopropyl groups are omitted for clarity. Only one position of the disordered butyl group is shown.

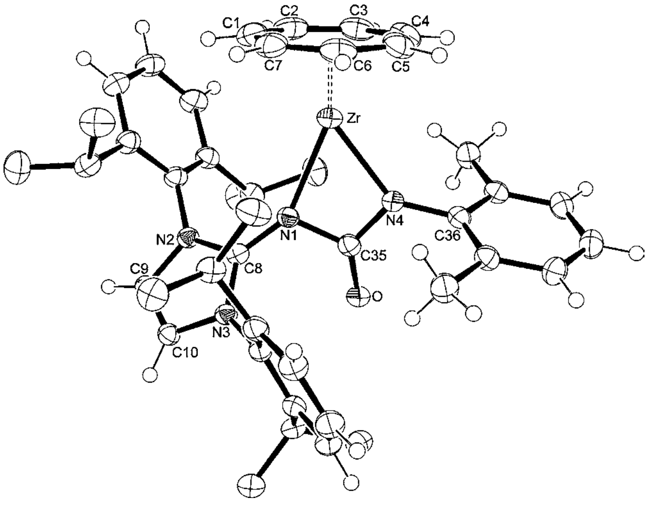
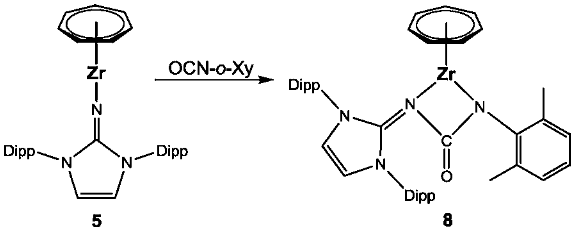


Figure 8. ORTEP diagram of **8** with thermal displacement parameters drawn at 50% probability. Hydrogen atoms of the isopropyl groups are omitted for clarity.

For the imidazolin-2-iminato complex [(η^8-C_8H_8)Sc(Im$^{\mathrm{Dipp}}$N)(THF)], the reaction with 2,6-dimethylphenyl isothiocyanate (SCN-*o*-Xy) afforded an *N*,*N*′-thioureato complex resulting from a [2 + 2] cycloaddition.[11b] Despite their isolobal relationship, attempts to isolate the corresponding compound from **5** and SCN-*o*-Xy failed, only giving indefinable products. Neither was it possible to react **5** with either CO_2 or CS_2 in a controlled manner. However, the reaction of **5** with 1 equiv of 2,6-dimethylphenyl isocyanate (OCN-*o*-Xy) was more clear-cut. Here, NMR spectroscopy and X-ray diffraction analysis (Figure 8) reveals the formation of [(η^7-C_7H_7)Zr{Im$^{\mathrm{Dipp}}$N(C=O)N-*o*-Xy}] (**8**) in reasonable yield (Scheme 6). The N=C bond of the isocyanate has added across the Zr−N1 bond in a [2 + 2] cycloaddition, leading to a four-membered metallacycle with an *N*,*N*′-ureato moiety. Alternatively, an N,O-bound ligand could be envisaged, but its formation is probably less favored because of potential steric interactions between the Dipp and Xy substituents. These two reaction pathways are

Scheme 6. Reaction of 5 with 2,6-Dimethylphenyl Isocyanate



well established for a number of imido complexes and are sometimes followed by cycloreversion reactions.[37a,40]

As expected, the *N*-(imidazolin-2-ylidene)-*N*′-(2,6-dimethylphenyl)ureato(1−) ligand in **8** coordinates to zirconium in an unsymmetric fashion, and stronger donation from the N4 (formerly isocyanate nitrogen) atom is evident from the shorter Zr−N4 bond of 2.2059(16) Å vs 2.3177(15) Å for the Zr−N1 bond; the latter has experienced a pronounced elongation of more than 0.3 Å in comparison to **5**. In contrast, a related zirconium complex bearing the dianionic *N*-(2,6-diisopropylphenyl)-*N*′-(*tert*-butyl)ureato(2−) ligand, originating from the reaction of an imido complex with an isocyanate, features almost identical Zr−N bond lengths of 2.155(4) and 2.168(4) Å.[40b] To reduce steric interaction, both the imidazoline ring and the isocyanide phenyl group in **8** are twisted out of a coplanar arrangement with the Zr−N1−C35−N4 plane; the corresponding dihedral angles are 44.9 and 70.5°, respectively. Finally, the elongated N1−C8 bond of 1.342(2)Å is significantly longer than in **5** (1.286(4) Å) or in Im^{Dipp}NH (1.2888(17) Å),[11b] which indicates a stronger contribution of the resonance form **IB** (Scheme 1), resulting in an ylidic imidazolium-amido-type character of the ligand.

Polymerization of *ε*-Caprolactone. Another example of the reactivity of [(η^7-C_7H_7)Zr(Im^{Dipp}N)] (**5**) involves its application in the catalytic ring-opening polymerization (ROP) of *ε*-caprolactone (*ε*-CL). Poly(esters) have lately received increasing attention because of their biodegradability and biocompatibility, the availability of their monomers from renewable sources, and their use as potential replacement for oil-based polymers.[41] In recent years, many metal complexes, most commonly bearing alkoxides as initiating groups, have been investigated as catalysts for the ROP of *ε*-CL,[42] including a number of zirconium complexes.[43]

Inspired by studies on phosphoraniminato complexes of the rare-earth metals,[44] we tested the imidazolin-2-iminato complex **5** as an initiator for the polymerization of *ε*-CL. Indeed, mixing catalytic amounts of **5** with *ε*-CL in THF affords a highly viscous mixture of poly(*ε*-CL) (Scheme 7). In agreement with the coordination−insertion mechanism,[41,42] we suppose that *ε*-CL first coordinates to zirconium via the carbonyl oxygen atom, followed by a nucleophilic attack of the monoanionic Im^{Dipp}N ligand on the carbonyl carbon atom, which then results in the relief of ring strain upon ring-opening. We then tested the performance of **5** in the ROP of *ε*-CL under four different conditions (Table 3); a typical ^{1}H NMR spectrum of the resulting poly(*ε*-CL) is shown in Figure 9. Significant transesterification or "backbiting" can result in cyclic rather than linear poly(*ε*-CL); for the former, no end groups are then found by NMR studies.[45] A polymerization experiment with a low catalyst:*ε*-CL ratio (1: 20) revealed a triplet at 3.64 ppm in the ^{1}H NMR spectrum of the corresponding poly(*ε*-CL), clearly indicating the presence of a $-CH_2OH$ end group and therefore a linear polymer (see the Supporting Information).[46]

Scheme 7. Polymerization of *ε*-Caprolactone Initiated by 5

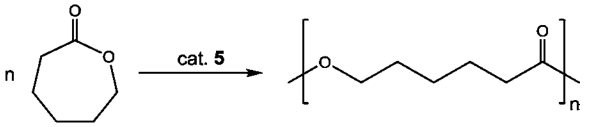


Table 3. GPC Results of the *ε*-Caprolactone Polymerization[a]

	A	B	C	D
catalyst:*ε*-CL	1: 200	1: 100	1: 200	1: 200
T (K)	303	303	333	303
V (mL)	10	10	10	15
yield[b] (%)	68	65	76	47
M_n(exptl)[c]	24024	21672	14224	26712
M_n(theor)	22800	11400	22800	22800
M_w[c]	34272	35448	25760	38080
PDI	1.43	1.64	1.81	1.43

[a] Conditions: 390 mg of *ε*-caprolactone, THF, 4 h. Given results are averaged over two runs. [b] Isolated yield. [c] Units of grams per mole. Determined by GPC analysis vs polystyrene standards and corrected with the appropriate response factor of 0.56.[47]

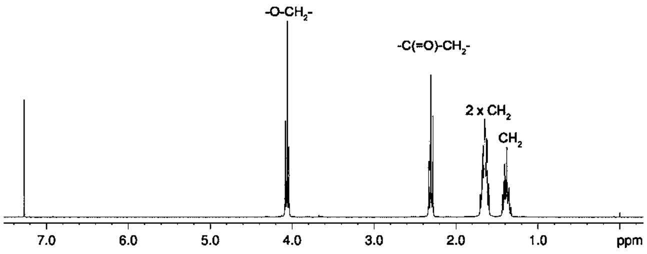


Figure 9. Typical ^{1}H NMR spectrum of poly(*ε*-CL) in $CDCl_3$.

In all cases, the polydispersity indices (PDIs) suggest that the initiation is not instantaneous and that there is consequently only a fair control over the molecular weight distribution. For the reactions at 30 °C (entries A, B, and D), the M_n values are higher than the theoretically expected molecular weight, suggesting that not all catalyst molecules participate in the polymerization process. Surprisingly, the isolated yields are only moderate. Increasing the temperature gives a slightly better yield (entry C), albeit with a concomitant increase of the PDI value and a significant decrease of M_n. As expected, higher dilution complicates the mass transport, leading to a lower yield (entry D), but results in a good PDI value of 1.43 due to a lower viscosity. Although there is certainly room for improvement, the polymerization study with **5** is one of the very few occasions where a cycloheptatrienyl complex acts as a homogeneous catalyst.[16,48] Furthermore, it supports the earlier observation that reactivity can arise from a highly polarized metal−nitrogen bond in imidazolin-2-iminato complexes.[11d]

■ CONCLUSIONS

In the present study, the preparation and characterization of the cycloheptatrienyl complex [(η^7-C_7H_7)Zr{η^3-$C_3H_3(TMS)_2$}-(THF)] (**3**) was achieved, which represents a rare example of a group 4 species containing a sterically demanding bis(trimethylsilyl)allyl ligand. The basic allyl ligand in **3** provides a tmeda-free route to introduce the monoanionic imidazolin-2-iminato ligand Im^{Dipp}N via an acid−base reaction with the corresponding imidazolin-2-imine Im^{Dipp}NH. The resulting complex [(η^7-C_7H_7)Zr(Im^{Dipp}N)] (**5**) exhibits an exceptional one-legged piano stool (pogo stick) geometry that was also established for isolobal cyclooctatetraenylimido complexes of the type [(η^8-C_8H_8)Ti(NR)]. Theoretical studies and also the reactivity of **5** toward the isocyanate OCN-*o*-Xy give further evidence for the strong analogy between imidazolin-2-iminato and conventional imido ligands; this can be exploited for the discovery of similar structural features and reactivity patterns, as recently successfully demonstrated for the development of highly active alkyne metathesis catalysts.[10]

■ EXPERIMENTAL SECTION

All synthetic and spectroscopic manipulations were carried out under an atmosphere of purified nitrogen gas, either in a Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen atmosphere from sodium benzophenone ketyl (THF) or by an MBraun GmbH solvent purification system (all other solvents). NMR spectra were recorded on Bruker DPX 200, Bruker AVIII 400, and Bruker DRX 400 spectrometers. The chemical shifts are expressed in parts per million (ppm) and are referenced to residual ^{1}H of the solvent or the ^{13}C resonance of the solvent. If required, the assignment of signals was supported by 2D experiments (^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC). A Bruker Vertex 70 spectrometer was used for recording the IR spectra. Elemental analyses were performed by combustion and gas chromatographical analysis with an Elementar varioMICRO instrument. GPC measurements were performed on a PSS SECcurity GPC system with Agilent Technologies 1200 series instrumentation equipped with three PSS columns using THF as the eluent with a constant flow of 1 mL/min at 308.15 K. [(η^7-C_7H_7)ZrCl(tmeda)] (**1**),[18a] K[$C_3H_3(TMS)_2$],[22a] Im^{Dipp}NH, and Im^{Dipp}NLi were synthesized as published previously.[5b,10a] ε-Caprolactone was purchased from Aldrich and purified by trap-to-trap distillation after being dried over CaH_2. All other reagents were obtained commercially and used as received.

[(η^7-C_7H_7)Zr(Im^{Dipp}N)(tmeda)] (2). A blue toluene/THF (20 mL/6 mL) suspension of [(η^7-C_7H_7)ZrCl(tmeda)] (0.800 g, 2.395 mmol) was slowly treated with Li(Im^{Dipp}N) (0.991 g, 2.419 mmol) in toluene (20 mL) at −78 °C. The mixture was stirred overnight, followed by solvent removal, extraction with toluene, and filtration through a pad of Celite. The solvent was evaporated from the red-brown solution, and the remaining solid was washed with pentane (red washings) and finally dried under vacuum. The product was obtained as a light brown solid in 79% yield (1.33 g). Single crystals were obtained from a concentrated toluene solution at −20 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.24 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, *p*-phenyl), 7.11 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, *m*-phenyl), 5.84 (s, 2 H, NCH), 4.82 (s, 7 H, C_7H_7), 3.27 (pseudo-sept, 4 H, CH isopropyl), 1.96 (s, 12 H, N−CH_3), 1.55 (s, 4 H, N−CH_2), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH_3), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 148.4 (*ipso*-phenyl), 129.3 (*p*-phenyl), 125.7 (*o*-phenyl), 123.9 (*m*-phenyl), 113.8 (NCH), 81.6 (C_7H_7), 58.3 (NCH_2), 49.3 (NCH_3), 28.8 (CH isopropyl), 25.9 (CH_3), 23.1 (CH_3); the NCN resonance was not observed. Anal. Calcd for $C_{40}H_{59}N_5Zr$ (701.2): C, 68.52; H, 8.48. Found: C, 68.45; H, 8.21.

[(η^7-C_7H_7)Zr{η^3-$C_3H_3(TMS)_2$}(THF)] (3). [(η^7-C_7H_7)ZrCl(tmeda)] (1.0 g, 2.994 mmol) was dissolved in THF (40 mL), and a solution of K[$C_3H_3(TMS)_2$] (0.710 g, 3.144 mmol) in THF (12 mL) was slowly added with a syringe at −78 °C. After the resulting solution was slowly warmed to room temperature and stirred for a total time of 3.5 h (note that stirring for prolonged times, e.g., overnight, degrades the product), the solvent was removed from the brown solution, and the residue was extracted with pentane/THF (ca. 12:1). Filtration through a pad of Celite gave a clear brown solution, which afforded a brown solid (0.945 g, 72%) after solvent removal and drying in vacuo at room temperature. Single crystals were obtained from a pentane/THF mixture at −30 °C. ^{1}H NMR (200 MHz, C_6D_6, ambient): δ = 6.59 (t, $^3J_{HH}$ = 16.3 Hz, 1 H, $H_{central}$), 5.21 (s, 7 H, C_7H_7), 3.18 (m, 4 H, THF), 1.57 (d, $^3J_{HH}$ = 16.3 Hz, 2 H, $H_{terminal}$), 0.93 (m, 4 H, THF), 0.25 (s, 18 H, TMS). ^{13}C NMR (50 MHz, C_6D_6, ambient): δ = 139.1 ($C_{central}$), 84.3 ($C_{terminal}$), 82.8 (C_7H_7), 74.0 (THF), 25.6 (THF), 1.0 (TMS). Anal. Calcd for $C_{20}H_{36}OSi_2Zr$ (439.9): C, 54.61; H, 8.25. Found: C, 54.18; H, 8.14.

[(η^7-C_7H_7)Zr{η^3-$C_3H_3(TMS)_2$}(Im^{Dipp}N)] (4). A solution of Im^{Dipp}NH (0.308 g, 0.764 mmol) in toluene (6 mL) was added to a solution of [(η^7-C_7H_7)Zr(η^3-$C_3H_3TMS_2$)(THF)] (0.336 g, 0.764 mmol) in toluene (8 mL), which resulted in the immediate formation of a brown suspension. After the suspension was stirred for 10 min, the brown solid was collected on a frit, washed with pentane, and dried (0.463 g, 79%). Single crystals were grown by the slow diffusion of pentane into a THF solution. ^{1}H and ^{13}C NMR spectra recorded at room temperature showed broad resonances, indicating a hindered rotation around the Zr−N bond at room temperature on the NMR time scale. Since we were only interested to prove the role of **4** as an intermediate, no temperature-dependent NMR study was performed. Anal. Calcd for $CH_{43}N_3Zr$ (771.4): C, 66.95; H, 8.49. Found: C, 67.23; H, 8.47.

[(η^7-C_7H_7)Zr(Im^{Dipp}N)] (5). [(η^7-C_7H_7)Zr(η^3-$C_3H_3TMS_2$)(THF)] (0.500 g, 1.137 mmol) in toluene (10 mL) was treated with a solution of Im^{Dipp}NH (0.463 g, 1.148 mmol) in toluene (5 mL). Upon being stirred at 45 °C for 22 h, the brown suspension slowly disappeared, and a red solution was obtained. Solvent removal gave a slightly oily red solid, which was washed with pentane (red washings). After drying, an orange solid (0.525 g, 79%) was isolated. Single crystals were obtained from a toluene/pentane mixture at −20 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.22 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, *p*-phenyl), 7.09 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, *m*-phenyl), 5.76 (s, 2 H, NCH), 5.07 (s, 7 H, C_7H_7), 2.86 (pseudo-sept, 4 H, CH isopropyl), 1.34 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 147.7 (*ipso*-phenyl), 134.2 (*o*-phenyl), 129.7 (*p*-phenyl), 124.3 (*m*-phenyl), 112.9 (NCH), 83.7 (C_7H_7), 28.9 (CH isopropyl), 24.3 (CH_3), 24.1 (CH_3); the NCN resonance was not observed. Anal. Calcd for $C_{34}H_{43}N_3Zr$ (585.0): C, 69.81; H, 7.41. Found: C, 69.39; H, 7.58.

[(η^7-C_7H_7)Zr(Im^{Dipp}N)(CN-*o*-Xy)] (6). A solution of CN-*o*-Xy (0.032 g, 0.244 mmol) in toluene (4 mL) was added to an orange-red solution of [(η^7-C_7H_7)Zr(Im^{Dipp}N)] (0.143 mg, 0.244 mmol) in toluene (6 mL), resulting in an immediate color change to dark red. Stirring was continued for 30 min, and a red powder (0.148 g, 85%) was obtained after solvent removal. Single crystals were grown by cooling a saturated benzene/pentane solution to −20 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.03 − 6.94 (m, 6 H, *m*- and *p*-phenyl), 6.80 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-phenyl isocyanide), 6.64 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, *m*-phenyl isocyanide), 5.80 (s, 2 H, NCH), 5.10 (s, 7 H, C_7H_7), 2.96 (pseudo-sept, 4 H, CH isopropyl), 2.04 (s, 6 H, CH_3 isocyanide), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 147.8 (*ipso*-phenyl), 140.0 (NCN), 135.5 (*ipso*-phenyl isocyanide), 134.7 (*o*-phenyl), 129.1 (*p*-phenyl), 128.7 (*p*-phenyl isocyanide), 127.8 (*m*-phenyl isocyanide), 123.6 (*m*-phenyl), 112.6 (NCH), 84.1 (C_7H_7), 28.9 (CH isopropyl), 24.2 (CH_3), 24.1 (CH_3), 18.7 (CH_3 isocyanide); the resonance for the *o*-phenyl of the isocyanide is probably hidden under the solvent, and the CN isocyanide resonance was not observed. Anal. Calcd for $C_{43}H_{52}N_4Zr$ (716.1): C, 72.12; H, 7.32. Found: C, 72.25; H, 7.35. IR (Nujol): ν(CN/cm^{-1}) = 2131.

[(η^7-C_7H_7)Zr(Im^{Dipp}N)(CN-*t*-Bu)] (7). A solution of CN-*t*-Bu (0.035 g, 0.419 mmol) in toluene (2 mL) was added to a solution of [(η^7-C_7H_7)Zr(Im^{Dipp}N)(tmeda)] (0.280 mg, 0.399 mmol) in toluene (6 mL). The resulting red solution was stirred for 30 min. After solvent removal, the oily residue was mixed with hexane (ca. 6 mL) and stored at −15 °C overnight. The supernatant was subsequently removed, and the procedure was repeated with the remaining solid. After drying, a red powder (0.165 g, 62%) was isolated. Single crystals were obtained from a toluene/pentane mixture at −20 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.23 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, *p*-phenyl), 7.13 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, *m*-phenyl), 5.82 (s,

Table 4. Crystallographic Data

	2	3	4	5	6	7	8
empirical formula	$C_{47}H_{67}N_5Zr$	$C_{20}H_{36}OSi_2Zr$	$C_{43}H_{65}N_3Si_2Zr$	$C_{34}H_{43}N_3Zr$	$C_{43}H_{52}N_4Zr$	$C_{39}H_{52}N_4Zr$	$C_{43}H_{52}N_4OZr$
fw	793.28	439.89	771.38	584.93	716.11	668.07	732.11
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
wavelength, λ (Å)	0.71073	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/m$	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	11.7720(2)	7.6044(12)	10.2512(2)	21.1024(5)	10.3414(4)	10.2512(2)	11.1996(4)
b (Å)	12.6377(2)	18.1370(2)	20.1854(2)	16.9179(4)	12.1335(4)	20.2799(2)	22.2814(6)
c (Å)	28.8396(6)	8.2034(12)	20.1059(2)	17.0954(4)	17.2704(6)	17.5953(2)	15.2844(4)
α (deg)	90	90	90	90	71.289(3)	90	90
β (deg)	94.632(2)	101.782(8)	94.238(8)	90	81.447(3)	99.343(8)	99.098(4)
γ (deg)	90	90	90	90	69.055(4)	90	90
vol (Å^3)	4276.48(13)	1281.31(19)	4149.03(10)	6103.2(2)	1915.46(12)	3668.50(3)	3766.1(2)
Z	4	2	4	8	2	4	4
no. of reflns collected	152295	14904	48648	77285	28284	52750	24519
no. of independent reflns	10596 (R_{int} = 0.0671)	2391 (R_{int} = 0.0692)	8610 (R_{int} = 0.0289)	10698 (R_{int} = 0.0482)	7850 (R_{int} = 0.0230)	7610 (R_{int} = 0.0248)	4720 (R_{int} = 0.0283)
GOF on F^2	0.903	1.080	1.058	1.005	1.130	1.076	1.109
ρ_{calcd} (g cm^{-3})	1.232	1.319	1.235	1.273	1.242	1.210	1.291
μ (mm^{-1})	0.30	5.1	3.0	3.1	2.6	2.7	2.7
Flack param				−0.005(8)			
$R(F_o)$, $[I > 2\sigma(I)]$	0.0305	0.0785	0.0253	0.0342	0.0280	0.0275	0.0325
$R_w(F_o^2)$	0.0664	0.2027	0.0645	0.0927	0.0693	0.0750	0.0852
$\Delta\rho$ (e Å^{-3})	0.71/−0.39	3.2/−2.1	0.32/−0.42	0.50/−0.76	0.40/−0.48	0.66/−0.46	0.40/−0.69

7 H, C_7H_7), 2.99 (pseudo-sept, 4 H, CH isopropyl), 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3), 0.77 (s, 9 H, CH_3 isocyanide). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 148.0 (*ipso*-phenyl), 139.2 (NCN), 135.0 (*o*-phenyl), 129.2 (*p*-phenyl), 123.7 (*m*-phenyl), 112.7 (NCH), 83.5 (C_7H_7), 29.3 (CH_3 isocyanide), 28.9 (CH isopropyl), 24.2 (CH_3), 24.1 (CH_3), the CN isocyanide resonance was not observed. Anal. Calcd for $C_{39}H_{52}N_4Zr$ (668.1): C, 70.11; H, 7.85. Found: C, 69.81; H, 7.70. IR (Nujol): ν(CN/cm^{-1}) = 2149.

[(η^7-C_7H_7)Zr(Im^{Dipp}N(C═O)N-*o*-Xy)] (8). [(η^7-C_7H_7)Zr(Im^{Dipp}N)] (0.298 g, 0.509 mmol) was dissolved in toluene (12 mL). The addition of OCN-*o*-Xy (0.075 g, 0.509 mmol) in toluene (4 mL) resulted in an immediate color change to brown-orange. After the resulting solution was stirred for 1 h, the solvent was removed, and the residue was washed with pentane (orange washings) and subsequently dried, affording a gray-brown powder (0.240 mg, 64%). ^1H NMR (400 MHz, C_6D_6, ambient): δ = 7.25 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, *p*-phenyl), 7.10 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, *m*-phenyl), 6.99 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *m*-phenyl isocyanate), 6.86 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, *p*-phenyl isocyanate), 6.07 (s, 2 H, NCH), 5.25 (s, 7 H, C_7H_7), 2.86 (pseudo-sept, 4 H, CH isopropyl), 1.93 (s, 6 H, CH_3 isocyanate), 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3), 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 159.9 (C═O), 150.5 (NCN), 146.1 (*ipso*-phenyl), 145.0 (*ipso*-phenyl isocyanate), 132.9 (*o*-phenyl isocyanate), 132.6 (*p*-phenyl), 130.5 (*p*-phenyl), 127.7 (*m*-phenyl isocyanate), 125.0 (*m*-phenyl), 123.4 (*p*-phenyl isocyanate), 118.2 (NCH), 85.7 (C_7H_7), 29.0 (CH isopropyl), 25.4 (CH_3), 23.8 (CH_3), 19.1 (CH_3 isocyanate). Anal. Calcd for $C_{43}H_{52}N_4OZr$ (732.1): C, 70.54; H, 7.16. Found: C, 70.78; H, 7.21. IR (Nujol): ν(CN/cm^{-1}) = 1638.

Polymerization of ε-Caprolactone. In a typical experiment, the desired amount of **5** was dissolved in THF and ε-caprolactone (0.390 g, 3.421 mmol) in THF (5 mL) was added in the glovebox. The Schlenk flask was immediately taken out, and the mixture was stirred at the desired temperature for 4 h with a powerful stirring bar. The polymer was subsequently precipitated in cold MeOH (300 mL) and dried to a constant weight for GPC analysis.

X-ray Diffraction Studies. Single crystals of each compound were examined under inert oil and transferred to an Oxford Diffraction diffractometer for data collection (Table 4). The structures were refined anisotropically on F^2 using the SHELXL-97 program.[49] Hydrogen atoms were located and refined isotropically (for all hydrogen atoms at the cycloheptatrienyl ligands and the NH hydrogen of **4**), incorporated as idealized methyl groups allowed to rotate but not tip, or allowed to ride on their attached carbon atoms. Compound **2** crystallized with one disordered toluene molecule. Compound **5** crystallized with two independent molecules per asymmetric unit. The *tert*-butyl group in **7** is disordered over two different orientations; the dimensions of the disordered group are not entirely satisfactory and should be interpreted with caution. The relatively high residual electron density of **3** (3 e Å^{-3} near the Zr atom) may be attributable to absorption errors.

Theoretical Calculations. The calculations were performed using the GAUSSIAN09 package.[50] All structures were fully optimized on the DFT level employing the B3LYP[51] and B97-D[52] functionals. For all main-group elements (C, H, and N) the all-electron triple-ζ basis set (6-311G**)[53] was used, whereas for the transition metal (Zr) the effective core potential double-ζ basis set (Stuttgart RSC 1997 ECP) was applied.[54]

■ ASSOCIATED CONTENT

Supporting Information

Presentations of all calculated structures together with Cartesian coordinates of their atomic positions, ^1H NMR spectrum of poly(ε-CL), computational details, relaxed potential energy scan, and contour plots of selected frontier orbitals in **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: m.tamm@tu-bs.de. Fax: (+49) 531-391-5387. Phone: (+49) 531-391-5309.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Wigley, D. E. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Interscience: New York, 1994; Vol. 42, pp 239−482.

(2) Selected reviews: (a) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633. (b) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355−366. (c) Schrock, R. R. *Dalton Trans.* **2011**, *40*, 7484−7495. (d) Zhang, S.; Nomura, K. *Catal. Surv. Asia* **2011**, *15*, 127−133. Nomura, K.; Zhang, W. *Chem. Sci.* **2010**, *1*, 161−173.

(3) Selected reviews: (a) Mountford, P. *Chem. Commun.* **1997**, 2127−2134. (b) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197−3246. (c) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216 − 217*, 65−97. (d) Duncan, A. P.; Bergman, R. G. *Chem. Rec.* **2002**, *2*, 431−445. (e) Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004**, 2387−2393. (f) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839−849. (g) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813−821.

(4) (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley-Interscience: New York, 1998. (b) Cundari, T. R. *Chem. Rev.* **2000**, *100*, 807−818.

(5) (a) Kuhn, N.; Göhner, M.; Grathwohl, M.; Wiethoff, J.; Frenking, G.; Chen, Y. *Z. Anorg. Allg. Chem.* **2003**, *629*, 793−802. (b) Tamm, M.; Petrovic, D.; Randoll, S.; Beer, S.; Bannenberg, T.; Jones, P. G.; Grunenberg, J. *Org. Biomol. Chem.* **2007**, *5*, 523−530.

(6) (a) Dehnicke, K.; Weller, F. *Coord. Chem. Rev.* **1997**, *158*, 103−169. (b) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19−65. (c) Diefenbach, A.; Bickelhaupt, F. M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 892−900.

(7) Wu, X.; Daniliuc, C. G.; Hrib, C. G.; Tamm, M. *J. Organomet. Chem.* **2011**, *696*, 4147−4151.

(8) (a) Kuhn, N.; Fawzi, R.; Steinmann, M.; Wiethoff, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 769−774. (b) Tamm, M.; Randoll, S.; Bannenberg, T.; Herdtweck, E. *Chem. Commun.* **2004**, 876−877. (c) Tamm, M.; Beer, S.; Herdtweck, E. *Z. Naturforsch.* **2004**, *59b*, 1497−1504. (d) Tamm, M.; Kunst, A.; Stadler, M.; Herdtweck, E. *Organometallics* **2007**, *26*, 761−764. (e) Zhang, S.; Tamm, M.; Nomura, K. *Organometallics* **2011**, *30*, 2712−2720.

(9) (a) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459−467. (b) Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6064−6070.

(10) (a) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890−8894. (b) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981−984. (c) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534−1545. (d) Haberlag, B.; Wu, X.; Brandhorst, K.; Grunenberg, J.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Chem.—Eur. J.* **2010**, *16*, 8868−8877. (e) Tamm, M.; Wu., X. *Chim. Oggi* **2010**, *28*, 10−13. (f) Wu, X.; Tamm, M. *Beilstein J. Org. Chem.* **2011**, *7*, 82−93.

(11) (a) Panda, T. K.; Randoll, S.; Hrib, C. G.; Jones, P. G.; Bannenberg, T.; Tamm, M. *Chem. Commun.* **2007**, 5007−5009. (b) Panda, T. K.; Trambitas, A. G.; Bannenberg, T.; Hrib, C. G.; Randoll, S.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2009**, *48*, 5462−5472. (c) Trambitas, A. G.; Panda, T. K.; Jenter, J.; Roesky, P. W.; Daniliuc, C.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2010**, *49*, 2435−2446. (d) Trambitas, A. G.; Panda, T. K.; Tamm, M. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2156−2171. (e) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Tamm, M. *J. Organomet. Chem.* **2010**, *695*, 2768−2773. (f) Trambitas, A. G.; Yang, J.; Melcher, D.; Daniliuc, C. G.; Jones, P. G.; Xie, Z.; Tamm, M. *Organometallics* **2011**, *30*, 1122−1229.

(12) (a) Blake, A. J.; Dunn, S. C.; Green, J. C.; Jones, N. M.; Moody, A. G.; Mountford, P. *Chem. Commun.* **1998**, 1235−1236. (b) Dunn, S. C.; Hazari, N.; Jones, N. M.; Moody, A. G.; Blake, A. J.; Cowley, A. R.; Green, J. C.; Mountford, P. *Chem.—Eur. J.* **2005**, *11*, 2111−2124.

(13) (a) Dunn, S. C.; Hazari, N.; Cowley, A. R.; Green, J. C.; Mountford, P. *Organometallics* **2006**, *25*, 1755−1770. (b) Arney, D. J.; Bruck, M. A.; Huber, S. R.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 3749−3755.

(14) Tamm, M. *Chem. Commun.* **2008**, 3089−3100.

(15) (a) Tamm, M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Sirsch, P.; Elsevier, C. J.; Ernsting, J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5530−5534. (b) Tamm, M.; Kunst, A.; Herdtweck, E. *Chem. Commun.* **2005**, 1729−1731. (c) Tamm, M.; Kunst, A.; Bannenberg, T.; Randoll, S.; Jones, P. G. *Organometalics* **2007**, *26*, 417−424. (d) Mohapatra, S. K.; Büschel, S.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *J. Am. Chem. Soc.* **2009**, *131*, 17014−17023. (e) Braunschweig, H.; Fuß, M.; Mohapatra, S. K.; Kraft, K.; Kupfer, T.; Lang, M.; Radacki, K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Chem.—Eur. J.* **2010**, *16*, 11732−11743. (f) Tagne Kuate, A. C.; Mohapatra, S. K.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *J. Organomet. Chem.* **2012**, *696*, 4281−4292.

(16) Green, M. L. H.; Ng, D. K. P. *Chem. Rev.* **1995**, *95*, 439−473.

(17) (a) Diamond, G. M.; Green, M. L. H.; Walker, N. M. *J. Organomet. Chem.* **1991**, *413*, C1−C4. (b) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Dalton Trans.* **1992**, 2259−2261.

(18) (a) Glöckner, A.; Bannenberg, T.; Tamm, M.; Arif, A. M.; Ernst, R. D. *Organometallics* **2009**, *28*, 5866−5876. (b) Glöckner, A.; Arif, A. M.; Ernst, R. D.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chim. Acta* **2010**, *364*, 23−29.

(19) (a) Glöckner, A.; Tamm, M.; Arif, A. M.; Ernst, R. D. *Organometallics* **2009**, *28*, 7041. (b) Glöckner, A.; Bauer, H.; Maekawa, M.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Sun, Y.; Sitzmann, H.; Tamm, M.; Walter, M. D. *Dalton Trans.* **2012**, DOI: 10.1039/C2DT12132H.

(20) Glöckner, A.; Bannenberg, T.; Büschel, S.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Chem.—Eur. J.* **2011**, *17*, 6118−6128.

(21) (a) Tamm, M.; Kunst, A.; Lügger, T.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2408−2414. (b) Glöckner, A.; Àrias, Ò.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2011**, *40*, 11511−11518.

(22) (a) Simpson, C. K.; White, R. E.; Carlson, C. N.; Wrobleski, D. A.; Kuehl, C. J.; Croce, T. A.; Steele, I. M.; Scott, B. L.; Young, V. G. Jr.; Hanusa, T. P.; Sattelberger, A. P.; John, K. D. *Organometallics* **2005**, *24*, 3685−3691. (b) Gren, C. K.; Hanusa, T. P.; Rheingold, A. L. *Main Group Chem.* **2009**, *8*, 225−235.

(23) (a) Solomon, S. A.; Layfield, R. A. *Dalton Trans.* **2010**, *39*, 2469−2483. (b) Chmely, S. C.; Hanusa, T. P. *Eur. J. Inorg. Chem.* **2010**, 1321−1337.

(24) Selected examples: (a) Harvey, M. J.; Hanusa, T. P.; Young, V. G. Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217−219. (b) Smith, J. D.; Hanusa, T. P.; Young, V. G. Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6455−6456. (c) Carlson, C. N.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2004**, *126*, 10550−10551. (d) Layfield, R. A.; Humphrey, S. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3067−3069. (e) Quisenberry, K. T.; Smith, J. D.; Voehler, M.; Stec, D. F.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2005**, *127*, 4376−4387. (f) Schormann, M.; Garratt, S.; Bochmann, M. *Organometallics* **2005**, *24*, 1718−1724. (g) Chmely, S. C.; Hanusa, T. P.; Brennessel, W. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 1−5.

(25) Alternatively, supine (*exo*) and prone (*endo*) can be used to distinguish the two orientations. See: Steinborn, D. *Grundlagen der Metallorganischen Komplexkatalyse, 2*; Auflage, Vieweg+Teubner Verlag: Wiesbaden, Germany, 2010.

(26) Larson, E. J.; Van Dort, P. C.; Dalley, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Organometallics* **1987**, *6*, 2141−2146.

(27) Ray, B.; Neyroud, T. G.; Kapon, M.; Eichen, Y.; Eisen, M. S. *Organometallics* **2001**, *20*, 3044−3055.

(28) Fernández-Galán, R.; Hitchcock, P. B.; Lappert, M. F.; Antiñolo, A.; Rodríguez, A. M. *J. Chem. Soc., Dalton Trans.* **2000**, 1743−1749.

(29) Selected examples: (a) Larson, E. J.; Van Dort, P. C.; Lakanen, J. R.; O'Neill, D. W.; Pederson, L. M.; McCandless, J. J.; Silver, M. E. *Organometallics* **1988**, *7*, 1183−1187. (b) Vance, P. J.; Prins, T. J.; Hauger, B. E.; Silver, M. E.; Wemple, M. E.; Pederson, L. M.; Kort, D. A.; Kannisto, M. R.; Geerligs, S. J.; Kelly, R. S.; McCandless, J. J.; Huffman, J. C.; Peters, D. G. *Organometallics* **1991**, *10*, 917−924. (c) Wielstra, Y.; Duchateau, R.; Gambarotta, S.; Bensimon, C.; Gabe, E. *J. Organomet. Chem.* **1991**, *418*, 183−190. (d) Antonelli, D. M.; Tjaden, E. B.; Stryker, J. M. *Organometallics* **1994**, *13*, 763−765.

(30) ^{1}H NMR for $C_3H_4(TMS)_2$: δ = 6.11−5.99 (m, 1 H), 5.42 (d, 1 H), 1.64 (d, 2 H), 0.04 (s, 9 H, TMS), 0.01 (s, 9 H, TMS).

(31) (a) Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, *92*, 2353−2358. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 2041−2054. (c) Michelman, R. I.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 5101−5102. (d) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G. *Organometallics* **1998**, *17*, 484−484. (e) Wallasch, M. W.; Weismann, D.; Riehn, C.; Ambrus, S.; Wolmershäuser, G.; Lagutschenkov, A.; Niedner-Schatteburg, G.; Sitzmann, H. *Organometallics* **2010**, *29*, 806−813. (f) Weismann, D.; Sun, Y.; Lan, Y.; Wolmershäuser, G.; Powell, A. K.; Sitzmann, H. *Chem.—Eur. J.* **2011**, *17*, 4700−4704.

(32) The Cambridge Structural Database (November 2011) contains 1876 structures with 5410 Zr−N distances. The distances range from 1.868 to 2.886 Å. Only 88 distances are shorter than 2.000 Å.

(33) Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689−708.

(34) Grimme, S. *WIREs Comput. Mol. Sci.* **2011**, *1*, 211−228.

(35) Meconi, G.; Kaltsoyannis, N. *Organometallics* **2005**, *24*, 1189−1197.

(36) Cloke, F. G. N.; Green, J.; Hazari, N.; Hitchcock, P. B.; Mountford, P.; Nixon, J. F.; Wilson, D. J. *Organometallics* **2006**, *25*, 3688−3700.

(37) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (b) Blake, A. J.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Schubart, M.; Scowen, I. J. *Chem. Commun.* **1997**, 1555−1556. (c) Bashall, A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Pugh, S. M.; Radojevic, S.; Schubart, M.; Scowen, I. J.; Trösch, D. J. M. *Organometallics* **2000**, *19*, 4784−4794.

(38) Tamm, M.; Kunst, A.; Bannnberg, T.; Herdtweck, E.; Schmid, R. *Organometallics* **2005**, *24*, 3163−3171.

(39) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1196−1200.

(40) Selected examples: (a) Blake, A. J.; Mountford, P.; Nikonov, G. I.; Swallow, D. *Chem. Commun.* **1996**, 1835−1836. (b) Blake, A. J.; McInnes, J. M.; Mountford, P.; Nikonov, G. I.; Swallow, D.; Watkin, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 379−391. (c) Dubberley, S. R.; Friedrich, A.; Willman, D. A.; Mountford, P.; Radius, U. *Chem.—Eur. J.* **2003**, *9*, 3634−3654. (d) Hanna, T. E.; Keresztes, I.; Lobkovsky, E.; Bernskoetter, W. H.; Chirik, P. J. *Organometallics* **2004**, *23*, 3448−3458. (e) Wang, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2005**, *24*, 3772−3779. (f) Guiducci, A. E.; Boyd, C. L.; Mountford, P. *Organometallics* **2006**, *25*, 1167−1187. (g) Tiong, P. J.; Nova, A.; Groom, L. R.; Schwarz, A. D.; Selby, J. D.; Schofield, A. D.; Clot, E.; Mountford, P. *Organometallics* **2011**, *30*, 1182−1201. (h) Chu, J.; Lu, E.; Liu, Z.; Chen, Y.; Leng, X.; Song, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 7677−7680.

(41) Selected reviews: (a) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. *J. Chem. Soc., Dalton Trans.* **2001**, 2215−2224. (b) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176. (c) Williams, C. K. *Chem. Soc. Rev.* **2007**, *36*, 1573−1580.

(42) Arbaoui, A.; Redshaw, C. *Polym. Chem.* **2010**, *1*, 801−826.

(43) Selected examples: (a) Thomas, D.; Arndt, P.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 1351−1357. (b) Arndt, P.; Spannenberg, A.; Baumann, W.; Becke, S.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2001**, 2885−2890. (c) Wang, H.; Chan, H.-S.; Okuda, J.; Xie, Z. *Organometallics* **2005**, *24*, 3118−3124. (d) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2006**, 887−889. (e) Gornshtein, F.; Kapon, M.; Botoshanksy, M.; Eisen, M. S. *Organometallics* **2007**, *26*, 497−507. (f) Ning, Y.; Zhan, Y.; Rodriguez-Delgado, A.; Chen, E. Y.-X. *Organometallics* **2008**, *27*, 5632−5640. (g) Schwarz, A. D; Thompson, A. L.; Mountford, P. *Inorg. Chem.* **2009**, *48*, 10442−10454. (h) Schwarz, A. D.; Herbert, K. R.; Paniagua, C.; Mountford, P. *Organometallics* **2010**, *29*, 4171−4188. (i) Saha, T. K.; Ramkumar, V.; Chakraborty, D. *Inorg. Chem.* **2011**, *50*, 2720−2722.

(44) Gröb, T.; Seybert, G.; Massa, W.; Weller, F.; Palaniswami, R.; Greiner, A.; Dehnicke, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 4373−4375.

(45) (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845−4856. (b) Dyer, H. E.; Huijser, S.; Schwarz, A. D.; Wang, C.; Duchateau; Mountford, P. *Dalton Trans.* **2008**, 32−35.

(46) (a) Gamer, M. T.; Roesky, P. W.; Palard, I.; Le Hellaye, M.; Guillaume, S. M. *Organometallics* **2007**, *26*, 651−657. (b) Jenter, J.; Roesky, P. W.; Ajellal, N.; Guillaume, S. M.; Susperregui, N.; Maron, L. *Chem.—Eur. J.* **2010**, *16*, 4629−4638.

(47) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889−899.

(48) (a) Tamm, M.; Baum, K.; Lügger, T.; Fröhlich, R.; Bergander, K. *Eur. J. Inorg. Chem.* **2002**, 918−928. (b) Tamm, M.; Dreßel, B.; Urban, V.; Lügger, T. *Inorg. Chem. Commun.* **2002**, *5*, 837−840. (c) Tamm, M.; Dreßel, B.; Lügger, T.; Fröhlich, R.; Grimme, S. *Eur. J. Inorg. Chem.* **2003**, 1088−1098.

(49) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(51) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(52) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787−1799.

(53) Cao, X.; Dolg, M. *J. Chem. Phys.* **2001**, *115*, 7348−7355.

(54) (a) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441. (b) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360−1366. (c) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.* **1993**, *97*, 5852−5859.