Metallocenes

Reactions of 2-Substituted Pyridines with Titanocenes and Zirconocenes: Coupling versus Dearomatisation

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Dedicated to Prof. Dr. Heinrich Lang on the occasion of his 60th birthday

Abstract: Reactions of group 4 metallocene sources with 2substituted pyridines were investigated to evaluate their coordination type between innocent and reductive dearomatisation as well as to probe the possibility for couplings. A dependence on the cyclopentadienyl ligands (Cp, Cp*), the metals (Ti, Zr), and the substrates (2-phenyl-, 2-acetyl-, and 2-iminopyridine) was observed. While 2-phenylpyridine is barely reactive, 2-acetylpyridine reacts vigorously with the Cp-substituted complexes and selectively with their Cp* analogues. With 2-iminopyridine, in all cases selective reactions were observed. In the isolated $[Cp_2Ti]$, $[Cp_2Zr]$, and $[Cp_*_2Zr]$ compounds the substrate coordinates by its pyridyl ring and the unsaturated side-chain. Subsequently, the pyridine was dearomatised, which is most pronounced in the $[Cp_*_2Zr]$ compounds. Using $[Cp_*_2Ti]$ leads to the unexpected paramagnetic complexes $[Cp_*_2Ti]^{III}(N,O-acpy)]$ and $[Cp_*_2Ti]^{III}(N,N'-impy)]$. This highlights the non-innocent character of the pyridyl substrates.

Introduction

Group 4 metallocene compounds rose in interest because they are useful reagents or catalysts in synthetic chemistry.^[1] Small metallacycles are often discussed as key intermediates in these reactions, and they can be obtained from 2-substituted pyridines competitively by either C-C coupling of two pyridine derivatives (Scheme 1, left) or coordination of one substrate via its pyridyl ring and the unsaturated side-chain (Scheme 1, right). As an early example for the latter reaction, in 1967, $[Cp_2Ti(N,N'-bipy)]$ (A) $(Cp = \eta^5$ -cyclopentadienyl) was synthesised by using bipyridine (**bipy**, Scheme 1)^[2] and $[Cp_2Ti(CO)_2]$ as metallocene source. Since then, A was examined in-depth by CV,^[3] EPR,^[4] X-ray crystallography,^[5] and quantum mechanical calculations^[6] to solve the problem of defining the titanium oxidation state and the classification of bipy as non-innocent ligand.^[2a] While bipy is a very well established pyridyl-containing bidentate ligand in group 4 metallocene chemistry, only few other compounds with 2-(2-pyridyl)-imidazoline, 2-(2-pyridyl)-imidazole, or 2-(2-pyridyl)-benzimidazole^[7] were described, however without structural information.

Instead of the coordination of the substrate, we examined C–C couplings in the reaction of 2-(trimethylsilylethynyl)pyri-

Scheme 1. Coupling or dearomatisation arising from bidentate coordination: Conceivable reactions with 2-substituted pyridines.

dine (**tmsepy**) with [Cp₂Ti(η^2 -Me₃SiC₂SiMe₃)] (Scheme 1, left), resulting in two regioisomeric titanacyclopentadienes.^[8] A similar C–C coupling was observed upon addition of 2-cyanopyridine (**cypy**) to [Cp*₂M(η^2 -Me₃SiC₂SiMe₃)] (M=Ti, Zr; Cp*= η^5 -pentamethylcyclopentadienyl).^[9]

Furthermore, we investigated reactions of zirconocene-(η^2 -Me₃SiC₂SiMe₃) complexes with 2-vinylpyridine (**vipy**) and obtained the neutral complexes [Cp₂Zr(vipy)] (**B**), [(ebthi)Zr(vipy)] (**C**),^[10] and [(thi)₂Zr(vipy)] (**D**)^[11] (ebthi = 1,2-ethylene-1,1'bis(η^5 -tetrahydroindenyl); thi = η^5 -tetrahydroindenyl). It is interesting to note that all these compounds have dearomatised pyridine

Chem. Eur. J. 2016, 22, 3361 - 3369

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504411.



rings, and therefore they can be best described as 1-zircona-2azacyclopent-3-enes with a formally reduced **vipy**. Additionally, similar compounds were afforded by an insertion of 2-butyne into the Zr–C bond of cationic $[Cp_2Zr(THF)(\eta^2-N,C-pyridyl]$ $[BPh_4]$.^[12]

Noteworthy are some other details regarding such type of ligands. Compounds are often described as 2-phenylpyridine complexes, although they contain 2-(pyridin-2-yl)benzen-1-idene as ligand (the *ortho*-metallated anionic 2-phenylpyridine; Scheme 2, right) and not its neutral form (Scheme 2, left).^[13] A clear separation of both complexation types is necessary.



Scheme 2. Attempted alkyne replacement at 1-4 with 2-phenylpyridine.

Along with the above mentioned **bipy**, **tmsepy**, **cypy**, and **vipy**, we investigated the reactions of 2-phenylpyridine (**phpy**), 2-acetylpyridine (**acpy**), and 2-(*N*-*n*-butyl-methylimino)pyridine (**impy**) with [Cp₂Ti(η^2 -Me_3SiC_2SiMe_3)] (1), [Cp₂Zr(py)(η^2 -Me_3SiC_2SiMe_3)] (2), and [Cp*₂M(η^2 -Me_3SiC_2SiMe_3)] (M=Ti (3), Zr (4); Scheme 1). We wanted to know whether a coupling or a coordination accompanied by dearomatisation is preferred for these substrates. For similar unsaturated bonds, couplings were already described, but such a reaction might be impeded by the pyridyl ring. Furthermore, **acpy** and **impy** should be suitable to study the influence of the heteroatoms located in β -position of the pyridine substituents.

Results and Discussion

Reactions of 2-phenylpyridine (phpy)

Motivated by the recent work of Beckhaus et al.,^[14] who isolated an unusual azatitanacyclopent-4-ene complex with a dearomatised phenyl ring, we treated **phpy** with the metallocene generators **1–4**. Beckhaus et al. used **1** and *N*-(di-*p*-tolylmethylene)aniline (*p*-tolyl)₂C=N-Ph, which also bears a phenyl group in conjugation to a C=N bond as in **phpy**. The reactions of **phpy** with **1–4** were carried out in nonpolar solvents such as benzene and *n*-hexane with a stepwise increased amount of **phpy** (up to 20 equiv). However, no reactions were observed, not even at elevated temperatures (up to 100 °C) and long reaction times (up to two weeks; Scheme 2).

To estimate the thermodynamic probability, we calculated the formation free energy of the desired $[Cp_2M^{IV}(N,C-phpy)]$ complexes (Scheme 2, left). The reaction of **1** with **phpy** is slightly endergonic by 2.8 kcal mol⁻¹, while that of $[Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)]$ is exergonic by 4.1 kcal mol⁻¹. Such low free energies reveal the very low thermodynamic probability at high temperature. For comparison, the formation free energy for the reaction of 1 and $(p-tolyl)_2C=N-Ph$ is exergonic by 4.1 kcalmol⁻¹, and the reaction is thermodynamically accessible.

To check the influence of coordinated pyridine, we computed the free energy change starting from $[Cp_2Zr(\eta^2-Me_3SiC_2SiMe_3)]$ and pyridine to $[Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)]$. It was found that the pyridine coordination has a free energy change of 0.2 kcalmol⁻¹, revealing the low coordination ability of the pyridine ligand. This calculation underpins the pyridine exchange examined in solution.^[15] Therefore, the energetic influence of the additional pyridine coordination is negligible.

Furthermore, we computed the reactions of $[Cp*_2M(\eta^2-Me_3SiC_2SiMe_3)]$ with **phpy**. For **3** no stable complex could be located, while with **4** the reaction is endergonic by 4.8 kcal mol⁻¹ and not accessible thermodynamically.

To gain access to the desired products, we investigated two other reaction paths. First, phpy was used as reactant and solvent in the reaction with 1-4. Second, a reduction of the corresponding metallocene dichlorides (with Mg, nBuLi, or Li as reducing agent) in the presence of phpy was tried. Unfortunately, both attempts did not result in the isolation of phpy complexes. In the second case, however, NMR experiments gave hints on a dearomatised phpy species (see the Supporting Information for further details). It is interesting to note that no ortho-metallation took place (Scheme 2), despite the fact that it is a frequent side reaction in transition-metal chemistry. This type of coordination is well examined in the synthesis of the salt [(ebi)Zr{ η^2 -(C,N)-2-(pyridin-2-yl)benzen-1-ide}][B(C₆F₅)₄] by the reaction of [(ebi)Zr{ η^2 -(C,N)-(6-phenyl-2-pyridyl)}] $[B(C_6F_5)_4]$ (ebi = 1,2-ethylene-bis-indenyl) with molecular hydrogen.^[16] However, no dearomatisation of the substrate is observed, since the *ortho*-metallation affords a σ -M–C bond.

Reactions of 2-acetylpyridine (acpy)

In contrast to the barely reactive **phpy**, we expected a much higher reactivity of **acpy** in the reactions with metallocene generators **1–4**, owing to the bidentate character of this substrate and the great oxophilicity of titanium and zirconium. The calculated formation free energy of the expected $[Cp'_2M^{\mathbb{N}}(N,O\text{-}acpy)]$ in singlet state for **1–4** is exergonic by 35.5, 43.0, 40.8, and 42.6 kcal mol⁻¹, respectively, indicating the thermodynamic accessibility of these exchange reactions.^[17]

Indeed, while dropping pure **acpy** to *n*-hexane solutions of the Cp substituted complexes **1** and **2** at ambient temperature (or even at -78 °C) the spontaneous precipitation of a brownish solid was observed. This residue is a mixture of several compounds, insoluble in nonpolar solvents and sparsely soluble in THF. Unfortunately, all attempts to isolate a defined product failed.

In contrast to this behaviour, the reactions of the Cp* complexes are more selective. Upon warming a mixture of **3** and **acpy**, a colour change from pale yellow to dark green was observed. Subsequently, the green solid was identified as the Ti^{III} complex **5** (Scheme 3), which was isolated in moderate yield (47%). In the case of the zirconium complex [Cp*₂Zr(η^2 -Me₃SiC₂SiMe₃)], the reaction with **acpy** already occurred at



Scheme 3. Synthesis of 5 and 6 by alkyne replacement with 2-acetylpyridine.

20 °C, indicated by the colour change from cyan to dark violet (Scheme 3). This afforded the Zr^{IV} compound **6**, a 1-zircona-2-aza-5-oxa-cyclopent-3-ene, again in moderate yield (43 %).

For a better understanding of the nature of complex **5**, we carried out EPR measurements at 27 °C in toluene solution, which clearly confirm the formation of a single d¹ titanium(III) complex with a *g* value of 1.9817 (Figure 1).^[18] In contrast to



Figure 1. a), c) EPR spectra: a) **5** and c) **9** at 27 °C in toluene and b), d) simulated spectra: b) **5** (g=1.9816; A_{TI}=8.5 G, A_N=1.54 G, Δ B=1.8 G) and d) **9** (g=1.9824; A_{TI}=8.7 G, A_{N1}=1.8 G, A_{N2}=2.4 G, Δ B=1.8 G).

this, the experimental data of **6** reveal unambiguously the formation of the 1-zircona(IV)-2-aza-5-oxa-cyclopent-3-ene, with no hints for an analogous paramagnetic zirconium(III) species. The complex formally consists of d⁰ zirconocene(IV) and the dianionic [acpy]^{2–} ligand (see the Structure Discussion below).

For compound **5**, our computations show a higher stability of the triplet state (by $\Delta G(S-T) = 1.9 \text{ kcal mol}^{-1}$), which indicates an equilibrium between singlet and triplet states (4%: 96%). In case of compound **6**, the singlet state is more stable by 6.0 kcal mol⁻¹ and therefore the sole isomer.

The compounds **5** and **6** have a remarkable thermal stability and decompose at temperatures above 200 °C. They can be stored at ambient temperature under argon atmosphere for a period of a month. Noteworthy is that both compounds decompose rapidly in the presence of oxygen, whereas it takes longer in the presence of water (about three days).

Reactions of 2-(N-n-butyl-methylimino)pyridine (impy)

In regard of the results with **acpy**, we expected a high reactivity of **impy**. The calculated formation free energy of $[Cp'_2M^{\mathbb{N}}(N,N'\text{-}impy)]$ in singlet states from **1–4** are exergonic by 31.5, 38.0, 24.3, and 28.7 kcal mol⁻¹, respectively, indicating the thermodynamic accessibility of these exchange reactions.

The reactions of **impy** with the metallocene generators **1–4** were performed in *n*-hexane or toluene. Depending on the Cp' ligand and the metals, we observed different reactivities. Interestingly, the Cp derivatives **1** and **2** formed the metallocene(IV) complexes $[Cp_2M^{IV}(N,N'-impy)]$ (**7**: M = Ti; **8**: M = Zr; Scheme 4)



Scheme 4. Alkyne replacement with 2-(N-n-butyl-methylimino)pyridine.

in a clean ligand exchange reaction without any hints of a metallocene(III) species.

For both compounds computations showed, that the singlet state is more stable by 1.1 kcal mol⁻¹ (Ti) and 8.5 kcal mol⁻¹ (Zr). In case of the titanium complex this reveals an equilibrium between the singlet and the triplet state (87 %:13%).

Both complexes can be synthesised in good yields (**7**: 72%; **8**: 71%) and show long-term stability under an argon atmosphere at ambient temperature. With decomposition temperatures of 106 °C (**7**) and 125 °C (**8**), they are less thermally stable than the above mentioned **acpy** complexes **5** and **6**. Furthermore, they are extremely sensitive to air and moisture. Noteworthy are some details of the NMR spectra of **7** and **8**. Owing to the intramolecular motion in **7**, low-temperature (-75 °C) measurements in [D₈]THF were required for the clear detection of all signals in the ¹H and the ¹³C NMR spectra (Figure 2).

It is interesting to note that the resonances of the β -CH₃ substituent as well as of the nitrogen-bonded *N*-CH₂ group are more prone to this movement than the Cp substituents and the terminal fragments of the *n*-butyl group. Opposing to this, the ¹H and ¹³C NMR spectra of **8** at 25 °C display two different resonances for the Cp substituents. This observation supports the concept of an oscillating **impy** ligand between the two Cp substituents in **7**, which is already known for 1,4-diazabuta-diene complexes of titanium.^[19] In contrast, the larger zirconium atom in **8** allows a fixation of the **impy** by a stronger metal–ligand interaction. For both compounds, this results in a bent structure in the solid state (see below).



Figure 2. Temperature-dependent 1H NMR spectra of 7 between 25 °C and -75 °C. Asterisks indicate the solvent [D_g]THF.

Furthermore, we were interested in the influence of the Cp* ligand on the reactions with **impy**. In case of the titanocene compound **3**, this again resulted in a paramagnetic Ti^{III} complex **9** in moderate yields (49%, Scheme 5). The triplet state is thermodynamically more dominant by 2.3 kcal mol⁻¹, and the ratio between the singlet and triplet state is 2% to 98%.



Scheme 5. Alkyne replacement with 2-(N-n-butyl-methylimino)pyridine.

However, the EPR spectrum of **9** at 27 °C (g = 1.9824) in toluene solution revealed unambiguously a single titanium(III) centre coordinated by both nitrogen atoms of **impy** (Figure 1).^[4a] The strong resonances in the spectra of **5** and **9** show a series of weak satellite resonances, which result from the hyperfine interactions with the ⁴⁷Ti (l=5/2) and ⁴⁹Ti (l=7/2) nuclei (Figure 1; $A_{TI}=8.5$ G in **5**; $A_{TI}=8.7$ G in **9**). Furthermore, these signals feature a super hyperfine splitting (shfs) by the coordinated ¹⁴N nuclei. However, the different M–N bonds in **9** resulted in two shfs values ($A_N=1.5$ G in **5**; $A_{N1}=1.8$ G, $A_{N2}=2.4$ G in **9**). The EPR spectra at -173 °C in toluene glass show for both compounds a rhombic titanium(III) centre, which is typical for Cp* substituted titanium (see the Supporting Information).

The observed EPR spectra of **5** and **9** at 27 °C are in good agreement with the determined data for the bis(cyclopentadienyl)titanium(III)-*N*,*N'*-bipyridyl hexafluorophosphate $[Cp_2Ti(N,N'-bipy)][PF_6]$ reported by McPherson, Stucky, et al.^[4a] It is necessary to note that no hints for a triplet excited state were found in our EPR measurements, as might be expected for neutral titanocene(III) complexes with a formal radical

anionic 2-substituted pyridine as ligand. This observation is in strong contrast to the previous work on the $[Cp'_2Ti(N,N'-bipy)]$ complexes and leads to the question of the formation and the nature of the observed neutral titanocene(III) complexes **5** and **9**.^[4-6]

Therefore, we carried out in situ NMR experiments and observed the direct formation of the complexes 5 and 9 indicated by a broad signal, the decrease of the starting materials and a rising sharp signal for Me₃SiC₂SiMe₃ (see the Supporting Information). In both reactions, the 2-substituted pyridine was not quantitatively converted, giving an explanation for the yields of 5 and 9 (< 50%). But, the NMR and MS spectra of the reaction solutions show no hints for other quantitatively formed side products as they can be imagined by Michael- or McMurry-like reductive coupling reactions^[20] or a comproportionation reaction towards 5 or 9. An analogous mechanism was recently discussed in the formation of a pyridonate-supported titanium(III) complex by Schafer et al.^[21] Furthermore, the in situ EPR experiments gave no hints for a second single electron containing species, which might be hidden in the NMR experiments. Unfortunately, these results yield no satisfactorily explanation for the formation of compounds 5 and 9 and their unusual spectroscopic data.

In contrast to $[Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)]$, the Cp*-substituted zirconium complex **4** did not react with **impy**, not even at elevated temperatures of 100 °C and several weeks of reaction time. However, the formation of the Cp*-analogous compound of **8** is exergonic ($\Delta G_{298} = -28.7 \text{ kcal mol}^{-1}$), indicating the thermodynamic accessibility of this complex. Thus, we investigated the reduction of $[Cp*_2ZrCl_2]$ with Li directly in the presence of **impy**. We observed a colour change in toluene from pale yellow to dark violet at ambient temperature within 12 h reaction time. The following separation of lithium chloride and workup gave the desired $[Cp*_2Zr^{IV}(N,N'-\text{impy})]$ (**10**) (Scheme 6) in good yield (74%). For compound **10**, the singlet state is more stable than the triplet state by 4.2 kcal mol⁻¹.

Owing to the steric demand of the Cp* ligand, **9** and **10** are more stable to air and moisture than **7** and **8**, but decompose in the same temperature range (**9**: $139 \degree$ C; **10**: $119 \degree$ C). They can be stored under argon atmosphere for several months.



Scheme 6. Reductive synthesis of 10.

Structure discussion

Especially of interest are the structural and electronic changes in the 2-substituted pyridines, caused by their coordination to group 4 metallocenes. The substrates that we used in this work are well-examined as bidentate ligands in classical coord-

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ination chemistry, for example [M](phy),^[22] [M](acpy),^[23] and [M](impy).^[24] In most of these complexes only the coordination sphere of the central metal atom was considered, while the bonding situation of the 2-substituted pyridine was neglected. However, DFT studies clarified the redox non-innocent character of **bipy** and especially the specific role of the three different oxidation levels of **bipy** ligands (neutral bipy⁰, π -radical anion [bipy¹]⁻, diamagnetic dianion [bipy]²⁻; Scheme 7).^[6]



Scheme 7. Oxidation levels of bipy.

A useful tool to distinguish the oxidation states of coordinated **bipy** is the bond distance of the *ipso*-carbon atoms linking the pyridines (C–C'). For example, in $[Cp_2Zr(N,N'-bipy)]^{[25]}$ (**E**) and $[Cp*_2Hf(4,4'-di-$ *tert*-butylbipyridyl)],^[26] both of which areformal [bipy]^{2–} complexes, these bonds are significantly short $ened as a consequence of strong <math>\pi$ -donation of the metal d² electrons into the π^* orbitals of **bipy**. This π -back-donation capability is known to be increased with a rising methylation degree at cyclopentadienyl rings owing to the increasing electron density at the metal centre.^[27]

With these results in mind, we examined the structural data of the herein described compounds by X-ray crystallography. The molecular structures of compounds **6**, **7**, **8**, and **9** are depicted in Figure 4 and 5. In all four complexes, the metal centre is surrounded by two Cp' ligands and the 2-substituted pyridine. The latter is coordinated by the pyridine nitrogen atom and the heteroatom (X=N or O) in the β -position (Figure 3). The five-membered metallacycles formed by N1, C5,

C6, X, and M show an envelope structure, which is reflected by β angles between 130.78(9)° in **8** and 156.63(9)° in **9** combined with small torsion angles N1-C5-C6-X between -2.0(2)° in **7** and 3.4(2)° in **9** (Table 1). The larger β angle in **9** (156.53(9)°) compared to 141.25(6)° in **7** shows a flattening of this envelope owing to the influence of the permethylated cy-



Figure 3. General assignment of the discussed complexes.



Figure 4. Molecular structure of **6** in the solid state. Hydrogen atoms are omitted for clarity; ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles $[\degree]$ are summarised in Table 1.

clopentadienyl ligands. This is in good agreement with the data for the analogous **bipy** complexes $[Cp_2Ti(N,N'-bipy)]$ ($\beta = 157^{\circ}$) and $[Cp*_2Ti(N,N'-bipy)]$ ($\beta = 180^{\circ}$).^[5] Furthermore, the larger β angle in **7** (141.25(6)°) compared to 130.78(9)° in **8** gives a hint for a larger ligand flipping energy barrier in **8**. This supports the oscillating **impy** ligand observed in solution in **7**, and the two NMR independent Cp substituents in **8**. The same bending behaviour was described for the complexes $[Cp_2Ti(N,N'-bipy)]$ (**A**) with a large β angle and $[Cp_2Zr(N,N'-bipy)]$ (**E**) with a smaller angle (Table 1).

To estimate the influence of the coordination on the structure of 2-substituted pyridines, we compared the bond lengths of free **acpy** to those in **6** (see Table 1 and the Supporting In-

Table 1. Selected bond lengths [Å] and angles [°], with BP86/TZVP computed values given in square brackets.							
Compound	M–N1	M—X	N1–C5	C5–C6	β	N1-C5-C6-X	
$\begin{array}{l} {\bf A} \ [Cp_2Ti(N,N'-bipy)]^{[a]} \\ {\bf B} \ [Cp_2Zr(N,N'-vipy)]^{[b]} \\ {\bf E} \ [Cp_2Zr(N,N'-bipy)]^{[c]} \end{array}$	2.146	2.117	1.374	1.422	156.7	-2.7	
	2.272(4)	2.272(5)	1.406(6)	1.386(7)	121.5	-10.5	
	2.164	2.160	1.395	1.397	137.1	2.1	
асру	-	-	1.3402(13)	1.4986(15)	-	-	
6 [Cp* ₂ Zr(<i>N</i> , <i>O</i> -acpy)]	2.169(2)	2.039(2)	1.421(3)	1.363(4)	152.7(1)	1.8(3)	
	[2.239]	[2.100]	[1.428]	[1.397]	[152.1]	[-1.5]	
7 [Cp ₂ Ti(<i>N</i> , <i>N</i> ′-impy)]	2.0869(10)	2.0384(10)	1.3918(14)	1.406(2)	141.25(6)	-2.0(2)	
	[2.093]	[2.043]	[1.402]	[1.421]	[143.8]	[2.7]	
8 [Cp ₂ Zr(<i>N</i> , <i>N</i> ′-impy)]	2.144(2)	2.086(2)	1.411(2)	1.394(3)	130.78(9)	0.2(3)	
	[2.207]	[2.141]	[1.411]	[1.419]	[136.0]	[2.4]	
9 [Cp* ₂ Ti(<i>N</i> , <i>N</i> ′-impy)]	2.1333(12)	2.1287(12)	1.397(2)	1.409(2)	156.63(9)	3.4(2)	
	[2.174]	[2.190]	[1.400]	[1.424]	[174.4]	[4.9]	
[a] Data taken from Ref. [5]. [b] Data taken from Ref. [10]. [c] Data taken from Ref. [25].							

Chem. Eur. J. **2016**, 22, 3361 – 3369

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Figure 5. Molecular structure of 7 (left), 8 (middle), and 9 (right) in the solid state. Hydrogen atoms are omitted for clarity; ellipsoids are set to 30% probability. Selected bond lengths [Å] and angles [°] are summarised in Table 1.

formation). The C5–C6 distance in **6** (1.363(4) Å) is impressively shortened by about 0.136 Å. The N1–C5 bond and the C6–O1 bond are elongated by 0.08 Å and 0.146 Å, respectively. Furthermore, in compound **6** C1–C2 (1.359(3) Å) and C3–C4 (1.341(5) Å) are localised double bonds, while in **acpy** the C–C distances of the pyridyl unit are well balanced and range between 1.373(2) Å (C2–C3) and 1.3881(14) Å (C4–C5). On the basis of these results, we suggest a dearomatised pyridyl unit [acpy]^{2–} and a [Cp*₂Zr^{IV}] fragment in **6**. To the best of our knowledge, **6** exhibits the shortest known C5–C6 distance for **acpy** complexes.

The comparison of the molecular structures of $[Cp_2Ti^{IV}(N,N'-impy)]$ (7), $[Cp_2Zr^{IV}(N,N'-impy)]$ (8), and $[Cp^*_2Ti^{III}(N,N'-impy)]$ (9) reveal only small differences concerning the **impy** ligand. The C5-C6 bonds range between 1.409(2) Å in 9 and 1.394(3) Å in 8, thus they can be described as elongated $C_{sp^2}-C_{sp^2}$ double bonds (cf. 1.34 Å). Furthermore, in all three compounds the C1–C2 and C3–C4 bonds are significantly shorter than the C2–C3 and C4–C5 bonds, indicating the same localised double bonds as observed in 6 (see the Supporting Information). Merely the N2–C6 bond is larger in the zirconium complex 8 than in the titanium compounds (cf. N2–C6: 1.378(3) in 8, 1.3514(2) in 7, 1.353(2) in 9). In agreement with the collected data, 7, 8, and 9 can be described as diazametallacyclopent-3-enes^[19,28] formed by the dearomatisation of **impy**.

Discussion of ¹H and ¹³C NMR data

Along with the discussed structural changes, we had a closer look on the ¹H and ¹³C NMR shifts of the 2-subsituted pyridines caused by the coordination. As a consequence of the strong π donation of metallocene d² electrons into the π^* orbitals of the pyridine substrates, a strong upfield shift of their resonances is observed. This illustrates their electron acceptance.^[29] A good indicator for the dearomatisation of the pyridyl units are the shifts of the C2 and the H(C2) signal.

These resonances were unambiguously determined for all described diamagnetic complexes by ¹H,¹³C HSQC and ¹H,¹H NOESY NMR experiments (Table 2). In the ¹³C NMR spectrum of **6**, the resonance of C2 is shifted by -27.0 ppm compared to free **acpy** and for H(C2) by -1.63 ppm. This is in good agreement with the C2 high-field shifts of about -18 ppm observed for [Cp₂Zr(vipy)] (**B**) and [(ebthi)Zr(vipy)] (**C**).^[10] In contrast to

Table 2. Selected NMR resonances [ppm] and shift differences [ppm] in $[D_6] benzene at 25\,^\circ\text{C}.$

Compound	¹³ C(2)	¹ H(C2)	$\Delta\delta$ (13C)	$\Delta\delta$ (¹ H)		
acpy impy	126.7 123.9	6.73 6.69	-			
6 $[Cp*_2Zr(N,O-acpy)]$ $[Cp*lr(Cl)(N,O-acpy)][PF_6]^{[a]}$	99.8 133.7	5.10 8.05	-27.0 +7.0	-1.63 +1.32		
7 [Cp ₂ Ti(<i>N</i> , <i>N</i> '-impy)] ^(b) 8 [Cp ₂ Zr(<i>N</i> , <i>N</i> '-impy)] 10 [Cp* ₂ Zr(<i>N</i> , <i>N</i> '-impy)]	103.9 101.5 101.3	5.25 5.44 5.47	-20.0 -22.3 -22.6	-1.44 -1.27 -1.22		
[a] Data taken from the previously reported measurement in CD_2Cl_2 . ^[22b] [b] Data taken from low temperature measurement in [D ₃]THF at -75 °C.						

these upfield shifts, the resonances of the cationic [Cp*Ir(Cl)-(*N*,*O*-acpy)][PF₆]^[23b] complex were shifted downfield (Table 2). In agreement with these observations and the shortened C5– C6 bond in **6**, these data support the concept of a [Cp*₂Zr^{IV}] unit with a formal [acpy]^{2–} ligand. Furthermore the ¹H and ¹³C NMR spectra of **7**, **8**, and **10** show an analogous upfield shift compared to free **impy**. The lower upfield shifts compared to **6** indicate a weaker but still significant dearomatisation in these compounds.

These observations, in combination with the isolation of the paramagnetic titanocene(III) species **5** and **9**, show that the 2-substituted pyridines **acpy** and **impy** are non-innocent ligands in group 4 metallocene complexes.

Conclusions

The reactions of the metallocene generators 1-4 with 2-substituted pyridines depend on the Cp' ligands (Cp, Cp*), the metal centres (Ti, Zr), and also the substrates (phpy, acpy, impy). During our investigations, all efforts to activate phpy using group 4 metallocenes were unsuccessful whereas acpy reacts vigorously with the Cp substituted complexes to a mixture of non-defined products. The reaction of the Cp* metallocene compound $[Cp_{2}^{*}Ti(\eta^{2}-Me_{3}SiC_{2}SiMe_{3})]$ (3) with acpy results in unexpected paramagnetic the titanium(III) complex $[Cp_{2}^{*}Ti^{III}(N,O-acpy)]$ (5). With $[Cp_{2}^{*}Zr(\eta^{2}-Me_{3}SiC_{2}SiMe_{3})]$ (4) the zirconium(IV) compound $[Cp_{2}T^{V}(N,O-acpy)]$ (6) was isolated. The latter shows a remarkably disturbed aromaticity and



a formal [acpy]²⁻ unit. This highlights the strong electron donation capability of Cp* zirconocene compared to the Cp derivative and the titanocenes. The reactions of **impy** and [Cp₂Ti(η^2 -Me_3SiC_2SiMe_3)] (1) as well as [Cp₂Zr(py)(η^2 -Me_3SiC_2SiMe_3)] (2) lead to the metallocene complexes [Cp₂M^{IV}(*N*,*N'*-impy)] (*M* = Ti in 7, *M* = Zr in 8). As in case of **acpy**, the reaction of **impy** and [Cp*₂Ti(η^2 -Me_3SiC_2SiMe_3)] (3) leads to the paramagnetic Ti^{III} complex [Cp*₂Ti^{III}(*N*,*N'*-impy)] (9). While **impy** is able to react with 2 to [Cp₂Zr^{IV}(*N*,*N'*-impy)] (8), an analogous formation of [Cp*₂Zr^{IV}(*N*,*N'*-impy)] (10) using 4 was not observed. However, 10 is accessible by reduction of [Cp*₂ZrCl₂] with lithium in the presence of **impy**.

The higher stability of the singlet states of the zirconocene complexes explains why they are the only detectable isomers (compare $\Delta G(S-T) = 6.0$ (6), 8.5 (8), and 8.5 kcal mol⁻¹ (10)). For the titanium compounds equilibria between the triplet and singlet states (compare $\Delta G(S-T) = -1.9$ (5), 1.1 (7), and -2.3 kcal mol⁻¹ (9)) were calculated, which makes the detection and analysis of the products difficult. Nevertheless, this work shows the non-innocent character of the 2-substituted pyridines and reveals the rising reactivity **phpy** < **impy** < **acpy** influenced by the heteroatoms located in β -position of the pyridine.

Experimental Section

All operations were carried out under argon with standard Schlenk techniques or in a glovebox. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. n-Butylamine (99.5%, Aldrich), 2-phenylpyridine (99%, Aldrich), and 2-acetylpyridine (99%, Aldrich) were freshly distilled prior to use. 2-(N-n-butyl-methylimino)pyridine,^[30] $[Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)] (Cp = \eta^5-cyclopentadienyl),^{[31]} [Cp_2Zr(py)(\eta^2-\eta^2-Me_3SiC_2SiMe_3)] (Cp = \eta^5-cyclopentadienyl),^{[31]} [Cp_2Zr(py)(\eta^2-Me_3SiC_2SiMe_3)] (Cp = \eta^5-cyclopentadienyl),^{[31]} (Cp = \eta^5-cyclopen$ $Me_{3}SiC_{2}SiMe_{3})],^{[32]} [Cp*_{2}Zr(\eta^{2}-Me_{3}SiC_{2}SiMe_{3})] (Cp*=\eta^{5}-pentamethyl$ cyclopentadienyl),^[33] and $[Cp_2^*Ti(\eta^2-Me_3SiC_2SiMe_3)]^{[34]}$ were prepared according to previously reported procedures. The following instruments were used: NMR: Bruker AV300 and AV400. ¹H and ¹³C chemical shifts were referenced to the solvent signal: [D₆]benzene $(\delta_{\rm H} = 7.16, \ \delta_{\rm C} = 128.0)$,^[35] [D₈]THF $(\delta_{\rm H} = 3.58, \ \delta_{\rm C} = 67.57)$ ^[36] For assignment of the NMR resonances we used a combination of twodimensional measurements. For ¹H-¹³C HSQC, ¹H-¹³C HMBC, and ¹H-¹H NOESY assignment, see the Supporting Information, Figure S1. IR: Bruker Alpha FT-IR-MS: Finnigan MAT 95-XP (Thermo-Electron). Elemental analysis: Leco Tru Spec elemental analyzer. Melting points: Mettler-Toledo MP 70. Melting points are uncorrected and were measured in sealed capillaries. In our calculations, we have used the real-size molecules 1-10 as well as the 2-substituted pyridines at the BP86 level with the TZVP basis set for non-metal elements and the effective core potential LANL2DZ basis set for Zr and Ti.^[37]

Crystals suitable for X-ray crystal structure analysis were obtained by cooling saturated warm *n*-hexane solutions (60 °C) of **6**, **7**, and **8** to ambient temperature; in the case of **9**, *n*-heptane was used. Crystals of **acpy** suitable for X-ray analysis were achieved by slow cooling neat drops of **acpy** under nitrogen atmosphere to -20 °C. Diffraction data for **acpy**, **6**, **7**, and **8** were collected on a Bruker Kappa APEX-II CCD diffractometer using Mo K α radiation. Diffraction data of **9** were collected on the same diffractometer using Cu K α radiation. The structures were solved by direct methods^[38] and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.^[39] Diamond was used for graphical representations.^[40]

Crystal data for **6**: $C_{27}H_{37}NOZr$, $M = 482.79 \text{ gmol}^{-1}$, triclinic, space group $P\bar{1}$, a = 8.6274(2), b = 9.2945(3), c = 15.9863(5) Å, a = 92.0441(6), $\beta = 97.9042(6)$, $\gamma = 109.7994(6)^{\circ}$, V = 1190.00(6) Å³, T = 150(2) K, Z = 2, 46596 reflections measured, 5756 independent reflections ($R_{int} = 0.0185$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0361$, $wR_2 = 0.0901$, final R values (all data): $R_1 = 0.0373$, $wR_2 = 0.0912$, 238 parameters.

Crystal data for **7**: $C_{21}H_{26}N_2$ Ti, $M=354.34 \text{ gmol}^{-1}$, monoclinic, space group $P2_1/c$, a=16.5370(9), b=8.4538(5), c=13.4579(7) Å, $\beta=99.4517(16)^\circ$, V=1855.88(18) Å³, T=150(2) K, Z=4, 35101 reflections measured, 4467 independent reflections ($R_{int}=0.0225$), final R values ($I > 2\sigma(I)$): $R_1=0.0289$, $wR_2=0.0777$, final R values (all data): $R_1=0.0324$, $wR_2=0.0810$, 219 parameters.

Crystal data for **8**: $C_{21}H_{26}N_2Zr$, $M=397.66 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, a=16.4175(11), b=8.6081(6), c=13.4787(9) Å, $\beta=100.0961(17)^\circ$, V=1875.4(2) Å³, T=150(2) K, Z=4, 21661 reflections measured, 4304 independent reflections ($R_{int}=0.0281$), final R values ($I>2\sigma(I)$): $R_1=0.0265$, $wR_2=0.0695$, final R values (all data): $R_1=0.0330$, $wR_2=0.0824$, 219 parameters.

Crystal data for **9**: $C_{31}H_{46}N_2$ Ti, $M = 494.60 \text{ gmol}^{-1}$, monoclinic, space group $P2_1/n$, a = 9.1871(2), b = 18.3010(4), c = 16.2386(3) Å, $\beta = 104.2994(8)^\circ$, V = 2645.66(10) Å³, T = 150(2) K, Z = 4, 20455 reflections measured, 4671 independent reflections ($R_{int} = 0.0330$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0349$, $wR_2 = 0.0969$, final R values (all data): $R_1 = 0.0366$, $wR_2 = 0.0988$, 319 parameters.

Crystal data for **acpy**: C₇H₇NO, $M = 121.14 \text{ gmol}^{-1}$, orthorhombic, space group *Pbca*, a = 12.1009(6), b = 7.7202(4), c = 13.7085(7) Å, V = 1280.67(11) Å³, T = 150(2) K, Z = 8, 11 204 reflections measured, 1540 independent reflections ($R_{int} = 0.0215$), final *R* values ($I > 2\sigma(I)$): $R_1 = 0.0375$, $wR_2 = 0.0966$, final *R* values (all data): $R_1 = 0.0448$, $wR_2 = 0.1041$, 83 parameters.

CCDC 1433272 (6), 1433273 (7), 1433274 (8), 1433275 (9), and 1433276 (acpy) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Preparation of 5: 2-Acetylpyridine (**acpy**) (0.121 g, 1.0 mmol) was added dropwise to a stirred solution of $[Cp*_2Ti(\eta^2-Me_3SiC_2SiMe_3)]$ (**3**) (0.379 g, 0.8 mmol) in *n*-hexane (10 mL) at 0 °C. The resulting mixture was slowly warmed to ambient temperature and heated to 55 °C for 2 d. The dark-green solution was concentrated to an approximate volume of 2 mL and filtered. The solution was stored at -78 °C over a period of 12 h resulting in the deposition of a dark-green solid. Removal of supernatant by syringe and drying in vacuo at ambient temperature for 3 h yielded **5** (0.165 g, 47%) as a green solid. It should be mentioned that **5** may be contaminated with **3**, which can be removed by recrystallization.

M.p.: 212 °C (dec. under Ar). ¹H NMR (25 °C, [D₆]benzene, 300.20 MHz): $\delta = 5-9$ ppm (broad). EPR (27 °C, toluene): g = 1.9816, A₁₁=8.5 G, A_N=1.54 G, $\Delta B = 1.8$ G; (-173 °C, toluene glass) $g_1 = 2.0018$, $g_2 = 1.9814$, $g_3 = 1.9645$, $\Delta B_1 = 1.8$ G, $\Delta B_2 = 4.3$ G, $\Delta B_3 = 4.6$ G. IR (Nujol, 32 scans): $\tilde{\nu} = 1628$ (w), 1600 (m), 1579 (s), 1558 (m), 1493 (m), 1322 (s), 1303 (m), 1279 (m), 1245 (m), 1158 (m), 1147 (m), 1021 (m), 996 (s), 802 (m), 756 (s), 743 (s), 649 cm⁻¹ (m). MS-Cl⁺ (isobutane): [M⁺] 439 (100), [Cp*₂Ti⁺] 318 (20), [Cp*⁺] 137 (97), [acpy+H⁺] 122 (100). M(C₂₇H₃₆NOTi) = 438,46 g mol⁻¹. Elemental analysis (%) calcd: C 73.96, H 8.28, N 3.19; found: C 73.81, H 8.32, N 3.26.

Preparation of 6: 2-Acetylpyridine (**acpy**) (0.060 g, 0.5 mmol) was added dropwise to a stirred solution of $[Cp*_2Zr(\eta^2-Me_3SiC_2SiMe_3)]$

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(4) (0.258 g, 0.5 mmol) in *n*-hexane (10 mL) at -78 °C. The mixture was slowly warmed to ambient temperature and stirred for 18 h. Subsequently, the dark-violet solution was concentrated to an approximate volume of 2 mL and filtered. The solution was stored at -78 °C over a period of 12 h resulting in the deposition of a dark-violet solid. Removal of supernatant by syringe and drying in vacuo at ambient temperature for 1 h yielded **6** (0.103 g, 43%) as a violet solid.

M.p.: 219 °C (dec. under Ar). ¹H NMR (25 °C, [D₆]benzene, 400.13 MHz): δ = 6.52 (m, 1 H, *CH*), 6.14 (m, 1 H, *CH*), 6.00 (m, 1 H, *CH*), 5.10 (m, 1 H, *CH*), 2.10 (s, 3 H, *CH*₃), 1.81 ppm (s, 30 H, Cp^{*}). ¹³C NMR (25 °C, [D₆]benzene, 100.62 MHz): δ = 144.1 (CH), 133.1 (*C*_{quart}), 132.2 (*C*_{quart}), 124.3 (CH), 119.5 (CH), 119.0 (Cp*_{quart}), 99.8 (CH), 19.7 (CH₃), 11.2 ppm (Cp*-CH₃). IR ATR (32 scans): $\tilde{\nu}$ = 2965 (m), 2900 (m), 2853 (m), 1596 (s), 1532 (w), 1494 (w), 1436 (s), 1377 (s), 1334 (m), 1277 (s), 920 (m), 707 (s), 650 cm⁻¹ (m). MS-Cl⁺ (isobutane): [*M*⁺] 481 (1), [Cp*⁺] 137 (100), [acpy+H⁺] 122 (47). M(C₂₇H₃₇NOZr) = 481.19 g mol⁻¹. Elemental analysis (%) calcd: C 67.17, H 7.72, N 2.91; found: C 66.95, H 7.75, N 2.99.

Preparation of 7: 2-(*N*-*n*-Butyl-methylimino)pyridine (**impy**) (0.176 g, 1.0 mmol) was added dropwise to a stirred solution of $[Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)]$ (1) (0.278 g, 0.8 mmol) in *n*-hexane (10 mL) at ambient temperature. The reaction mixture gradually changed its colour from pale brownish to dark-red within 24 h. The resulting solution was concentrated to an approximate volume of 4 mL, filtered, and slowly cooled to -78 °C. Removal of supernatant by syringe, washing with cooled *n*-hexane (-78 °C, 3×3 mL) and drying in vacuo at ambient temperature for 3 h yielded **7** (0.205 g, 72%) as dark-red solid.

M.p.: 106 °C (dec. under Ar).¹H NMR (-75 °C, [D₈]tetrahydrofurane, 400.13 MHz): $\delta = 7.57$ (m, 1H, CH), 6.95 (m, 1H, CH), 6.43 (m, 1H, CH), 5.38 (s, 10H, Cp), 5.25 (t, 1H, CH), 3.41 (m, 2H, CH₂), 2.34 (s, 3H, CH₃), 1.32 (m, 4H, 2× CH₂), 0.94 ppm (t, 3H, CH₃). ¹³C NMR $(-75 \degree C, [D_8]$ tetrahydrofurane, 100.62 MHz): $\delta = 150.5$ (CH), 140.4 (C_{quart.}), 131.8 (C_{quart.}), 128.2 (CH), 120.2 (CH), 105.5 (Cp), 103.9 (CH), 55.4 (CH₂), 37.8 (CH₂), 21.8 (CH₂), 14.9 (CH₃), 13.2 ppm (CH₃). IR (Nujol, 32 scans): $\tilde{v} = 3096$ (w), 3080 (w), 3038 (w), 1913 (w), 1716 (w), 1584 (s), 1547 (w), 1497 (m), 1337 (m), 1307 (w), 1287 (s), 1250 (s), 1221 (w), 1163 (w), 1153 (m), 1132 (m), 1109 (m), 1065 (m), 1020 (m), 1008 (m), 984 (m), 904 (m), 842 (m), 833 (m), 814 (s), 801 (s), 791 (s), 734 (s), 660 (w), 610 (w), 564 (m), 514 (w), 481 (w), 465 cm⁻¹ (w). MS-Cl⁺ (isobutane): [*M*⁺] 354 (100), [impy+H⁺] 177 (67). $M(C_{21}H_{26}N_2Ti) = 354.16 \text{ g mol}^{-1}$. This complex is extremely airsensitive and could not be analysed satisfactorily by CHN analysis. **Preparation of 8**: To a stirred solution of $[Cp_2Zr(py)(\eta^2 -$ Me₃SiC₂SiMe₃)] (2) (0.235 g, 0.5 mmol) in *n*-hexane (10 mL), 2-(*N*-n-

butyl-methylimino)pyridine (**impy**) (0.088 g, 0.5 mmol) was added dropwise at ambient temperature. The reaction mixture was stirred at 60 °C for 24 h. The resulting solution was concentrated to an approximate volume of 4 mL, filtered and slowly cooled to -78 °C. Removal of supernatant by syringe, washing with cooled *n*-hexane (-78 °C, 3×3 mL) and drying in vacuo at ambient temperature for 3 h yielded **8** (0.132 g, 67%) as brownish solid.

M.p.: 125 °C (dec. under Ar). ¹H NMR (25 °C, [D₆]benzene, 300.13 MHz): δ = 7.48 (m, 1 H, *CH*), 6.53 (m, 1 H, *CH*), 6.42 (m, 1 H, *CH*), 5.74 (s, 5 H, Cp), 5.44 (m, 1 H, *CH*), 5.25 (s, 5 H, Cp), 3.44 (m, 2 H, *CH*₂), 1.79 (s, 3 H, *CH*₃), 1.33 (m, 2 H, *CH*₂), 1.18 (m, 2 H, *CH*₂), 0.86 ppm (t, 3 H, *CH*₃). ¹³C NMR (25 °C, [D₆]benzene, 75.48 MHz): δ = 147.8 (*CH*), 127.2 (*CH*), 117.4 (*CH*), 109.3 (C_{quart}), 107.6 (*Cp*), 103.5 (*Cp*), 101.5 (*CH*), 54.8 (*CH*₂), 38.0 (*CH*₂), 21.0 (*CH*₂), 14.4 (*CH*₃), 12.3 ppm (*CH*₃). IR (Nujol, 32 scans): $\tilde{\nu}$ = 3113 (w), 3096 (w), 3077 (w), 3039 (w), 1911 (w), 1716 (w), 1598 (s), 1320 (s), 1288 (s), 1234 (m), 1218 (m), 1169 (m), 1151 (m), 1135 (m), 1075 (w), 1062 (w), 1016 (m), 1007 (m), 978 (m), 900 (w), 824 (m), 798 (s), 787 (s), 732 (s), 557 (m), 426 (m), 400 cm⁻¹ (m). MS-CI⁺ (isobutane): $[M^+]$ 396 (100), [impy+H⁺] 177 (41). M(C₂₁H₂₆N₂Zr)=396.11 g mol⁻¹. Elemental analysis (%) calcd: C 63.43, H 6.59, N 7.04; found: C 63.58, H 6.49, N 7.01.

Preparation of 9: 2-(*N*-*n*-Butyl-methylimino)pyridine (**impy**) (0.100 g, 0.57 mmol) was added dropwise to a stirred solution of Cp*₂Ti(η^2 -Me₃SiC₂SiMe₃) (**3**) (0.236 g, 0.50 mmol) in *n*-hexane (10 mL) at 0 °C. The mixture was slowly warmed to ambient temperature and heated to 55 °C for 3 d. Then the dark-brown solution was concentrated to an approximate volume of 2 mL and filtered. The filtrate was freed of all volatiles in vacuo resulting in **9** (0.121 g, 49%) as a brown solid.

M.p.: 139 °C (dec. under Ar). ¹H NMR (25 °C, [D₆]benzene, 300.13 MHz): δ = 1.5–2.1 (broad), 4–6 ppm (broad). EPR (27 °C, toluene): g = 1.9824, A_{TI} = 8.7 G, A_{N1} = 1.8 G, A_{N2} = 2.4 G, Δ B = 1.5 G; (-173 °C, toluene glass) g_1 = 2.0019, g_2 = 1.9821, g_3 = 1.9675, Δ B₁ = 6.9 G, Δ B₂ = 6.5 G, Δ B₃ = 7.6 G. IR ATR (32 scans): $\tilde{\nu}$ = 3071 (w), 2949 (m), 2895 (m), 2851 (s), 1879 (w), 1604 (w), 1573 (m), 1555 (m), 1477 (m), 1434 (m), 1374 (s), 1345 (m), 1320 (s), 1278 (s), 1246 (s), 1161 (w), 1142 (w), 1128 (m), 1105 (m), 1042 (m), 1018 (s), 988 (m), 948 (m), 901 (w), 794 (m), 724 (s), 708 cm⁻¹ (s). MS-Cl⁺ (isobutane): [M^+] 493 (68), [Cp*₂Ti⁺] 318 (11), [impy+H⁺] 177 (5) [Cp*⁺] 137 (3). M(C₃₁H₄₅N₂Ti) = 493,58 g mol⁻¹. Elemental analysis (%) calcd: C 75.44, H 9.19, N 5.68; found: C 75.13, H 9.43, N 5.80.

Preparation of 10: 2-(*N*-*n*-Butyl-methylimino)pyridine (**impy**) (0.088 g, 0.5 mmol) was added dropwise to a stirred suspension of $[Cp*_2ZrCl_2]$ (0.216 g, 0.5 mmol) and lithium sand (0.007 g, 1.0 mmol) in toluene (10 mL) at ambient temperature. The pale yellow reaction mixture was stirred over 2 d. Within 2 h, the colour switches to red-brownish and finally to dark-violet at the end of the reaction time. This solution was freed of all volatiles in vacuo, the residue dissolved in *n*-hexane (10 mL) and filtered. The dark-violet solution was concentrated to an approximate volume of 1 mL and stored at 6°C for 2 d resulting in the deposition of **10** (0.201 g, 74%) as a violet solid.

M.p.: 119 °C (dec. under Ar). ¹H NMR (25 °C, [D₆]benzene, 400.13 MHz): δ = 7.14 (m, 1H, *CH*), 6.51 (m, 1H, *CH*), 6.30 (m, 1H, *CH*), 5.47 (m, 1H, *CH*), 3.51 (m, 2H, *CH*₂), 2.04 (s, 3H, *CH*₃), 1.80 (s, 30H, Cp*), 1.57 (m, 2H, *CH*₂), 1.33 (m, 2H, *CH*₂), 0.97 ppm (m, 3H, *CH*₃). ¹³C NMR (25 °C, [D₆]benzene, 75.48 MHz): δ = 147.08 (*C*H), 131.97 (C_{quart}), 123.86 (*C*H), 120.19 (*C*H), 116.32 (C_{quart}), 115.66 (*C*quart,), 111.82 ppm (Cp*-*C*H₃). IR ATR (32 scans): $\tilde{\nu}$ = 2954 (m), 2899 (m), 2855 (m), 2721 (w), 1638 (w), 1589 (m), 1565 (m), 1497 (m), 180 (m), 1450 (s), 1431 (s), 1375 (s), 1299 (m), 1289 (s), 1227 (m), 1165 (m), 726 (s), 700 cm⁻¹ (m). MS-CI⁺ (isobutane): [*M*⁺] 536 (100), [Cp*₂Zr⁺] 360 (2), [impy+H⁺] 177 (1). M(C₃₁H₄₆N₂Zr) = 537.95 g mol⁻¹. Elemental analysis (%) calcd: C 69.22, H 8.62, N 5.21; found: C 69.11, N 8.61, H 5.10.

Acknowledgements

We are grateful for the GC measurement and hydrogen detection by L. Dura. Furthermore, we thank our technical and analytical staff for assistance. Financial support by the DFG (RO 1269/9-1) is gratefully acknowledged.

Keywords: dearomatisation \cdot metallacycles \cdot metallocenes \cdot pyridines \cdot reduction

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Received: November 3, 2015 Published online on January 25, 2016

Chem. Eur. J. 2016, 22, 3361 - 3369

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