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A general benzylic C–H activation and C–C coupling reaction of zirconocenes mediated by C–N bond cleavage in *tert*butylisocyanide – unusual formation of iminoacyl complexes

Reactions of a zirconocene complex with *tert*-butylisocyanide and methylbenzenes result in the formation of zirconocene η^2 -iminoacyl cyanide complexes by C–C coupling with a benzyl fragment through C–H bond activation of a methyl group of the methylbenzene and C–N cleavage at the isocyanide. A dimeric cyanide bridged zirconocene complex is formed as a sideproduct of this process.





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Introduction

Coupling of small unsaturated molecules to transition metal fragments is a well-known and straight-forward approach for the generation of a variety of cyclic and acyclic functionalised molecules. Incorporation of heteroatom containing substrates provides a general route to highly functionalised heterocycles which circumvents multistep-synthesis.¹ In this context, isocyanides are interesting coupling partners as they are isoelectronic with CO, one of the most important C₁ building blocks; however, their coordination chemistry is more diverse due to the additional substituents.² Reactions of isocyanides were studied for many of the transition metals, giving e.g. metallaaziridine or iminoacyl complexes upon insertion into M-C bonds of the corresponding alkyl complexes. For early transition metals, insertion and coupling of isocyanides with cyclic³ and acyclic⁴ alkyl ligands is well precedented and typically affords η^2 -iminoacyl complexes. End-on coordination of

A general benzylic C–H activation and C–C coupling reaction of zirconocenes mediated by C–N bond cleavage in *tert*-butylisocyanide – unusual formation of iminoacyl complexes†‡

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Reactions of the zirconocene alkyne complex $[rac-(ebthi)Zr(\eta^2-Me_3SiC_2SiMe_3)]$ $(rac-(ebthi) = rac-1,2-ethylene-1,1'-bis(\eta^5-tetrahydroindenyl))$ with *tert*-butylisocyanide and methylbenzenes were investigated. Depending on the stoichiometry, the solvent and the reaction temperature different products were obtained. Starting with the end-on coordination of the isocyanide to the zirconium centre (**2**), elevated reaction temperatures and an excess of *tert*-butylisocyanide resulted after the elimination of the alkyne in the formation of zirconocene η^2 -iminoacyl cyanide complexes **3a–d**. These complexes are formed by coupling with a benzyl fragment through C–H bond activation of a methyl group of methylbenzene. The dimeric cyanide bridged zirconocene complex **4** is formed as a side-product of this process. The unexpected dimer and the heterometallacycles were fully characterised, including X-ray crystallography.

the isocyanide to the metal centre via the C atom⁵ is known to be the initial step for this process.

Recently, some of us have reported that the reaction of the alkyne complex $[rac-(ebthi)Zr(\eta^2-Me_3SiC_2SiMe_3)]$ (1) with 2,6-dimethylphenyl isocyanide (XyNC) results - depending on the reaction temperature and time as well as the Zr/isocyanide ratio - in the coupling of the alkyne with two, three or four equivalents of isocyanide. As a result, metallaaziridine complexes, azametallacycloallenes, and fused heterocyclic systems were obtained (Scheme 1).6 Notably, although reactions with the Hf analogue $[rac-(ebthi)Hf(\eta^2-Me_3SiC_2SiMe_3)]$ gave the corresponding isostructural coupling products, use of the permethylated complex [Cp*2Zr(η2-Me3SiC2SiMe3)] and other nonbridged metallocene precursors did not allow for coupling of more than two equivalents of the isocyanide, thus highlighting the importance of the bridging cyclopentadienyl ligand for isocyanide coupling. Release of the unusual fused heterocyclic ligand by demetalation/protonation was possible and furnished highly functionalised pyrroles.

Reactions of *ansa*-metallocenes with other common isocyanides such as *t*-BuNC were performed in the past; however, coupling of the CN units has not been reported. For example, treatment of a SiMe₂ bridged zirconocene alkyne complex with an excess of *t*-BuNC resulted in only the end-on coordination of the isocyanide.^{3b} Also, with non-bridged metallocenes $[Cp_2M]$ (M = Zr, Hf), Erker and co-workers reported the formation of addition/insertion products which – even in the presence of excess *t*-BuNC – possess besides an end-on isocya-



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 $[\]dagger$ This work is dedicated to mentor and friend Robin N. Perutz on the occasion of his 70th birthday, in recognition of his numerous important contributions to C–H bond activation and mechanistic organometallic chemistry in general.

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Scheme 1 Top: Coupling of up to four equivalents of XyNC with complex 1 (Xy = 2,6-dimethylphenyl, M = Zr, Hf). Bottom: Examples of end-on isocyanide complexes.

nide ligand an η^2 -iminoacyl group.^{4d} For us, these findings raised the question whether for reactions of isocyanides with group 4 metallocenes the reactivity is dominated by the cyclopentadienyl ligand or rather by the isocyanide substituent. To follow up on previous studies, we have thus performed the reactions of the well-studied alkyne complex $\mathbf{1}^7$ with *t*-BuNC and observed the formation of unusual coupling products through a series of bond activation reactions.

Results and discussion

Reactions of [rac-(ebthi)Zr] with t-BuNC

Addition of *t*-BuNC to a benzene solution of complex **1** at room temperature results in an immediate colour change from green to orange and well-known coordination of isocyanide to the Zr centre occurs. The molecular structure of the coordination product **2** (Scheme 2) was confirmed by X-ray analysis and shows the expected five-coordinate Zr centre (Fig. 1). The bond parameters of the coordinated alkyne and the isocyanide



Scheme 2 Synthesis of complexes 2, 3a-e and 4. 3a in toluene; 3b in benzene with excess of *p*-xylene; 3c in benzene with excess of *m*-xylene; 3d in benzene with excess of *o*-xylene; 3e in benzene with excess of mesitylene.



Fig. 1 The molecular structure of complex 2. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

are in the expected range and correspond to a shortened C–C double bond in the alkyne ligand which is well in line with the value found for the isocyanide free complex 1 (1: 1.300(10), 2: 1.304(2) Å, *cf.* $\sum r_{cov}(C=C) = 1.34 Å^8$) and a dative Zr–isocyanide interaction (Zr1–C9 2.280(2) Å), respectively. In comparison to the related *ansa*-complex [Me₂Si(η⁵⁻C₅H₄)₂Zr(CN-*t*-Bu) (η²-Me₃SiC₂SiMe₃)]^{3b} (C) this Zr–C distance is only slightly smaller (*cf.* 2.293(2) Å). Moreover, the CN stretching vibrations of both compounds are similar (2: $\tilde{\nu}$ (CN) 2111, C: 2116 cm⁻¹). In contrast, for [Cp₂Zr(CN-*t*-Bu)(η²-Me₃SiC₂SiMe₃)]^{3b} (D) this band was found at 2124 cm⁻¹, which suggests a slightly stronger Zr–C bond in the *ansa*-complexes 2 and C.

Next, we investigated the possibility of isocyanide coupling to 2 and added further t-BuNC in an NMR scale reaction using C_6D_6 as the solvent. To our surprise, isomerisation of *t*-BuNC to *t*-BuCN occurs as evidenced by a ¹H NMR signal at 0.9 ppm as well as three resonances in ¹³C NMR at 27.5, 27.7 and 125.1 ppm. Notably, this reaction can also be performed catalytically (1.7 mol% 2, Fig. S19‡). To avoid a so far unknown solvent effect we then followed exactly the same protocol as used before for reactions with XyNC (Scheme 1).⁶ Heating the mixture of 2 and excess t-BuNC at 60-80 °C in toluene instead of benzene results in the formation of a brownish-red solution from which a pale yellow material could be isolated after recrystallisation from *n*-hexane. ¹H NMR spectroscopic analysis of compound 3a reveals the presence of only one intact t-BuNC group along with two doublets (δ 3.88 and 4.22 ppm; Fig. 2, marked with asterisks) that can be assigned to the CH_2 group based on a ^{2}J coupling of 15.2 Hz. These signals are absent when using toluene- d_8 (Fig. S18[‡]). With the previous experiment in benzene in mind, this CH₂ group should thus have its origin in the C-H activation of the CH₃ group. This assumption is further confirmed by the molecular structure (Fig. 3, left), which shows a benzyl fragment coupled with an isocyanide to give an iminoacyl ligand in η^2 -coordination to the Zr centre. Additionally, a cyanide ligand binds to the metal (C-N 1.143(2) Å), thus giving a five-coordinate complex. Formation of this unusual complex is proposed to occur by a series of C-H (in toluene solvent) and C-N bond cleavage (in the isocyanide) as well as C-C coupling events (between the benzyl ligand and the intact isocyanide ligand). Notably, reaction times can be reduced significantly when reactions are per-



Fig. 2 ¹H NMR spectra of products **3a–d** obtained after *n*-hexane workup (C_6D_6). The spectrum of **3e** was taken from the crystallised product. Asterisks indicate the CH₂ group formed by benzylic C–H activation. Triangles can be assigned to an additional [*rac*-(ebthi)Zr] species **4**.

formed at 110 °C in toluene; however, along with **3a** poorlydefined product mixtures are obtained (Fig. S17[‡]).

In order to evaluate whether formation of this unusual zirconocene complex occurs *via* a general type of benzylic C–H activation we next investigated reactions with other methylbenzenes, including *p*-xylene, *m*-xylene, *o*-xylene and mesitylene. These could formally undergo twofold C–H activation at two methyl groups, thus giving dinuclear Zr complexes. Indeed, in all cases, the same set of doublets can be detected in the ¹H NMR spectra of the reaction product (Fig. 2). Spectroscopic evidence of activation of two CH₃ groups was not found.

Notably, in the NMR spectra of complexes **3b** and **3d**, an additional set of four doublets is observed that can be assigned to the presence of a second [rac-(ebthi)Zr] species **4** (*vide infra*). Fig. 2 also shows that the reaction of the *m*-xylene derivative (**3c**) is much less selective, which unfortunately made isolation of this reaction product impossible.

The molecular structures of complexes 3d and 3e show similar features as for 3a with the iminoacyl group in

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Table 1 Summary of selected experimental and calculated bond lengths of complexes 3a, 3d, and 3e. Data in italics correspond to the values obtained from DFT calculations

	3a	3d	3e
Zr–C1	2.2396(15)	2.229(2)	2.2318(13)
	2.278	2.277	2.279
Zr-CX ^a	2.3241(15)	2.331(2)	2.3198(13)
	2.306	2.304	2.306
Zr–N1	2.2275(12)	2.2254(17)	2.2351(11)
	2.283	2.283	2.284
C1-N1	1.2655(19)	1.271(3)	1.2676(17)
	1.277	1.278	1.277
CX-N2	1.143(2)	1.143(3)	1.1452(18)
	1.175	1.175	1.175

^a CX represents the carbon atom of the cyanide.

^N-inside' orientation (Fig. 3). In all three species the Zr–C1 bond lengths are shorter than typical Zr–C σ -bonds (see Table 1, *cf.* Zr–C in Cp₂ZrMe₂ 2.280(5)/2.273(5) Å)⁹ which are well in line with literature-known zirconocene iminoacyl complexes, bearing a (C–C=N–C) unit coordinated in η^2 -mode, where these values range from 2.267(4) Å in [(Me₂Si)₂(η^5 -C₅H₃)₂Zr(Cl) (η^2 -i-PrNCXy)]¹⁰ to 2.156(2) Å in [Cp₂Zr(-N(*t*-Bu)C-anthracene-)].¹¹

The C1–N1 distances in complexes **3a**, **3d**, and **3e** are equal and correspond to double bonds (*cf*. $\sum r_{cov}(C=N) = 1.27$ Å),⁸ which is in agreement with related structures where these values are found to be between 1.293(5) in Erker's¹² and 1.242(2) Å in Bullock's¹³ zirconocene iminoacyl complexes. The CX–N2 bond of all iminoacyl complexes is best described as a triple bond, which confirms the presence of a cyanide ligand coordinated to the metal centre (Table 1, *cf*. $\sum r_{cov}(C=N) =$ 1.14 Å).⁸ This is supported by two CN vibration bands for these complexes, which range from 2121 to 2118 cm⁻¹ for the cyanide ligand and from 1625 to 1618 cm⁻¹ for the iminoacyl ligand (Table S8‡).

In addition, we were interested in the nature of the Zr–E (E = C, N) bonds in these complexes. Therefore, natural bond orbital (NBO) and natural localised molecular orbital (NLMO) analysis was performed using the NBO6.0¹⁴ package for



Fig. 3 Molecular structures of complexes 3a (left), 3d (middle) and 3e (right). Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Complex 3d co-crystallises with the dimer 4 in a 1:1 ratio; 4 was omitted for clarity, see ESI‡ for details.



Fig. 4 Representation of selected Natural Localised Molecular Orbitals (NLMO) calculated for the optimised structure of complex 3a.

Gaussian09¹⁵ (Fig. 4 and Table S11[‡]). NLMO40 reveals the Zr–N bond as a dative bond with contributions from the sp⁴ hybrid lone-pair of the nitrogen atom (82%) and the d orbital of zirconium (11%). The C=N π -bond of the iminoacyl ligand is described by NLMO47 as consisting of two pure p orbitals. The Zr–C1 bond consists of a sp² hybrid at C1 (70%) and a d orbital at the zirconium centre (25%, NLMO48). In agreement with the data from the molecular structure of the cyanide ligand one LP at the N2 atom (NLMO43), one CX–N2 σ bond (NLMO59) and two orthogonal π bonds (NLMO60 and 61, Table S11,[‡] p. S47) were found. The CX–Zr bond (NLMO53) consists of a CX sp hybrid (76%) and an sd⁷ hybrid at the Zr centre (23%). These findings further support the assignment of cyanide coordinated iminoacyl complexes **3a–e** as depicted in Scheme 2.

Notably, complex **3d** co-crystallises with the cyanide bridged dimeric Zr(m) complex **4** (Fig. 5), which was observed spectroscopically and also formed in reactions with *p*-xylene and mesitylene. Only in the case of **3e** the product free of **4** could be obtained by crystallization from benzene. Although the cyanide units are disordered in **4**, in combination with the ¹³C NMR shift of 213.6 ppm (Fig. S35‡) and the C≡N vibration at 1892 cm⁻¹ (Table S8‡), it is possible to clearly distinguish between C and N and thus confirm the structural assignment (Fig. 5).

Furthermore, the $[Zr-CN]_2$ isomer of 4 is energetically preferred compared to the $[Zr-NC]_2$ isomer ($\Delta_R G = -70.2$ kJ mol⁻¹). The formal Zr(III) complex 4 can be readily detected by



Fig. 5 Molecular structure of complex **4**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms, the lower occupancy sites and co-crystallised **3d** are omitted for clarity.

NMR spectroscopy at room temperature, which suggests antiferromagnetic coupling between both Zr centres. To confirm this, the Complete Active Space (CAS(2,2)) SCF method¹⁶ was employed to obtain a multi-determinant open-shell singlet wave function and describe the bonding situation in 4 appropriately. The orbital localisation scheme indicates that the radical of each zirconium centre is delocalised over one Zr–CN unit and 4 can be formally described as a biradicaloid with $\beta^{17} = 13\%$ (Fig. S47,‡ p S54).¹⁸

At this point it should be mentioned that compound 4 cannot be obtained simply by heating compounds 3a-e (Fig. S22 and S23[‡]).

Mechanistic considerations

To explain the selective formation of iminoacyl complexes **3a–e** with *t*-BuNC as opposed to the formation of **B** and its subsequent products with XyNC (Scheme 1),⁶ simple thermochemistry calculations were carried out on the basis of the optimised structures using the pure density functional BP86¹⁹ in combination with the LANL2DZ²⁰ basis set and the corresponding ECP for Zr and the TZVP²¹ basis set for all other atoms (notation BP86/LANL2DZ/TZVP). We first compared Gibbs free energies for the transformation of **A** to **B** for the zirconocene complexes. For the reaction of *t*-BuNC this process is endergonic with $\Delta_{\rm R}G = +8.1$ kJ mol⁻¹, which might provide an explanation and is in line with the observed reactivity,⁶ and the corresponding reaction with XyNC is exergonic by -9.9 kJ mol⁻¹. It should however be noted that these values are rather small and in the range of the error of the DFT method.

In order to gain insight into the formation of complexes **3a–e** and **4**, we performed a series of ¹H NMR experiments (Fig. S6–S15[‡]), the results of which are discussed below exemplarily for the formation of **3a**. Heating (T = 80 °C) a mixture of complex **2**, excess *t*-BuNC and toluene results in the formation of complex **3a** and isobutane (δ 0.86 (d), 1.63 ppm (dec)). Along with this, *t*-BuCN and an unidentified paramagnetic species are produced, as evidenced by a significant decrease of NMR signal intensity (Fig. S1–S3[‡]). Also, Me₃SiC₂SiMe₃ (δ 0.16 ppm) and isobutene (δ 1.57 (trip), 4.67 ppm (sep)) are observed. Formation of complex **4** occurs only after full consumption of *t*-BuNC and not by the degradation of **3a**. The latter was confirmed by the stability test of mixtures of **3b/4** and **3e/4** (Fig. S22 and S23[‡]). Furthermore, in some of the

NMR monitoring experiments a signal at δ 4.45 ppm was found which could indicate the presence of H₂. Based on these observations we propose the following mechanism for the formation of complexes **3a-e** and **4** (Scheme 3):

- The reaction of complex 2 at elevated temperatures leads to a homolytic cleavage of the C-N bond to form a zirconocene radical species along with a t-Bu radical.

- Formation of isobutene occurs from this radical, either by disproportionation or H₂ elimination.

- Reaction of the *t*-Bu radical or the Zr radical species with t-BuNC forms t-BuCN (C-N activation). Examples of radical induced isocyanide-to-nitrile isomerisation are known.²²

- Reaction of the *t*-Bu radical with methyl arene produces a benzyl radical and isobutane (C-H activation).

- Recombination of zirconocene and benzyl radicals forms a transient zirconocene benzyl cyanide complex, which subsequently inserts t-BuNC to yield an iminoacyl complex (C-C coupling).

- Formation of 4 occurs from 2 and its decomposition products in the absence of t-BuNC.

The first step of this sequence is computed to be endergonic, which is in line with the lack of reactivity at room temperature (Scheme 3). All other proposed steps are strongly exergonic.

Since we propose the presence of a paramagnetic species as well as a formal cyanide during the formation of both 3a-e and 4 from isocyanide, C-N cleavage should be a fundamental reaction step. Therefore, we calculated bond dissociation energies (BDEs) for the uncoordinated isocyanides which clearly reveal the preferred formation of the tert-butyl radical compared to the *m*-xylene radical (BDE (*t*-BuNC) = $378.5 \text{ kJ mol}^{-1}$ and BDE (XyNC) = $460.0 \text{ kJ mol}^{-1}$). In the coordination sphere

- Me₃SiC₂SiMe₃

Scheme 3 Proposed mechanism for the formation of iminoacyl complexes. Compounds in solid boxes were fully characterised. Dashed boxes show products identified by NMR spectroscopy.

of the zirconocene this energy is further reduced (BDE: (2) = 84.7, (A) = 163.5, and (D) 103.6 kJ mol⁻¹). Since the difference in BDEs between 2 and D is very small compared to A, it can be assumed that the influence of the isocyanide on the observed reactivity is much greater than that of the metallocene ligand.

Similar types of C-N bond cleavage in t-BuNC have been reported before, e.g. in a Sm complex, where the formation of a CN bridged trinuclear complex was observed.²³ Also, Andersen and Lukens have shown that the cleavage of *t*-BuNC by Cp₃Zr results in the oxidation of the Zr centre to form Cp₃ZrCN.²⁴

The last step of the proposed mechanism includes the insertion of another equivalent of t-BuNC into the Zr-C bond of a benzyl complex which furnishes iminoacyl complexes. Isocyanide insertion is well-known and shows broad applicability and a wide substrate range.² As this step of the proposed reaction sequence is strongly exergonic for all methylbenzenes used and for the XyNC derivative, it is assumed that isocyanide activation has a significant influence on the observed reaction (cf. p. S43). Although stoichiometric and catalytic benzylic C-H bond activation with group 8-10 metals has been reported on several occasions,²⁵ the corresponding reactions of early transition metal complexes that give well-defined complexes are much less common. Examples include the formation of Nb²⁶ and Y benzyl complexes,²⁷ as well as thermal activation of a mesityl group to give η^3 -mesityl and eventually an alkylidene ligand with Zr.28 Notably, in some cases not only alkyl C-H activation, but also competing aromatic C-H activation is observed (e.g. Pt,^{25b,c} Nb²⁶). Although in our case we have no clear evidence of similar aromatic activation processes, this could additionally explain the poor yields of some of the η^2 iminoacyl products.

Conclusions

We have presented the reactions of the alkyne complex [rac-(ebthi) $Zr(\eta^2-Me_3SiC_2SiMe_3)$] with *t*-BuNC in the presence of a series of methylbenzenes. In all cases, an unusual sequence of C-H and C-N activation as well as C-C coupling events occurs, which was not observed for related reactions with the aromatic isocyanide XyNC. This reactivity pattern appears to be mostly determined by the nature of the isocyanide, which is known to be prone to the cleavage of the CN fragment. Notably, the observed reactivity occurs systematically for a broad range of methylbenzenes, further highlighting the potential of early transition metals, in particular group 4 metallocenes, for a rich coupling chemistry of unsaturated substrates. However, we would like to point out that the results of the present study should not be understood in terms of selective synthesis of iminoacyl complexes, but rather as a case-study of possible (unwanted) reactivities under drastic reaction conditions (metallocene(III) intermediates, high temperature, and methyl arenes as solvents).



Experimental

All operations were carried out under argon with standard Schlenk techniques or in a glove box. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk flasks equipped with Young-type Teflon valve stopcocks. The metallocene compound rac-(ebthi) $Zr(\eta^2-Me_3SiC_2SiMe_3)$ (1) was synthesised as previously described in the literature.⁷ Commercially available t-BuNC (Sigma Aldrich) was dried over molecular sieves and degassed prior to use. The following instruments were used for characterisation: NMR: Bruker AV300 and AV400 spectrometers. ¹H and ¹³C NMR chemical shifts are given in ppm and were referenced to the solvent signals: $[D_6]$ benzene $(\delta_{\rm H} = 7.16; \delta_{\rm C} = 128.06 \text{ ppm})$. Signal assignment was done by homo- and heteronuclear chemical shift correlation (COSY, HMBC) and ¹H NOE experiments. Detailed NMR spectra can be found in the ESI‡ (pp. S17-S21). IR: Bruker Alpha FT-IR spectrometer. Raman spectra were recorded on a LabRAM HR 800 Raman Horiba spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by different laser sources: 633 nm (17 mW, air cooled), 784 nm laser diode (100 mW, air-cooled) or 473 nm Ar+ Laser (20 mW, air-cooled). Full spectra are depicted in the ESI[‡] (pp. S22-S27). MS: Finnigan MAT 95-XP from Thermo-Electron. CHN analysis: Leco Tru Spec elemental analyser. Melting points: Mettler-Toledo MP 70 (melting points were uncorrected and were measured in sealed capillaries).

Synthesis of complex 2

To a solution of rac-(ebthi) $Zr(\eta^2-Me_3SiC_2SiMe_3)$ (1) (0.284 g, 0.50 mmol) in benzene (10 mL) t-BuNC (0.058 mL, 0.51 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 20 min at ambient temperature all volatiles were removed in a vacuum resulting in an orange solid of complex 2. Yield: 0.238 g (73%). Mp: 116 °C (decomp. under Ar). ¹H NMR (300 MHz, $[D_6]$ benzene, 297 K): $\delta = 0.41, 0.58$ (s, each 9H, SiMe₃), 1.14 (s, 9H, *t*-Bu), 4.71 (d, ${}^{3}J$ = 2.8 Hz, 1H, CH=CH ebthi), 5.20 (d, ${}^{3}J$ = 2.8 Hz, 1H, CH=CH ebthi), 5.36 (d, ³J = 3.1 Hz, 1H, CH=CH ebthi), 5.74 (d, ${}^{3}J$ = 3.1 Hz, 1H, CH=CH, ebthi) ppm (CH₂ resonances of the ebthi ligand appear as broad multiplets between 1.32 and 2.48 ppm, 20 H). (1.40 and 3.58 (m, each 1H, CH₂ THF). ¹³C NMR (75 MHz, $[D_6]$ benzene, 297 K): δ = 2.2, 3.7 (SiMe₃), 23.27, 23.36, 23.39, 23.6, 23.8, 24.0, 24.01, 24.2, 26.8, 27.9 (CH₂ ebthi), 30.2 (CH₃ t-Bu), 56.4 (Cq t-Bu), 96.2, 96.6, 97.9, 106.6, (CH=CH ebthi), 112.1, 113.6, 113.7, 118.1, 118.9, 120.8, (*Cq* ebthi), 180.2, 182.5, 191.9 (*C*=*C* resp. $C \equiv N$) ppm (25.8 and 67.8 CH₂ THF). IR (ATR, cm⁻¹): $\nu = 2108$ (w, C=N). MS: m/z (CI): 528 (100) [M⁺-t-Bu], 171 $[Me_3SiC_2SiMe_3]^+$ (5), 84 (21) $[(CH_3)_{3d}]NC]^+$. Elemental analysis calcd (%) for C₃₃H₅₁NSi₂Zr·0.25 THF (C₃₄H₅₃NSi₂Zr 621.28 g mol⁻¹): C 65.53, H 8.57, N 2.25; found: C 64.89, H 8.48, N 2.03.

Synthesis of complex 3a

To a solution of rac-(ebthi) $Zr(n^2-Me_3SiC_2SiMe_3)$ (1) (0.263 g, 0.50 mmol) in toluene (15 mL) t-BuNC (0.054 ml, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further t-BuNC (0.1 mL, 1.0 mmol) was added. After heating the reaction mixture for 12 days at 80 °C, all volatiles were removed in a vacuum and the remaining oil was washed twice with 2 mL of n-hexane. The formed pale yellow powder was dissolved in diethyl ether, filtered and the solution was kept at -78 °C, which resulted in the formation of small pale yellow crystals of 3a. These were isolated by decanting the mother liquor and drying in a vacuum. Yield: 0.115 g (41%). Mp: 162-164 °C (decomp. under Ar). ¹H NMR (300 MHz, $[D_6]$ benzene, 297 K): $\delta = 1.41$ (s, 9H, t-Bu), 3.88 (d, ${}^{2}J$ = 15.2 Hz, 1H, CH₂-Ph), 4.22 (d, ${}^{2}J$ = 15.2 Hz, 1H, CH₂-Ph), 4.41 (d, ${}^{3}J$ = 2.8 Hz, 1H, CH=CH), 4.91 (d, ${}^{3}J$ = 2.8 Hz, 1H, CH=CH), 5.71 (d, ${}^{3}J$ = 2.9 Hz, 1H, CH=CH), 5.94 (d, ${}^{3}J$ = 2.9 Hz, 1H, CH=CH), 7.13 (m, 4H, Ph), 7.17 (m, 1H, Ph) ppm (CH₂ resonances of the ebthi ligand appear as broad multiplets between 1.94 and 3.14 ppm, 20 H). ¹³C NMR (75 MHz, $[D_6]$ benzene, 297 K): δ = 22.7, 23.0, 23.2, 23.3, 23.60, 23.69, 23.72, 24.7, 27.3, 27.6 (CH2 ebthi), 30.3 (CH3 t-Bu), 42.5 (CH2 Ph), 62.0 (Cq t-Bu), 98.1, 104.8 105.8, 106.5 (CH=CH, ebthi), 117.2, 120.7, 122.6, 123.8, 123.9, 126.7 (Cq ebthi), 127.3, 128.4, 129.0, 130.4 (CH-Ph), 138.0 (Cq-Ph), 157.4 (C=N), 231.1 (C=N) ppm. IR (ATR, cm⁻¹): ν = 2120 (w, C \equiv N). MS: m/z (CI): 555 [M], 528 $[M^+-C\equiv N]^+$, 174 $[Me_{3d}-NC-CH_2-Ph]^+$. Elemental analysis calcd (%) for C₃₃H₄₀N₂Zr (555 g mol⁻¹): C 71.30, H 7.25, N 5.04; found: C 71.32, H 7.37, N 4.86.

Synthesis of complex 3b

To a solution of rac-(ebthi) $Zr(\eta^2-Me_3SiC_2SiMe_3)$ (1) (0.263 g, 0.50 mmol) in benzene (10 mL) t-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further t-BuNC (0.114 mL, 1.0. mmol) and an excess (1 mL, 8.5 mmol) of p-xylene were added. After heating the reaction mixture for 12 days at 80 °C, all volatiles were removed in a vacuum and the remaining deep brown oil was washed with three 1 mL portions of cold n-hexane. The obtained yellow-brown sticky solid was dissolved in diethyl ether, which was subsequently removed in a vacuum. After addition of 1 mL of benzene light brown yellow crystals were obtained after one week at room temperature. These were isolated by filtration, washed twice with cold pentane and dried in a vacuum. Yield: 0.125 g of a mixture of $3\mathbf{b} + 4$ (1:0.25). Several crystallisation steps from benzene or diethyl ether yielded only a small amount of crystals of pure 3b. ¹H NMR (300 MHz, [D₆]benzene, 297 K): δ = 1.45 (s, 9H, *t*-Bu), 2.15 (s, 3H, *Me*-xylene), 3.93 (d, ${}^{2}J$ = 15.2 Hz, 1H, *CH*₂-xylene), 4.27 (d, ²J = 15.2 Hz, 1H, CH₂-xylene), 4.50 (d, ³J = 2.8 Hz, 1H, CH=CH ebthi), 5.01 (d, ³*J* = 2.8 Hz, 1H, CH=CH ebthi), 5.75 (d, ³*J* = 2.9 Hz, 1H, CH=CH ebthi), 5.98 (d, ${}^{3}J$ = 2.9 Hz, 1H, CH=CH ebthi), 7.05, 7.07, 7.13, 7.15 (br., 4H, CH xylene) ppm (CH₂

resonances of the ebthi ligand appear as broad multiplets between 1.90 and 2.98 ppm, 20 H). NMR (100 MHz, [D₆] benzene, 297 K): $\delta = 21.1$ (*Me*-Ph) 22.8, 23.06, 23.22, 23.4, 23.6, 23.70, 23.73, 24.7, 27.3, 27.6 (*C*H₂ ebthi), 30.3 (*Me*-t-Bu), 42.0 (*C*H₂-Ph), 62.0 (*Cq*-t-Bu), 98.2, 104.7 105.8, 106.5 (*C*H=*C*H, ebthi), 117.2, 120.6, 122.5, 123.82, 123.86, 126.7 (*Cq*-ebthi), 127.3, 129.3, (*C*H-Ph), 134.9, 136.8 (*Cq*-Ph), 157.4 (*C*=N), 231.3 (*C*=N) ppm. IR (ATR, cm⁻¹): $\nu = 2110$ (w, C=N). MS: *m/z* (CI): 569 [M]⁺, 542 [M⁺-C=N]⁺, 188 [Me_{3d}-NC-CH₂-xylene]⁺.²⁹

Synthesis of complex 3d

To a solution of rac-(ebthi) $Zr(\eta^2-Me_3SiC_2SiMe_3)$ (1) (0.263 g, 0.50 mmol) in benzene (10 mL) t-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further t-BuNC (0.115 mL, 1.0 mmol) and an excess (1 mL, 8.30 mmol) of mesitylene were added. After heating the reaction mixture for 12 days at 80 °C, all volatiles were removed in a vacuum and the remaining dark oil was washed twice with 1 mL of n-hexane. The obtained orange-red sticky solid was dissolved in diethyl ether, which was subsequently removed in a vacuum. After adding a mixture of ether/n-hexane (1:1), filtration from the insoluble oily precipitate and standing for three weeks at -78 °C, orange-red crystals formed which were isolated and identified as a 1:1 mixture of 3d and 4 by NMR spectroscopy. When pure diethyl ether is used for crystallisation a 1:4 (3d:4) mixture was obtained. ¹H NMR (400 MHz, $[D_6]$ benzene, 297 K): $\delta = 1.49$ (s, 9H, *t*-Bu, 3d), 2.08 (s, 3H, Me-Ph, 3d), 3.14-0.9 (m, 40H, CH₂-ebthi, 3d + 4), 3.89 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph, 3d), 4.44 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph, 3d), 4.56 (m, 2H, ebthi, 3d + 4), 4.75 (d, J = 2.9 Hz, 1H, 4), 4.90 (d, ${}^{3}J$ = 2.9 Hz, 1H, ebthi, 3d), 5.31 (d, ${}^{3}J$ = 2.9 Hz, 1H, 4), 5.56 (d, ${}^{3}J$ = 2.9 Hz, 1H, 4), 5.79 (d, ${}^{3}J$ = 2.9 Hz, 1H, ebthi, **3d**), 5.90 (d, ${}^{3}J$ = 2.9 Hz, 1H, CH-ebthi, **3d**), 7.01–7.13 (m, 3H, Ph, 3d), 7.35 (dd, J = 7.5, 1.5 Hz, 1H Ph, 3d) ppm. ¹³C NMR (75 MHz, $[D_6]$ benzene, 297 K): $\delta = 21.4$ (*Me*-Ph, 3d), 22.7, 22.8, 23.2, 23.5, 23.6, 23.72, 23.73, 23.8, 23.9, 24.5, 24.6, 25.5, 24.8, 25.5, 26.0, 29.4, 30.3, 32.0 (CH₂-ebthi, 3d + 4), 30.0 (Me-t-Bu, 3d), 39.5 (*CH*₂-Ph, 3d), 62.8 (*Cq-t*-Bu, 3d), 96.6, 98.4, 100.3, 100.6 (CH-ebthi, 4), 98.5, 105.0, 105.6, 106.1 (CH-ebthi, 3d), 113.3, 116.0, 126.0, 127.5, 129.6 (Cq-ebthi, 4), 117.0, 121.3, 122.7, 122.8, 123.7, 126.1 (Cq-ebthi, 3d), 131.1, 130.4, 127.48, 126.7 (CH-Ph, 3d), 136.71, 136.72 (Cq-Ph, 3d), 157.5 (C=N, 3d), 213.6 (C=N, 4), 230.0 (C=N, 3d) ppm. MS: m/z (CI): 760 $[M]^+$ (4) 569 $[M]^+$ (3d), 542 $[M^+-C\equiv N]^+$, 188 $[Me_{3d}-NC-CH_2 C_6H_4Me$]⁺.²⁸

Synthesis of complex 3e

To a solution of *rac*-(ebthi)Zr(η^2 -Me₃SiC₂SiMe₃) (1) (0.263 g, 0.50 mmol) in benzene (10 mL) *t*-BuNC (0.057 mL, 0.5 mmol) was added. Immediately a colour change from green to orange was observed. After stirring the reaction mixture for 2 h at room temperature further *t*-BuNC (0.115 mL, 1.0 mmol) and an excess (1 mL, 7.25 mmol) of mesitylene were added. After heating the reaction mixture for 12 days at 80 °C, all volatiles were removed in a vacuum and the remaining dark oil was

washed several times with 1 mL of n-hexane. The formed orange sticky solid was dissolved in diethyl ether, which was subsequently removed in a vacuum. After adding a mixture of ether/n-hexane (1:1), filtration and standing for one week at -78 °C, light orange crystals formed which were isolated and identified as a 2:1 mixture of 3e and 4 by NMR spectroscopy. ¹H NMR (300 MHz, $[D_6]$ benzene, 297 K): $\delta = 1.47$ (s, 9H, *t*-Bu, 3e), 2.22 (m, 6H, Me-Ph, 3e), 3.14-0.9 (m, 30H, CH₂-ebthi, 3e + 4), 3.96 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph, 3e), 4.20 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph, **3e**), 4.56 (d, J = 2.9 Hz, 0.5H, ebthi, 4), 4.61 (d, ${}^{3}J =$ 2.8 Hz, 1H, ebthi, 3e), 4.75 (d, J = 2.9 Hz, 0.5H, ebthi, 4), 4.99 $(d, {}^{3}J = 2.8 \text{ Hz}, 1\text{H}, \text{ebthi}, 3\text{e}), 5.31 (d, J = 2.9 \text{ Hz}, 0.5\text{H}, 4), 5.56$ $(d, J = 2.9 \text{ Hz}, 0.5 \text{H}, 4), 5.75 (d, {}^{3}J = 2.9 \text{ Hz}, 1 \text{H}, \text{ebthi}, 3 \text{e}), 5.99$ $(d, {}^{3}I = 2.9 \text{ Hz}, 1\text{H}, \text{CH-ebthi}, 3e), 6.80 (s, 1\text{H}, \text{Ph}, 3e), 6.92 (s, 1)$ 2H, H-Ph, 3e); (6.72 and 2.17 (m, traces of free mesitylene)) ppm. ¹³C NMR (100 MHz, $[D_6]$ benzene, 297 K): $\delta = 21.4$ (Me-Ph, 3e), 22.8, 22.91, 22.95, 23.21, 23.62, 23.72, 23.73, 24.7, 27.4, 27.5 (CH2-ebthi, 3e), 22.7, 23.20, 23.6, 23.7, 24.5, 24.8, 25.5, 26.0, 29.4, 30.3 (CH2-ebthi, 4), 30.2 (Me-t-Bu, 3e), 42.4 (CH2-Ph, 3e), 62.0 (Cq-t-Bu, 3e), 96.6, 98.4, 100.3, 100.6 (CHebthi, 4), 98.2, 104.8 105.7, 106.4 (CH-ebthi, 3e), 113.3, 116.0, 126.0, 127.5, 129.6 (Cq-ebthi, 4), 117.2, 120.8, 122.6, 123.8, 123.9, 126.7 (Cq-ebthi, 3e), 128.4, 128.8 (CH-Ph, 3e), 137.9, 138.3 (Cq-Ph, 3e), 157.5 (C=N, 3e), 213.6 (C=N, 4), 231.7 (C=N, 3e) ppm. MS: m/z (CI): 760 $[M]^+$ (4), 583 $[M]^+$ (3e), 556 $[M^+-C=N]^+$, 201 $[Me_{3d}-NC-CH_2-C_6H_4Me_2]^+$. The *n*-hexane fractions were combined and the volume was reduced in a vacuum. After one week at -78 °C a grey precipitate could be isolated. Recrystallisation from benzene afforded colourless crystals of pure 3e which were suitable for X-ray crystallography. 3e: ¹H NMR (300 MHz, $[D_6]$ benzene, 297 K): $\delta = 1.47$ (s, 9H, t-Bu), 2.22 (m, 6H, Me-Ph), 3.14-0.9 (m, 20H, CH2-ebthi), 3.96 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph), 4.20 (d, ${}^{2}J$ = 15.5 Hz, 1H, CH₂-Ph), 4.61 (d, ${}^{3}J$ = 2.8 Hz, 1H, ebthi), 4.99 (d, ${}^{3}J$ = 2.8 Hz, 1H, ebthi), 5.75 (d, ${}^{3}J$ = 2.9 Hz, 1H, ebthi), 5.99 (d, ${}^{3}J$ = 2.9 Hz, 1H, CH-ebthi), 6.80 (s, 1H, Ph), 6.92 (s, 2H, Ph), (6.72 and 2.17 (m, traces free mesitylene) ppm. 13C NMR (75 MHz, [D6] benzene, 297 K): δ = 21.4 (Me-Ph), 22.8, 22.91, 22.95, 23.2, 23.6, 23.72, 23.73, 24.7, 27.4, 27.5 (CH2-ebthi), 30.2 (Me-t-Bu), 42.4 (CH2-Ph), 62.0 (Cq-t-Bu), 98.2, 104.8 105.7, 106.4 (CH-ebthi), 117.2, 120.8, 122.6, 123.8, 123.9, 126.7 (Cq-ebthi), 128.4, 128.8 (CH-Ph), 137.9, 138.3 (Cq-Ph), 157.5 (C=N), 231.7 (C=N), (21.3, 127.4, 137.6 free mesitylene) ppm.

Conflicts of interest

There are no conflicts to declare.

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