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Reactivity Study of Pyridyl-Substituted 1-Metalla-2,5-diaza-cyclopenta-2,4-dienes of Group 4 Metallocenes

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Dedicated to Prof. Dr. Angelika Brückner on the occasion of her 60th birthday

Abstract: In this work the reactivity of 1-metalla-2,5-diazacyclopenta-2,4-dienes of group 4 metallocenes, especially of the pyridyl-substituted examples, towards small molecules is investigated. The addition of H_2, CO_2, $Ph{-}C{\equiv}N$, $2\text{-py}{-}C{\equiv}N$, 1,3-dicyanobenzene or 2,6-dicyanopyridine results in exchange reactions, which are accompanied by the elimination of a nitrile. For CO_2, a coordination to the five-membered cycle occurs in case of $Cp^*_2Zr(N{=}C(2\text{-py}){-}C(2\text{-py}){=}N)$. A 1,4-diaza-buta-1,3-diene complex is formed by H-transfer in the conversion of the analogous titanocene compound with $CH_3{-}C{\equiv}N$, $PhCH_2{-}C{\equiv}N$ or acetone. For $CH_3{-}C{\equiv}N$ a coupling product of three acetonitrile molecules is established additionally. In order to split off the metallocene from the coupled nitriles, we examined reactions with HCl, $PhPCl_2$, $PhPSCl_2$ and $SOCl_2$. In the last case, the respective thiadiazole oxides and the metallocene dichlorides were obtained. A subsequent reaction produced thiadiazoles.

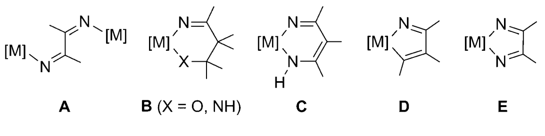
Introduction

In many catalytic reactions all-C as well as heterometallacycles are predicted as important intermediates. Therefore, their synthesis, structure and especially their reactivity are of considerable interest.[1]

In recent years, we gained access to nitrogen-containing heterometallacycles of group 4 metallocenes by reactions of $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ ($Cp' = Cp = \eta^5$-cyclopentadienyl, $Cp'_2 =$ *rac*-ebthi = *rac*-1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl), $Cp' = Cp^* = \eta^5$-pentamethylcyclopentadienyl; M = Ti, Zr) with nitriles.[2] We studied the synthesis and structure of the obtained complexes and were now interested in their reactivity. In the literature several conversions of group 4 metallocenes with $R{-}C{\equiv}N$ were already reported, but we noticed that only for some of these products the reactivity was investigated. These conversions resulted in new group 4 metallocene compounds or in a split-off of $[Cp'_2M]$.

An example for the first case is the formation of the diimine complex $Cp^*_2Zr[N{=}C(H,p\text{Tol})]_2$ upon addition of H_2 to $Cp^*_2Zr(N{=}C(p\text{Tol}){-}C(p\text{Tol}){=}N)$.[3] Other products of reactions of group 4 metallocenes with nitriles are known to dimerise to dinuclear compounds (Scheme 1, **A**)[4] or to couple with acetone, anilines,[5] dimethyl acetylenedicarboxylate[6] or further nitriles[7] to heterometallacycles (**B**, **C**).

For the second case, the split-off of $[Cp'_2M]$ (M = Ti, Zr) from the nitrile complexes, two different reaction types were reported. The first is the hydrolysis, which was investigated for diverse compounds and afforded, for example, amines,[8] azaindoles,[7c] ketones,[8a, 9] pyrroles[10] or other heterocycles.[11] The second one is the exchange of $[Cp'_2M]$ (M = Ti, Zr) by S_2Cl_2,[9c, 12] PCl_3[13a] or other electrophiles.[13b] For the 1-metalla-2-aza-cyclopenta-2,4-dienes of group 4 metallocenes (**D**), the products of an alkyne–nitrile C–C coupling, similar exchanges by $NiCl_2(PPh_3)_2$ and a subsequent reaction with alkynes to pyridines were intensively investigated.[14]



Scheme 1. Selected examples of group 4 metallocene complexes, established in reactions with nitriles.

In our research, we focused especially on the 1-metalla-2,5-diaza-cyclopenta-2,4-dienes (**E**). These were established by C–C couplings of aryl nitriles at $[Cp^*_2M]$ (M = Ti, Zr) and isolated in high yields.[15] This method could also be extended to dicyanobenzenes, thus forming tri- and tetranuclear compounds.[16] Exploring the reactivity of $Cp^*_2M(N{=}C(Ph){-}C(Ph){=}N)$ (M = Ti, Zr) towards H_2, CO_2 or $CH_3{-}C{\equiv}N$ showed that the C–C bond of the five-membered metallacycles was easily cleaved.[15a] This resulted in the elimination of one $Ph{-}C{\equiv}N$ and its replacement by the substrate. Unfortunately, experiments to hydrolyse the complexes were unsuccessful. In case of the macrocyclic products, their rapid decomposition under inert conditions impeded the investigation of their reactivity.[16]

Recently, we isolated pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes in the reactions of $Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, Zr) with cyanopyridines.[17] In contrast to their aryl-substituted analogues these compounds are easier to access and more stable. This was rationalised by DFT calculations and proven by testing the catalytic activity of $Cp^*_2Ti(N{=}C(R){-}C(R){=}N)$ (R = Ph, 2-py, 4-py) in the ring-opening polymerisation of ε-caprolactone.[17] Moreover, the tetranuclear $[Cp^*_2Ti(N{=}C(m\text{-}C_6H_3N){-}C{=}N)]_4$, obtained in the reaction of $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with 2,6-dicyanopyridine, did not decompose rapidly under inert conditions. These differences might influence the reactivity of the 1-metalla-2,5-diaza-cyclopenta-2,4-dienes significantly. The higher stability of the pyridyl-substituted compounds should enable different reactions or a higher selectivity towards new metallocene complexes. Furthermore, the split-off of $[Cp^*_2M]$ is more probable to result in stable organic substances. Besides, the compounds contain vacant coordination sites with the N atoms of the pyridine ring, which might lead to fascinating new complexes.[18] Owing to this, the investigation of the reactivity of the pyridyl-substituted compounds is of considerable interest.

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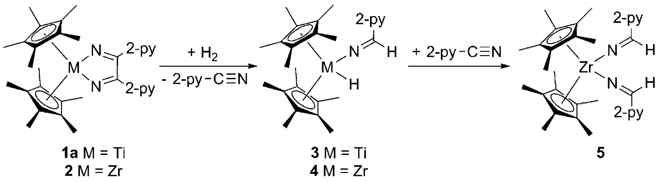
Results and Discussion

Firstly, we investigated reactions of Cp*$_2$M(N=C(2-py)–C(2-py)=N) (**1a**: M = Ti, **2**: M = Zr)[17] with H_2, CO_2 and CH_3–C≡N. By comparing the results to those of the phenyl-substituted analogues we wanted to estimate the influence of the substituents at the 1-metalla-2,5-diaza-cyclopenta-2,4-dienes on their reactivity. Secondly, we tested the possibility of separating the metallocene and the coupled nitriles to gain access to unsaturated organic compounds.

Reactions with H_2

The conversions of **1a** and **2** with H_2 were monitored by NMR spectroscopy and the spectra are given in the Supporting Information. Upon warming to 50 °C for one day both compounds started to react with H_2 to free 2-cyanopyridine and the hydride complexes **3** and **4** (Scheme 2). Therefore, the cleavage of the C–C bond of the five-membered cycle was necessary. The typical resonances of the imine N=CH groups are found at 9.22 (**3**) and 9.78 ppm (**4**) in the ^{1}H NMR and at 155.4 (**3**) and 160.1 ppm (**4**) in the ^{13}C NMR spectra. For the titanium compound a completion of this conversion could not be achieved by further warming. Instead, **1a** and **3** seemed to decompose. Thus, **3** was not isolable and was solely characterised by NMR spectroscopy.



Scheme 2. Reaction of **1a** and **2** with H_2.

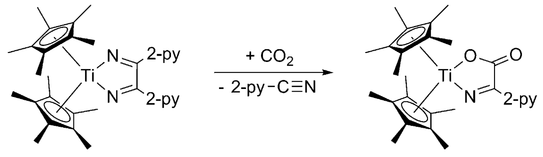
In case of the zirconium compound the diimine complex **5** was formed additionally upon further warming to 50 °C. Therefore, the free 2-py–C≡N inserted into the M–H bond of **4** (Scheme 2). Similar insertions were already described for diverse zirconocene hydride species.[13b,19] In the ^{1}H and ^{13}C NMR spectra the typical resonances of the imine N=CH moieties were with 9.96 and 160.4 ppm, respectively, in the same range as for **3** and **4**. A complete conversion of **2** to **4** and further to **5** could not be achieved. Thus, **4** and **5** were, like **3**, not isolated and are solely described by NMR spectroscopy.

The comparison of these results to those of reactions of the aryl-substituted analogues with H_2 shows that the obtained products are similar.[3,15a] The difference is that, in those cases the conversions could be completed within 3 days of warming, without hints for follow-up products. Moreover, the analogous zirconium compounds, with two Ph[15a] or *p*Tol[3] groups instead of 2-py, reacted already at ambient temperature with H_2.

To understand this difference, we computed the Gibbs free energies for the formation of **3** and **4** from **1a** and **2** ($\Delta G = -2.2$ and 0.8 kcal mol^{-1}, respectively) and of **5** from **4** ($\Delta G = -12.3$ kcal mol^{-1}). The values for the first step are less exergonic than those for the analogous phenyl-substituted compounds (Ti: $\Delta G = -7.3$ kcal mol^{-1}, Zr: $\Delta G = -5.8$ and -8.8 kcal mol^{-1}). This explains the necessity of higher temperatures for the conversions of the pyridyl-substituted complexes **1a** and **2**.

Reactions with CO_2

As in case of H_2, at ambient temperature no reaction of **1a** with CO_2 was observed. Thus, the solution was saturated with CO_2 and warmed to 50 °C for 4 d. This resulted in free 2-py–C≡N and in **6** (Scheme 3) by the formal C–C coupling of the remaining coordinated 2-cyanopyridine and CO_2. Complex **6** was isolated as a brown solid in high yield. In the ^{13}C NMR and the IR spectra the typical signals of the C=O and C=N moieties of the five-membered metallacycle were found at 165.7 (C=O), 154.9 ppm (or 157.5) (C=N), and 1647 (C=O), 1578 cm^{-1} (C=N), respectively.



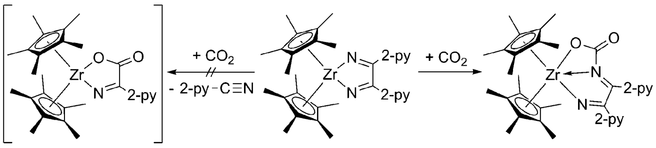
Scheme 3. Reaction of **1a** with CO_2.

A similar exchange reaction with CO_2 has been observed for the analogous complex Cp*$_2$Ti(N=C(Ph)–C(Ph)=N) (**1b**). In contrast to the conversion of **1a** this proceeded at ambient temperature within minutes.[15a] The reaction of **1b** with CO_2 provides more Gibbs free energy ($\Delta G = -10.0$ kcal mol^{-1}) than that of **1a** with CO_2 ($\Delta G = -0.7$ kcal mol^{-1}), which is consistent with the experiment.

Coupling of CO_2 and a C≡N bond at an organometallic compound was rarely observed. To the best of our knowledge only two further examples are known in which CO_2 inserted into the M–C bond of η^2-iminoacyl complexes.[20] Aside from that, coupling of Ph–C≡N and CO_2 to a four-membered bridge (N=C–C–O) in a bimetallic complex was described.[21] These conversions are of considerable interest, in regard of the CO_2-fixation and -activation as well as of potential further reactions.

Considering this, we also investigated the reaction of the zirconium complex **2** with CO_2. For the analogous compound Cp*$_2$Zr(N=C(Ph)–C(Ph)=N) the addition of CO_2 at ambient temperature afforded a mixture.[15a] The higher stability of the pyridyl-substituted cycle **2** is supposed to induce a higher selectivity. We observed an immediate colour change from yellow to brown upon bubbling CO_2 through a solution of **2** at ambient temperature. The subsequent work-up resulted in the isolation of brown crystals of **7** in high yield (Scheme 4).

The molecular structure of **7** is depicted in Figure 1. It shows that by the reaction of **2** with CO_2 a new C–N bond was formed (C1–N1) and that the CO_2 was coordinated via one of its O atoms to the Zr centre. As a consequence of this, the O2-



7a **2** **7**, 80 %

Scheme 4. Reaction of **2** with CO_2.

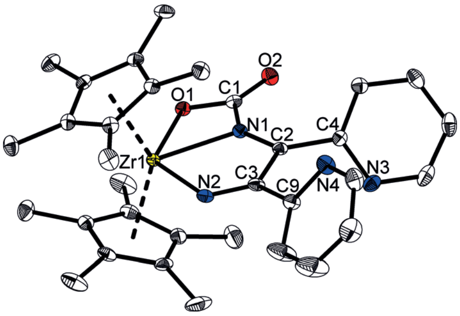


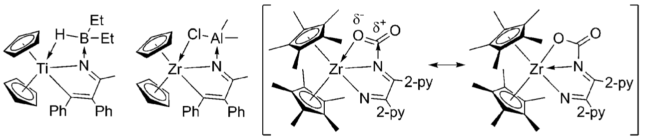
Figure 1. Molecular structure of **7** in the solid state. H atoms are omitted for clarity. The thermal ellipsoids correspond to 30 % probability. Selected bond lengths [Å] and angles [°]: O1-Zr1 2.276(1), N1-Zr1 2.222(2), N2-Zr1 2.201(2), C1-O1 1.286(2), C1-N1 1.450(2), C2-N1 1.286(2), C3-N2 1.270(2), C2-C3 1.518(3), O2-C1-O1 130.0(2), C2-N1-C1 136.7(2), N1-C2-C3 108.6(2), N2-C3-C2 117.4(2), C2-N1-Zr1 123.8(1), C3-N2-Zr1 120.2(1).

C1-O1 angle is reduced to 130.0(2)° and the C1=O1 double bond is elongated to 1.286(2) Å. The new four-membered metallacycle is planar with a mean deviation from the best plane of 0.002 Å.

Furthermore, the characterisation of **7** by X-ray crystallography offers us the opportunity to determine the impact of the coordination of CO_2 on the five-membered metallacycle in **2**. The C2–N1 distance (1.286(2) Å) in **7** is slightly longer than the C3–N2 bond (1.270(2) Å), which is the same as in **2** (1.274(2), 1.273(2) Å).[17] The C–C bond in **7** (C2–C3 1.518(3) Å) is in comparison to **2** (1.543(2) Å) slightly shortened, but is still in the range of an elongated C_{sp^2}–C_{sp^2} single bond. The N–Zr distances (N1–Zr1 2.222(2), N2–Zr1 2.201(2) Å) are longer than in **2** (2.124(1), 2.134(1) Å), which is more pronounced in case of N1–Zr1. The angles in the five-membered cycle are likewise influenced by the coordination. The N1-C2-C3 angle (108.6(2)°) in **7** is smaller than the N2-C3-C2 angle (117.4(2)°), which is in the same range as in **2** (117.0(1), 116.3(1)°). The C-N-Zr angles were both widened in comparison to **2**, which is again more distinct in case of C2-N1-Zr1 (**7**: C2-N1-Zr1 123.8(1), C3-N2-Zr1 120.2(1)°; **2**: 113.80(9), 114.09(8)°).

The five-membered cycle remained nearly planar (mean deviation from the best plane: 0.03 Å). The angle between this plane and that of the four-membered cycle (Zr1-O1-C1-N1) is 6.76(9)°. In summary, the coordination of CO_2 has only a slight impact on the bond lengths and angles in the five-membered ring in **7**. Besides, the resonances of the C=N bonds in the IR spectra are in the same range as for **2** (**7**: 1665, 1581 cm^{-1}; **2**: 1654, 1583 cm^{-1}).[17] But, the coordination of CO_2 influences the NMR spectra. In case of **2** four multiplets in the ^1H NMR as well as six signals in the ^{13}C NMR spectra were assigned to the two coupled 2-cyanopyridine units. The coordination of CO_2 results in a doubling of these resonances for **7**.

The formation of **7** is in many aspects quite remarkable. Firstly, in contrast to all other reactions observed so far for 1-metalla-2,5-diaza-cyclopenta-2,4-dienes of group 4 metals this is the first time the C–C bond of the five-membered metallacycle remained intact. Secondly, related group 4 metallocene complexes were isolated only once.[22] In those cases $HBEt_2$ or $ClAlMe_2$ were coordinated to 1-metalla-2-aza-cyclopenta-2,4-dienes (Scheme 5, **A** and **B**). Regarding these compounds, **7** might be described as Lewis acid-base adduct (Scheme 5) in which the lone pair of the N1 atom stabilises the formal cationic C1 atom, which was formed by the coordination of CO_2 to the Zr centre. Moreover, complexes, which are similar to **7**, were assumed as intermediates in the metallacycle transfer reactions to main-group elements like sulfur.[12b] However, heating **7** to 50 °C resulted in the elimination of CO_2 and the formation of **2** and not in the elimination of $[Cp^*_2Zr]$. This is a good indicator for a Lewis acid-base adduct.



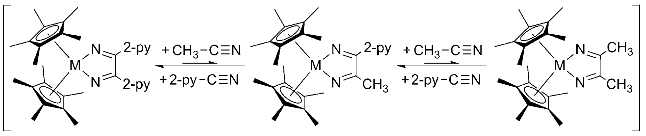
A **B** **7**

Scheme 5. Adduct complexes comparable to **7**.

A third aspect, which makes the formation of **7** so remarkable, is that DFT calculations predicted an exchange reaction to **7a** (Scheme 4) to be thermodynamically more probable ($\Delta G = -0.9$ kcal mol^{-1}, for **7**: $\Delta G = 0.1$ kcal mol^{-1}). Thus, the selective reaction to **7** must be kinetically favoured. In case of the analogous titanium complex **1a** the Gibbs free energy for a similar coordination is highly endergonic ($\Delta G = 11.1$ kcal mol^{-1}). Therefore, it is in comparison to the exchange thermodynamically not favourable.

Reactions with CH_3–C≡N

Regarding the fact that the reactivity of the aryl- and pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes towards H_2 and CO_2 was similar, we expected an exchange of one 2-cyanopyridine upon addition of CH_3–C≡N to **1a** or **2**. Thus, an equilibrium between **1a**/**2**, $Cp^*_2M(N{=}C(2\text{-py}){-}C(CH_3){=}N)$ and $Cp^*_2M(N{=}C(CH_3){-}C(CH_3){=}N)$ (M = Ti, Zr) would be established (Scheme 6).

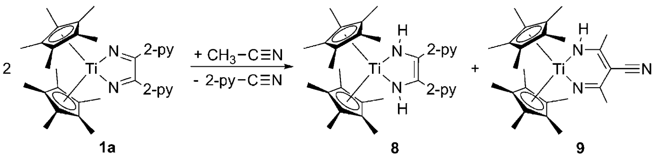


1a M = Ti
2 M = Zr

Scheme 6. Possible exchange reaction at **1a** and **2** with CH_3–C≡N.

Dissolving **1 a** and **2** separately in CH_3–C≡N resulted for, both compounds, in free 2-py–C≡N, but the expected products were not identified. For a better understanding of this, we computed the formation free energies of the stepwise exchange of both 2-py–C≡N moieties in **1 a** and **2** by CH_3–C≡N. All four values are endergonic by 1.1 (Ti) and 1.9 kcal mol^{-1} (Zr) for the first step as well as 3.9 (Ti) and 4.6 kcal mol^{-1} (Zr) for the second step, and therefore in contrast to the analogous conversions of the phenyl-substituted complexes (Ti: −1.5 and −2.2 kcal mol^{-1}; Zr: −1.4 and −0.9 kcal mol^{-1}).[15a] Regarding this, the exchange of one 2-py–C≡N by CH_3–C≡N might be possible, although the resulting equilibrium favours **1 a** (ratio 87:13) or **2**, respectively (97:3). The second exchange is unlikely to proceed. This difference in the reactivity of the phenyl- and pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes is quite fascinating, but even more interesting is the outcome of the reactions that occurred instead.

In case of the zirconium complex **2**, we obtained a mixture of diverse compounds. Unfortunately, separation attempts were not successful and no definite zirconocene species were identified. The titanium complex **1 a** was converted to two new compounds. The solubility of these products is very similar, though slightly different in *n*-hexane. Thus, it was possible to isolate a small amount of both substances in high purity as purple (**8**) and yellow solid (**9**; Scheme 7).



Scheme 7. Reaction of **1 a** with excess CH_3–C≡N.

The purple solid was identified as the 1,4-diaza-buta-1,3-diene complex **8**. Formally, it was established by the addition of two H atoms to the five-membered metallacycle in **1 a**. Comparable complexes of group 4 metals were already described, but mostly, they were formed by a C–C coupling of isonitriles[23] or by coordination of 1,4-diaza-buta-1,3-dienes.[24] To the best of our knowledge, solely three such group 4 metallocene compounds were obtained by a C–C coupling of two nitriles and an H-transfer. The first one was established by warming $Cp^*_2Ti(N{=}C(Fc){-}C(Fc){=}N)$ [Fc =-(η^5-C_5H_4)Fe(η^5-C_5H_5)] to 80 °C,[15b] the second, a trinuclear compound, was obtained upon addition of adiponitrile to $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[16] and the third was achieved in the reaction of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with $PhCH_2$–C≡N.[2c] In case of the zirconocene complex the source of the additional H atoms is supposed to be the deprotonation of further $PhCH_2$–C≡N. For the other two compounds their origin is unknown. The additional H atoms in **8** seem to be provided by the CH_3–C≡N. A subsequent coupling of the remaining fragment (CH_2–CN) at [Cp^*_2Ti] might have formed the six-membered metallacycle in **9**. In order to prove that CH_3–C≡N is the source of the additional H atoms in **8**, we investigated the reaction of **1 a** with CD_3–C≡N. The ^{1}H NMR spectrum of the reaction mixture was identical to that of the conversion of **1 a** with CH_3–C≡N, except for the absence of the signals of the N–H moieties of **8** and **9** and of the Me groups of **9**. This confirmed our assumption of acetonitrile being the source of the additional H atoms in **8** (spectra are given in the Supporting Information).

The characterisation of compound **8** by X-ray crystallography (Figure 2) offered us the opportunity to directly compare this 1-metalla-2,5-diaza-cyclopent-3-ene to the 1-metalla-2,5-diaza-cyclopenta-2,4-diene **1 a**. The C–N bonds are with 1.363(2) and 1.365(1) Å in the range of C_{sp^2}–N_{sp^2} single bonds and distinctly longer than in **1 a**: 1.274(2), 1.271(2) Å.[15a] In contrast to this, the C–C bond is shortened from 1.531(2) Å in **1 a** to 1.402(2) Å in **8**. Furthermore, complex **8** is folded along the N–N axis (angle between the planes defined by Ti1, N1, N2 and N1, C1, C2, N2: 24.53(5)°), thus showing an envelope conformation, while **1 a** was nearly planar (mean deviation from the best plane 0.02 Å).

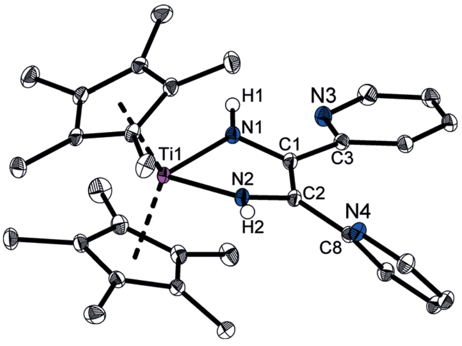


Figure 2. Molecular structure of **8** in the solid state. H atoms, except for H1 and H2, are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [°]: C1-C2 1.402(2), C1-N1 1.363(2), C2-N2 1.365(1), N1-Ti1 2.024(1), N2-Ti1 2.026(1), N1-C1-C2 113.6(1), N2-C2-C1 114.0(1), C1-N1-Ti1 114.35(8), C2-N2-Ti1 113.23(8).

The conversion of the cyclopentadiene in **1 a** to a cyclopentene in **8** by H-transfer has only a slight impact on the position of the Cp* and pyridyl group resonances in the ^{1}H and ^{13}C NMR spectra. In comparison to **1 a**, they are only slightly shifted for **8**. The signals of the N–H moieties were identified at 7.99 ppm in the ^{1}H NMR and at 3345 cm^{-1} in the IR spectrum.

The second product of the reaction of **1 a** with CH_3–C≡N is **9** (Scheme 7). It was established by a trimerisation of CH_3–C≡N at [Cp^*_2Ti], accompanied by an H-transfer. In consequence to this, **9** contains a C≡N triple, a C=N double as well as a C–N single bond and one of the former three methyl groups lost all its H atoms. The six-membered cycle in **9** is therefore highly unsymmetrical. Owing to this, two resonances were identified in the ^{1}H NMR (2.01 and 2.19 ppm) and in the ^{13}C NMR spectrum (24.2 and 27.8 ppm) for the CH_3 groups. The signal of the N–H group in the ^{1}H NMR spectrum was found at 4.27 ppm. Resonances at 124.6, 158.8 and 165.1 ppm in the ^{13}C NMR spectrum were assigned to the C≡N triple, the C=N double and the C–N single bond respectively. In the IR spectrum of **9**, resonances for the N–H (3278 cm^{-1}), the C≡N (2156 cm^{-1}) and the C=N unit (1603 and 1546 cm^{-1}) were identified.

The structure of **9** was confirmed by X-ray crystallography (Figure 3). It shows the nearly planar six-membered metallacycle (mean deviation from the best plane: 0.02 Å) and the three unequal C–N bonds. While C5–N3 (1.153(3) Å) corresponds to a C≡N triple bond, C3–N2 (1.278(3) Å) is a C=N double bond and C1–N1 (1.313(3) Å) a shortened C–N single bond. The remaining bond lengths of the six-membered cycle indicate an unusual bonding situation. The N–Ti bond lengths (N1–Ti1 2.078(2), N2–Ti1 1.887(2) Å) differ significantly from each other. The C1–C2 distance (1.418(3) Å) is shorter than a $C_{sp}{}^2$–$C_{sp}{}^2$ single and longer than a C_{sp^2}=C_{sp^2} double bond. Whereas, the C2–C3 distance (1.442(4) Å) is in the range of a C_{sp^2}–C_{sp^2} single bond. This bonding situation was in case of a tetrameric tungsten complex, with similar six-membered cycles, explained by a partial M=N double bond character, which influences the other bonds in the metallacycle as well.[25]

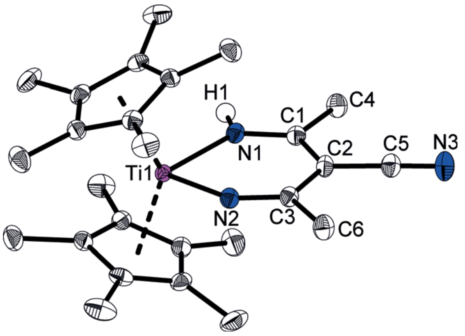


Figure 3. Molecular structure of **9** in the solid state. H atoms, except for H1 are omitted for clarity. The thermal ellipsoids correspond to 30 % probability. Selected bond lengths [Å] and angles [°]: C1-N1 1.313(3), C1-C2 1.418(3), C1-C4 1.502(3), C2-C5 1.416(3), C2-C3 1.442(4), C3-N2 1.278(3), C3-C6 1.508(3), C5-N3 1.153(3), N1-Ti1 2.078(2), N2-Ti1 1.887(2), N1-C1-C2 122.8(2), N2-C3-C2 120.2(2), C1-N1-Ti1 131.0(2), C3-N2-Ti1 140.8(2), N3-C5-C2 178.4(3).

The formation of **9** by a trimerisation of CH_3–C≡N is remarkable. Coupling reactions of titanocene fragments with nitriles to comparable six-membered titanacycles (Scheme 1, **C**) were already described, but in those cases only two nitriles were involved. Thus, they contained an H atom or a CH_2 unit as substituent instead of the C≡N group.[7a,26] Moreover, a trimerisation of CH_3–C≡N to a six-membered cycle as in **9** was solely observed for a tungsten complex.[25] In comparable compounds, formed in reactions of diverse metal species with CH_3–C≡N, both N atoms of the established metallacycles were protonated.[27]

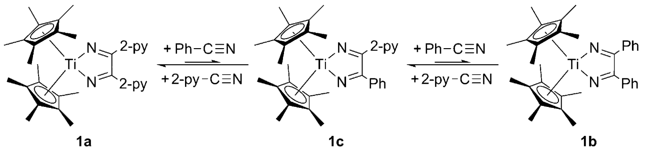
Though complexes, which are similar to **8** and **9** were already described, their formation by the reaction of **1a** with CH_3–C≡N is fascinating. On the one hand, it is interesting that an excess of acetonitrile is needed for this conversion, although formally a 2:3 ratio of the substrates should be sufficient. On the other hand, for the analogous compound $Cp^*{}_2Ti(N{=}C(Ph){-}C(Ph){=}N)$ (**1b**) the addition of acetonitrile resulted simply in an exchange of the nitriles and not in an H-transfer or a trimerisation.[15a] Still, we suppose the first steps of both reactions to be similar. In the beginning one nitrile should be eliminated and CH_3–C≡N coordinated to the metal. In case of the phenyl-substituted complex a subsequent C–C coupling leads to a five-membered metallacycle with a Ph and a CH_3 substituent. Such an exchange might be possible for **1a** too ($\Delta G = 1.1$ kcal mol^{-1}), but it should result in an equilibrium in favour of **1a**. The excess of acetonitrile might influence this and promote the generation of a complex with 2-py–C≡N and CH_3–C≡N coordinated to [$Cp^*{}_2$Ti]. Instead of the formation of the five-membered cycle, the next step could be an H-transfer to the coordinated 2-cyanopyridine. Further coupling and rearrangement steps might afford **8** and **9**.

Reactions with other nitriles

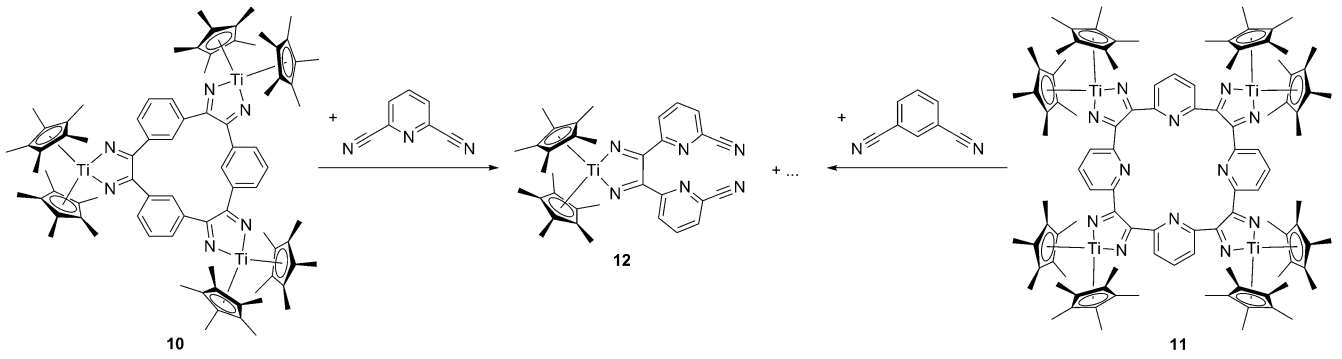
To confirm our assumed formation path, especially the nitrile-exchange step, we investigated the reactivity of **1a** towards other nitriles. At first we studied the conversion with $PhCH_2$–C≡N, which also contains acidic α-protons. This resulted in free 2-cyanopyridine and in **8**, but not in an exchange of the nitriles. The source of the additional H atoms might have been $PhCH_2$–C≡N. Unfortunately, we were not able to identify products, which contain the remainders of the nitrile. A similar reaction to **8** and free 2-py–C≡N was observed upon addition of acetone to **1a**.

In addition, we examined the reactivity of **1a** towards Ph–C≡N, which contains no H atoms neighbouring the C≡N moiety and thus might hinder the formation of **8**. Besides, DFT calculations predicted that a stepwise exchange of both 2-py–C≡N units by two Ph–C≡N molecules is thermodynamically unlikely (1st step: $\Delta G = 4.1$ kcal mol^{-1}, 2nd step: $\Delta G = 4.6$ kcal mol^{-1}). As for $PhCH_2$–C≡N, no reaction was observed at ambient temperature. But, warming a 1:1 mixture of **1a** and Ph–C≡N partly resulted in the formation of the mixed species **1c** (Scheme 8). The symmetric complex **1b** was not established. Upon warming a solution of **1a** with an excess of Ph–C≡N both compounds **1c** and **1b** formed, but **1c** only in minor concentration and **1b** in traces. This demonstrates that the exchange of 2-py–C≡N in **1a** by another nitrile is possible, although it is thermodynamically not probable, and that a high concentration or temperature is necessary to achieve it. The reverse reaction of **1b** with 2-py–C≡N to **1a**, **1c** and Ph–C≡N already proceeded at ambient temperature within 2 d. In the resulting mixture the main component was **1a**.

Moreover, we were interested to determine if a nitrile exchange is also possible for the multinuclear analogues of **1a** and **1b**. This might probably lead to mixed di-, tri- or tetranuclear species. As recently published, the reaction of $Cp^*{}_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with 1,3-dicyanobenzene or 2,6-dicyanopyridine



Scheme 8. Exchange reaction with Ph–C≡N.



Scheme 9. Exchange of dicyano compounds in the macrocyclic complexes **10** and **11** under formation of **12**.

afforded the tri- and tetranuclear compounds **10**[16] and **11**[17] (Scheme 9).

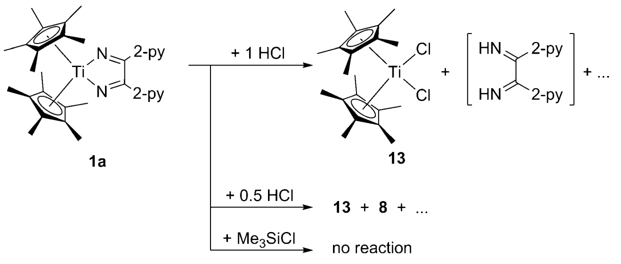
The reaction of **10** with 2,6-dicyanopyridine proceeded at ambient temperature. Thereby, a 1:2 ratio was sufficient for the complete conversion of **10**. The observed products are free 1,3-dicyanobenzene and several titanocene species.

These are suspected to be mono- or dinuclear 1-titana-2,5-diaza-cyclopenta-2,4-dienes. The addition of an excess of 2,6-dicyanopyridine to **10** (ratio 5:1), led to only three compounds, which are assumed to be the possible mononuclear species. The main product in all cases is **12** (Scheme 9). This complex was already established by the coupling of two equivalents 2,6-dicyanopyridine at $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[17] In case of the addition of 1,3-dicyanobenzene to **11** (ratio 3:1) no reaction was observed at ambient temperature. Upon warming to 60 °C for 12 h a mixture formed, with **12** as main component. In contrast to the reaction of **10** with 2,6-dicyanopyridine no elimination of the dicyano compound was observed and the conversion was incomplete. This resembles the reactions of the mononuclear species **1a** and **1b** with Ph–C≡N and 2-py–C≡N, respectively. Unfortunately, these conversions of **10** and **11** did not result in the isolation of mixed di-, tri- or tetranuclear compounds.

The investigated reactions of **1a** and **2** with H_2, CO_2, CH_3–C≡N and other nitriles showed several differences in comparison to those of the phenyl-substituted analogues. In some cases the improved stability of the pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes induced longer reaction times and higher temperatures, in others it caused different reactions and resulted in new metallocene compounds. For our attempts to split off the $[Cp^*_2M]$ from the coupled nitriles these findings are very promising.

Attempts to separate $[Cp^*_2M]$ from the coupled nitriles

At first, we tried to generate diimines by the treatment of **1a** with HCl or Me_3SiCl. Complex **1a** reacted vigorously with ethereal HCl, resulting in $Cp^*_2TiCl_2$ (**13**) and numerous other compounds (Scheme 10). The diimine was not isolated, probably due to decomposition as in case of its phenyl-substituted analogue (in reaction of **1b** with HCl).[15a,28] For directing this further conversion to the respective diketone, we performed it with 1 equiv HCl_{aq}. But still, we observed the formation of a mixture. Furthermore, we tried to increase the selectivity by applying only 0.5 equiv of ethereal HCl. This resulted in a mixture as well, in which we identified **1a**, **13** and **8** among other compounds. Though, we were not able to isolate the respective diimine, these experiments showed us, that in principle the separation of the metallocene and the coupled nitriles should be possible. In order to obtain a more stable diimine, we added Me_3SiCl to **1a**. Unfortunately, no reaction occurred (Scheme 10), not at ambient temperature and not upon warming to 60 °C for 8 d.

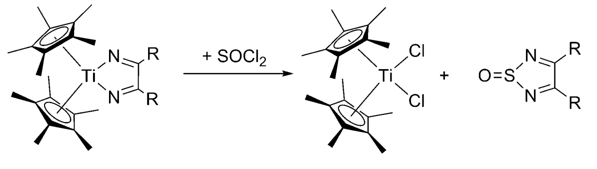


Scheme 10. Attempts to generate diimines by reactions of **1a** with HCl or Me_3SiCl.

In our further attempts to separate $[Cp^*_2M]$ from the coupled nitriles we tried to generate five-membered heterocycles by the reaction with $PhPCl_2$, $PhPSCl_2$, Me_2SiCl_2 or $SOCl_2$. For comparable compounds, like 1-metallacyclopenta-2,4-dienes or 1-metalla-2-aza-cyclopenta-2,4-dienes of group 4 metallocenes, such conversions were already realised.[9c,12] These produced phospholes, thiophene oxides, thiacyclopentenes or isothiazoles. The addition of $PhPCl_2$, $PhPSCl_2$ or Me_2SiCl_2 to **1a** resulted in **13** and in free 2-py–C≡N.[29] Formal phospholes, siloles or products, which contain the remainders of $PhPCl_2$ or $PhPSCl_2$, were not identified. The reaction with $SOCl_2$ was tested for the 1-titana-2,5-diaza-cyclopenta-2,4-dienes $Cp^*_2Ti(N{=}C(R){-}C(R){=}N)$ with R = 2-py (**1a**), R = 6-CN-2-py (**12**) and R = 2-Br-5-py (**14**).[30] The outcome of these conversions was for all compounds similar. Therefore, we describe in the following mainly the reaction of **1a** with $SOCl_2$.

The addition of $SOCl_2$ to **1a** at −78 °C followed by warming of the mixture to ambient temperature afforded the dichloride

13 and the thiadiazole oxide **15a** (Scheme 11). The separation of these two products was difficult. Their solubility is similar and thus the isolated crystal fractions consisted of yellow crystals of **15a** and red ones of **13**, which were separated manually. Due to this method, the yield of pure **15a** was rather low (40%).



1a R = 2-py
12 R = 6-CN-2-py
14 R = 2-Br-5-py

13

15a R = 2-py
15b R = 6-CN-2-py
15c R = 2-Br-5-py

Scheme 11. Reaction with $SOCl_2$.

Interestingly, if **13** and **15a** were not separated, a subsequent reaction started. This resulted in the thiadiazole **16a**, in the elimination of the Cp* ligand and in a formal Ti species [Cp*Ti] with only one Cp* ligand (Scheme 12). The eliminated Cp* ligand was identified as decamethylfulvalene (Cp^*_2),[31] tetramethylfulvene[32] and pentamethylcyclopentadiene (Cp*H),[33] by comparison of the typical NMR signals to those published in the literature (below all three species are mentioned as [Cp*] for a better readability). In order to complete this conversion the mixture was warmed to 60 °C for 38 h. Afterwards, we identified [Cp*], the formal [Cp*Ti] species, the thiadiazole **16a** and, unfortunately, still **15a**. Thus, $Cp^*_2TiCl_2$ (**13**) seems to be necessary for the conversion of **15a** to **16a**. To test this assumption, we dissolved pure **15a** and warmed it to 85 °C. This did not result in any kind of reaction. Then, we added an excess of **13** and again warmed the mixture to 85 °C. Here, the conversion of **15a** to **16a** started.

An explanation for this might be the formation of the formal [Cp*Ti] species. We suppose that by the reaction of **15a** with **13**, the Cp* ligand is eliminated and the O atom transferred to the titanium. Subsequent to this, a complex could be formed, which might resemble the tetrameric $[(Cp^*Ti)_4O_6]$.[34] Unfortunately, we were not able to isolate and characterise this new compound in detail. But, we suppose that the difference to the literature known example could be, that it contains Cl and O atoms as bridging ligands between the [Cp*Ti] moieties (Scheme 12). A higher amount of chlorine in comparison to oxygen in this complex would explain the necessity of an excess of $Cp^*_2TiCl_2$ for the complete conversion of **15a** to **16a**.

As mentioned above, the reactions of the other pyridyl-substituted 1-titana-2,5-diaza-cyclopenta-2,4-dienes with $SOCl_2$ are similar to that of **1a**. The difference is that, the subsequent reactions were in both cases faster than for **15a**. Thus, we were not able to isolate **15b** or **15c** in pure form. But, **16c** was obtained as crystals (Figure 4). The values of the bond lengths of the five-membered cycle (N1–S1 1.625(2), C1–N1 1.331(3), C1–C1A 1.436(5) Å) and the fact that it is nearly planar (mean deviation from the best plane 0.007 Å) indicate some electron delocalisation, as already described for other thiadiazoles.[35] The pyridyl substituent and the five-membered cycle are tilted by 42.77(9)° (angle between the planes defined by S1, N1, C1, C1A, N1A and C2, C3, N2, C4, C5, C6).

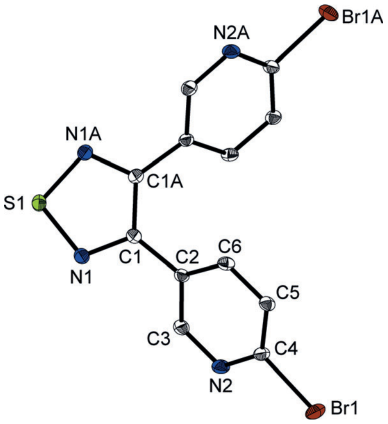
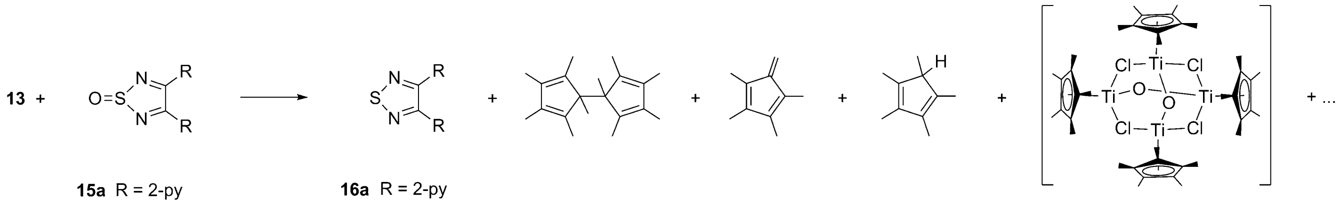


Figure 4. Molecular structure of **16c** in the solid state. H atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [°]: N1-S1 1.625(2), C1-N1 1.331(3), C1-C1A 1.436(5), C1-C2 1.481(4), N1-C1-C2 119.3(2), N1-C1-C1A 112.9(1), C1-N1-S1 107.6(2), N1-S1-N1A 99.0(2).

In order to obtain **16a** in pure form, we studied the reactions of $SOCl_2$ with $Cp^*_2Ti(N(H)–C(2\text{-}py)=C(2\text{-}py)–N(H))$ (**8**) and $Cp^*_2Zr(N=C(2\text{-}py)–C(2\text{-}py)=N)$ (**2**). In case of **8**, we expected at first the formation of a dihydrothiadiazole oxide, which could be converted to **16a** by the elimination of water. The dichloride **13** should remain intact and might be separated more easily. But the reaction afforded an inseparable mixture of **16a**, **13**, [Cp*] and the formal [Cp*Ti] species. The addition of $SOCl_2$ to the zirconocene complex **2** resulted in $Cp^*_2ZrCl_2$ and in **15a**.



15a R = 2-py
15b R = 6-CN-2-py
15c R = 2-Br-5-py

16a R = 2-py
16b R = 6-CN-2-py
16c R = 2-Br-5-py

Scheme 12. Subsequent reaction of **13** and **15** to **16**, [Cp*] and the formal [Cp*Ti] species.

In contrast to the conversions of the titanium compound **1 a**, no subsequent reaction to **16 a** occurred although the mixture was warmed to 80 °C for 3 d.

In order to compare the reactivity towards $SOCl_2$ between the pyridyl- and the phenyl-substituted complexes, we investigated the reaction of **1 b** with $SOCl_2$ as well. This produced the thiadiazole **16 d** and **13** (**16 d** was identified by comparison of the typical NMR data to those published in the literature[36]). The formation of the thiadiazole oxide **15 d**, of the formal [Cp*Ti] species and of [Cp*] was not observed.

Conclusions

Herein, we presented a detailed study on the reactivity of 1-metalla-2,5-diaza-cyclopenta-2,4-dienes of group 4 metallocenes towards small molecules. At first, we investigated the reactions of the pyridyl-substituted complexes $Cp^*_2M(N{=}C(2\text{-py}){-}C(2\text{-py}){=}N)$ (**1 a**: M = Ti, **2**: M = Zr) with H_2, CO_2, $CH_3{-}C{\equiv}N$ and other nitriles. We observed several differences by comparing the results to those of the analogous aryl-substituted compounds.

In some cases the improved stability of the pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes effected longer reaction times and higher temperatures. This was observed for the conversion of **1 a** with H_2 and CO_2 as well as of **2** with H_2, in which the obtained products were similar to those of the aryl-substituted analogues. In other cases different reactions were caused by the higher stability and resulted in new metallocene species. The reaction of **2** with CO_2 afforded a fascinating coordination product, while the conversion of the phenyl-substituted analogue resulted in a mixture. The special feature of this reaction of **2** is that the five-membered metallacycle stayed intact. The higher stability of the pyridyl-substituted cycle also induced a different reaction with $CH_3{-}C{\equiv}N$. In case of the phenyl-substituted complexes the addition of acetonitrile resulted in an exchange of the nitriles. In the reaction with **1 a**, the 1,4-diaza-buta-1,3-diene complex **8** was established by an H-transfer and a six-membered cycle in **9** by a remarkable coupling of three former $CH_3{-}C{\equiv}N$ moieties. Similar H-transfers were observed for $PhCH_2{-}C{\equiv}N$ and acetone, which generated **8** as well.

The exchange of the nitriles was also accomplished for **1 a**, but only upon the addition of $Ph{-}C{\equiv}N$, which lacks acidic protons neighbouring the $C{\equiv}N$ moiety. Besides, an excess of $Ph{-}C{\equiv}N$ and elevated temperatures were necessary for this reaction. The same was observed upon addition of 1,3-dicyanobenzene or 2,6-dicyanopyridine to the trinuclear compound **10** or the tetranuclear complex **11**, respectively. An explanation for this seems again to be the higher stability of the pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes in comparison to their phenyl-substituted analogues.

In light of these results, we examined in the second part of this work reactions to separate the $[Cp^*_2M]$ from the coupled nitriles. Our first experiments, using HCl, Me_3SiCl, $PhPCl_2$, $PhPSCl_2$ and Me_2SiCl_2 and the titanium complex **1 a** were unsuccessful. If a reaction occurred, it resulted in a mixture or in the formation of $Cp^*_2TiCl_2$ and the free nitrile. But, the addition of $SOCl_2$ to different 1-titana-2,5-diazacyclopenta-2,4-dienes afforded at first the thiadiazole oxides **15** and the dichloride **13**. In a subsequent reaction these were converted to the thiadiazoles **16**, [Cp*] and to a formal [Cp*Ti] species.

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. $Cp^*_2M(N{=}C(2\text{-py}){-}C(2\text{-py}){=}N)$ (**1 a**: M = Ti, **2**: M = Zr),[17] $Cp^*_2Ti(N{=}C(Ph){-}C(Ph){=}N)$ (**1 b**),[15a] $[Cp^*_2Ti(N{=}C(m\text{-}C_6H_4){-}C{\equiv}N)]_3$ (**10**),[16] $[Cp^*_2Ti(N{=}C(m\text{-}C_6H_3N){-}C{\equiv}N)]_4$ (**11**),[17] $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[37] and $Cp^*_2Ti(N{=}C(2\text{-Br-5-py}){-}C(2\text{-Br-5-py}){=}N)$ (**14**)[17] were synthesised according to the published procedures. 2-Cyanopyridine, $PhCH_2{-}C{\equiv}N$, benzonitrile and Me_2SiCl_2 (all Sigma–Aldrich) were purified by distillation and stored under argon. 2,6-Dicyanopyridine (Sigma–Aldrich) was purified by sublimation. The solid 1,3-dicyanobenzene (Sigma–Aldrich) was dried in vacuum prior to use. Ethereal HCl (HCl in diethyl ether, 2.0 M, Sigma–Aldrich), Me_3SiCl (Sigma–Aldrich), $PhPCl_2$ (Acros) and $PhPSCl_2$ (TCI) were used as received. $SOCl_2$ was purified according to the published procedure.[38] The following instruments were used: NMR spectra: Bruker AV300 and AV400. ^1H and ^{13}C chemical shifts are given in ppm and were referenced to the solvent signals: [D$_6$]benzene ($\delta_H = 7.16$ ppm, $\delta_C = 128.0$ ppm), $CDCl_3$ ($\delta_H = 7.26$ ppm, $\delta_C = 77.2$ ppm), [D$_6$]DMSO ($\delta_H = 3.33$ ppm, $\delta_C = 39.5$ ppm), [D$_8$]THF ($\delta_H = 3.58$ ppm, $\delta_C = 67.6$ ppm); IR: Bruker Alpha FT-IR spectrometer; MS: Finnigan MAT 95-XP from Thermo-Electron; elemental analysis: Leco Tru Spec elemental analyzer; melting points: Mettler-Toledo MP70. Melting points are uncorrected and were measured in sealed capillaries.

Diffraction data for **7**, **8** and **16 c** were collected on a Bruker Kappa APEX II Duo diffractometer using $Mo_{K\alpha}$ radiation for **7** and **8** and $Cu_{K\alpha}$ radiation for **16 c**. For **9** the diffraction data were collected on a STOE-IPDS II diffractometer using $Mo_{K\alpha}$ radiation. The structures were solved by direct methods 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 7: $C_{33}H_{38}N_4O_2Zr$, $M = 613.89$, monoclinic, space group $C2/c$, $a = 28.5767(7)$, $b = 12.9297(3)$, $c = 16.4976(4)$ Å, $\beta = 109.2273(7)^\circ$, $V = 5755.6(2)$ Å^3, $T = 150(2)$ K, $Z = 8$, 60 815 reflections collected, 6952 independent reflections ($R_{int} = 0.0370$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0297$, $wR_2 = 0.0710$, final R values (all data): $R_1 = 0.0395$, $wR_2 = 0.0774$, 371 parameters.

Crystal data for 8: $C_{32}H_{40}N_4Ti$, $M_r = 528.58$, monoclinic, space group $C2/c$, $a = 19.3954(9)$, $b = 16.1976(7)$, $c = 18.8007(9)$ Å, $\beta = 110.995(1)^\circ$, $V = 5514.3(4)$ Å^3, $T = 150(2)$ K, $Z = 8$, 76 393 reflections collected, 6672 independent reflections ($R_{int} = 0.0236$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0321$, $wR_2 = 0.0865$, final R values (all data): $R_1 = 0.0363$, $wR_2 = 0.0911$, 352 parameters.

Crystal data for 9: $C_{26}H_{37}N_3Ti$, $M_r = 439.48$, orthorhombic, space group $P2_12_12_1$, $a = 9.9475(3)$, $b = 13.8264(3)$, $c = 17.3814(4)$ Å, $V = 2390.6(1)$ Å^3, $T = 150(2)$ K, $Z = 4$, 42 072 reflections collected, 5762 independent reflections ($R_{int} = 0.0547$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0299$, $wR_2 = 0.0662$, final R values (all data): $R_1 = 0.0365$, $wR_2 = 0.0675$, 287 parameters.

Crystal data for 16 c: $C_{12}H_6Br_2N_4S$, $M_r = 398.09$, monoclinic, space group $C2/c$, $a = 14.8696(5)$, $b = 7.7513(3)$, $c = 13.3462(4)$ Å, $\beta = 122.7486(14)^\circ$, $V = 1293.76(8)$ Å^3, $T = 150(2)$ K, $Z = 4$, 4364 reflections collected, 1142 independent reflections ($R_{int} = 0.0197$), final R values

($I > 2\sigma(I)$): $R_1 = 0.0261$, $wR_2 = 0.0674$, final R values (all data): $R_1 = 0.0270$, $wR_2 = 0.0681$, 87 parameters.

CCDC 1468162 (**7**), 1468163 (**8**), 1468164 (**9**) and 1468165 (**16c**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Computational details

Structure optimisations were carried out at the BP86[41] density functional level of theory with the TZVP basis set[42] for C, H, N O as well as LANL2DZ[43] for Ti and Zr by using Gaussian 09 program package.[44] The optimised geometries are characterised as energy minimums at the potential energy surface from frequency calculations at the same level of theory (BP86/TZVP), that is, the energy minimum structure has only real frequencies, while the transition-state structure has only one imaginary frequency. Furthermore, the thermal corrections to enthalpy and Gibbs free energy at 298 K from the frequency analysis are added to the total electronic energy. Therefore, we either used the corrected enthalpy (ΔH) or the Gibbs free energy (ΔG) at 298 K for our energetic comparisons. The energetic data and the Cartesian coordinates are given in the Supporting Information.

Reactions with H_2

Preparation of 3: Cp*$_2$Ti(N=C(2-py)–C(2-py)=N) (**1a**) was dissolved in C_6D_6 and the red solution was transferred into a sealable J-Young NMR tube. The sample was degassed using a freeze-pump-thaw method and filled with 1 atm of H_2 at −196 °C. Subsequently, it was first warmed to ambient temperature, then heated to 50 °C for 1 d. ^{1}H and ^{13}C NMR spectra were recorded before and after the addition of H_2 and after the heating. Compound **3** could not be isolated and characterised in detail because of its incomplete formation and its subsequent reaction upon further warming. ^{1}H NMR (400 MHz, 297 K, C_6D_6): $\delta = 1.80$ (s, 30 H, C_5Me_5), 6.64 (m, 1 H, py), 7.12 (m, 1 H, py), 8.24 (m, 1 H, py), 8.55 (m, 1 H, py), 9.22 ppm (s, 1 H, N=CH). The signal of the Ti–H moiety could not be identified; ^{13}C NMR (100 MHz, 297 K, C_6D_6): $\delta = 12.2$ (C_5*Me*$_5$), 114.0 (*C*$_5$Me$_5$), 117.6, 119.3, 123.4, 135.6 (C_{py}), 149.8 (*ipso*C_{py}), 155.4 ppm (N=CH).

Preparation of 4 and 5: Cp*$_2$Zr(N=C(2-py)–C(2-py)=N) (**2**) was dissolved in C_6D_6 and the yellow solution was transferred into a sealable J-Young NMR tube. The sample was degassed using a freeze-pump-thaw method and filled with 1 atm of H_2 at −196 °C. Subsequently, it was first warmed to ambient temperature, then heated to 50 °C. After 1 d of warming, **4** started to form and after 4 d compound **5** was established. Both complexes could not be isolated and characterised in detail because of their incomplete formation.

Analytical data of 4: ^{1}H NMR (400 MHz, 297 K, C_6D_6): $\delta = 1.87$ (s, 30 H, C_5Me_5), 4.80 (s, 1 H, Zr-H), 6.54 (m, 1 H, py), 7.08 (m, 1 H, py), 7.66 (m, 1 H, py), 8.72 (m, 1 H, py), 9.78 ppm (s, 1 H, N=CH); ^{13}C NMR (100 MHz, 297 K, C_6D_6): $\delta = 11.8$ (C_5*Me*$_5$), 115.1 (*C*$_5$Me$_5$), 119.2, 123.1, 125.9, 132.5 (C_{py}), 155.7 (*ipso*C_{py}), 160.1 ppm (N=CH).

Analytical data of 5: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.72$ (s, 30 H, C_5Me_5), 6.84 (m, 2 H, py), 7.30 (m, 2 H, py), 7.94 (m, 2 H, py), 8.64 (m, 2 H, py), 9.96 ppm (s, 2 H, N=CH); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 11.4$ (C_5*Me*$_5$), 117.6 (*C*$_5$Me$_5$), 116.7, 123.5, 137.3 (C_{py}), 149.8 (*ipso*C_{py}), 160.4 ppm (N=CH). The forth C_{py} signal could not be identified.

Reactions with CO_2

Synthesis of 6: Cp*$_2$Ti(N=C(2-py)–C(2-py)=N) (**1a**; 0.159 g, 0.3 mmol) was given into a three-necked-flask equipped with a pressure release valve and dissolved in toluene under stirring. CO_2 (using solid CO_2) was passed through a P_4O_{10} filled column and then bubbled through the solution of **1a** for at least 30 min to saturate the solution and the atmosphere. Subsequently, the flask was closed and warmed to 50 °C for 4 d. All volatiles were removed in vacuum. The remaining brown solid was dissolved in *n*-hexane. Upon cooling to −78 °C a brown precipitate formed, which was separated by decanting and dried in vacuum to give pure **6**. Yield: 0.124 g (0.26 mmol, 88 %); m.p.: 186 °C (dec. under Ar); ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.73$ (s, 30 H, C_5Me_5), 6.64 (m, 1 H, py), 7.26 (m, 1 H, py), 8.59 (m, 1 H, py), 8.71 ppm (m, 1 H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 11.6$ (C_5*Me*$_5$), 124.1 (*C*$_5$Me$_5$), 123.0, 124.1, 135.8, 149.9 (C_{py}), 154.9, 157.5 (*ipso*C_{py} or C=N), 165.7 ppm (C=O); IR (ATR): $\tilde{\nu} = 2905$ (w), 1647 (vs, C=O), 1578 (m, C=N), 1377 (s), 743 cm^{-1} (s); MS: *m/z* (CI): 467 (100) [*M*+H]$^+$, 318 (9) [Cp*$_2$Ti]$^+$, 137 (49) [Cp*+2 H]$^+$, 105 (68) [(2-py–C≡N)+H]$^+$; elemental analysis calcd (%) for $C_{27}H_{34}N_2O_2Ti$ (466.45 g mol^{-1}): C 69.52, H 7.35, N 6.01; found: C 69.43, H 7.27, N 6.33.

Synthesis of 7: A toluene solution of Cp*$_2$Zr(N=C(2-py)–C(2-py)=N) (**2**; 0.285 g, 0.5 mmol) was transferred into a three-necked-flask equipped with a pressure release valve. CO_2 (using solid CO_2) was passed through a P_4O_{10} filled column and then bubbled through the solution. The colour changed immediately from yellow to brown. All volatiles were removed in vacuum and the brown residue was dissolved in a toluene/*n*-hexane mixture (3:2). The solution was allowed to stand at −78 °C and a brown solid formed. It was isolated by decanting and dried in vacuum to give pure **7**. Crystals suitable for an X-ray crystal structure analysis were obtained by cooling a warm toluene/*n*-hexane mixture (3:2, 50 °C) of **7** slowly to ambient temperature. Yield: 0.245 g (0.40 mmol, 80 %); m.p.: 215–218 °C (dec. under Ar); ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.81$ (s, 30 H, C_5Me_5), 6.51 (m, 1 H, py), 6.54 (m, 1 H, py), 7.19 (m, 1 H, py), 7.22 (m, 1 H, py), 7.87 (m, 1 H, py), 8.00 (m, 1 H, py), 8.12 (m, 1 H, py), 8.45 ppm (m, 1 H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 10.9$ (C_5*Me*$_5$), 118.9 (*C*$_5$Me$_5$), 122.0, 122.1, 124.4, 127.1, 135.5, 135.9, 147.2, 148.1 (C_{py}), 152.1, 152.4 (*ipso*C_{py}), 157.5, 161.2, 165.4 ppm (C=N or C=O); IR (ATR): $\tilde{\nu} = 2905$ (w), 1704 (vs, C=O), 1665 (m, C=N), 1581 (m, C=N), 1222 (s, C-O), 737 cm^{-1} (s); MS: *m/z* (CI): 596 (2) [*M*−O]$^+$, 136 (100) [Cp*+H]$^+$, 105 (39) [(2-py–C≡N)+H]$^+$; elemental analysis calcd (%) for $C_{33}H_{38}N_4O_2Zr$ (613.92 g mol^{-1}): C 64.56, H 6.24, N 9.13; found: C 64.32, H 6.15, N 9.57.

Reactions with CH_3–C≡N

Synthesis of 8 and 9: Cp*$_2$Ti(N=C(2-py)–C(2-py)=N) (**1a**; 0.284 g, 0.5 mmol) was dissolved in CH_3–C≡N (10 mL) and the solution was stirred for 24 h. The colour changed from red to brown. All volatiles were removed in vacuum and the remaining brown solid washed with *n*-hexane to give at first a dark-violet and then a brown fraction. The remaining yellow residue was dried in vacuum to give **9** in high purity. Cooling the dark-violet solution to −78 °C resulted in a brown solid, which was separated by decanting. The dark-violet filtrate was evaporated to dryness to give pure **8**. For a higher yield of both products the brown solid and the brown solution were worked up further. Crystals of **8** suitable for X-ray analysis were obtained by cooling a saturated *n*-hexane solution of **8** to −78 °C. Crystals of **9** suitable for X-ray analysis formed at ambient temperature by slow evaporation of a C_6D_6 solution.

Analytical data of 8: Yield: 0.082 g (0.16 mmol, 29%); m.p.: 193 °C (dec. under Ar); ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.79$ (s, 30H, C_5Me_5), 6.47 (m, 2H, py), 6.85 (m, 2H, py), 7.36 (m, 2H, py), 7.99 (s, 2H, N-H), 8.57 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta =$ 12.0 ($C_5\mathit{Me}_5$), 117.8 (C_5Me_5), 119.7, 123.8, 134.4, 149.5 (C_{py}), 144.3 ppm (ipsoC_{py} or C=NH); IR (ATR): $\tilde{\nu} = 3345$ (vw, N-H), 2894 (w), 1578 (s, C=C), 1442 (s, C-N), 780 cm^{-1} (vs); MS: m/z (CI): 528 (100) $[M]^+$, 318 (4) $[Cp^*_2Ti]^+$, 137 (96) $[Cp^*+2H]^+$, 105 $[(2\text{-py}-C{\equiv}N)+H]^+$; elemental analysis calcd (%) for $C_{32}H_{40}N_4Ti$ (528.57 g mol^{-1}): C 72.72, H 7.63, N 10.60; found: C 72.56, H 7.66, N 10.63.

Analytical data of 9: Yield: approximately 0.069 g (0.016 mmol, 29%; contaminated by unidentified impurities). ^{1}H NMR (400 MHz, 297 K, C_6D_6): $\delta = 1.57$ (s, 30H, C_5Me_5), 2.01 (d, $^4J(^1H\text{-}^1H) = 0.9$ Hz, 3H, 4-Me), 2.19 (s, 3H, 6-Me), 4.27 ppm (s, 1H, N-H); ^{13}C NMR (100 MHz, 297 K, C_6D_6): $\delta = 11.5$ ($C_5\mathit{Me}_5$), 24.2 (6-Me), 27.8 (4-Me), 78.0 (C2), 120.3 (C_5Me_5), 124.6 (C5), 158.8 (C3), 165.1 ppm (C1) (Numbering is consistent with molecular structure Figure 3); IR (ATR): $\tilde{\nu} = 3278$ (vw, N-H), 2905 (w), 2156 (m, C≡N), 1603 (m, C=N), 1546 (w, C=N), 417 cm^{-1} (vs); MS: m/z (CI): 440 (83) $[M+H]^+$, 318 (2) $[Cp^*_2Ti]^+$, 137 (100) $[Cp^*+2H]^+$, 123 (3) $[(N{=}C(CH_3){-}C(CN){=}C(CH_3){-}N(H)) + 2H]^+$.

Reactions with $SOCl_2$

Preparation of 15a: A toluene solution of $Cp^*_2Ti(N{=}C(2\text{-py}){-}C(2\text{-py}){=}N)$ (**1a**; 0.263 g, 0.5 mmol) was cooled to −78 °C and then a 0.2 M toluene solution of $SOCl_2$ (2.5 mL, 0.5 mmol) was added. Subsequently, the mixture was warmed to ambient temperature to complete the conversion to **13** and **15a**. By cooling the mixture to −78 °C a red precipitate of **13** formed, which was separated by decanting. The filtrate was concentrated. After the addition of *n*-hexane to it, the solution was cooled to −78 °C. Yellow and red crystals formed, which were separated manually. The yellow crystals were identified as **15a**, the red ones as **13**.

Analytical data of 15a: Yield: 0.050 g (0.20 mmol, 40%); m.p.: 105 °C (dec. under Ar); ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.50$ (m, 2H, py), 6.93 (m, 2H, py), 7.53 (m, 2H, py), 7.96 ppm (s, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 124.7$, 125.1, 136.4, 148.4 (C_{py}), 150.8, 167.6 ppm (ipsoC_{py} or C=N); IR (ATR): $\tilde{\nu} = 1581$ (m, C=N), 1432 (w, C=N), 1123 (s), 540 cm^{-1} (vs); MS: m/z (CI): 257 (100) $[M+H]^+$, 241 (87) $[M-O]^+$, 105 (14) $[(2\text{-py}-C{\equiv}N)+H]^+$.

Conversion of 15a to 16a: A mixture of **15a** and **13** was dissolved in C_6D_6 and given into a sealable J-Young NMR tube and allowed to stand at ambient temperature for 3 d. Subsequently, it was warmed to 60 °C for 38 h. NMR spectra were measured after 3 d at ambient temperature, after 2, 14, 26 and 38 h at 60 °C. They revealed the conversion of **15a** and **13** to **16a**, decamethylfulvalene (Cp^*_2), tetramethylfulvene, pentamethylcyclopentadiene (Cp*H) and the formal [Cp*Ti] species.

Analytical data of 16a: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.59$ (m, 2H, py), 7.09 (m, 2H, py), 7.70 (m, 2H, py), 8.25 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 123.3$, 124.1, 136.1, 148.9 (C_{py}), 153.3, 161.0 ppm (ipsoC_{py} or C=N).

Analytical data of Cp^*_2: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.15$ (s, 6H, 1/1′-Me), 1.67 (s, 12H, Me), 1.76 ppm (s, 12H, Me); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 11.1$ (Me), 19.7 (Me), 60.2 ppm (C1/C1′). The remaining signals were not unambiguously identified.

Analytical data of tetramethylfulvene: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 1.69$ (s, 6H, Me), 1.85 (s, 6H, Me), 5.33 ppm (s, 2H, CH_2).

Analytical data of Cp*H: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 0.99$ (d, $^3J = 7.8$ Hz, 3H, 1-Me), 1.74 (m, 6H, Me), 1.80 (s, 6H, Me), 2.42 ppm (m, 1H, Cp-H).

Analytical data of the formal [Cp*Ti] species: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 2.08$ (C_5Me_5); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta =$ 13.3 ($C_5\mathit{Me}_5$), 134.0 ppm (C_5Me_5).

Preparation of 15b and 16b: $Cp^*_2Ti(N{=}C(6\text{-CN-2-py}){-}C(6\text{-CN-2-py}){=}N)$ (**12**) was synthesised in situ from $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.488 g, 1.0 mmol) and 2,6-dicyanopyridine (0.285 g, 2.2 mmol) as described in the published procedure.[17] It was dissolved in toluene and the solution was cooled to −78 °C. A 0.2 M toluene solution of $SOCl_2$ (5.0 mL, 1.0 mmol) was added. This resulted in the formation of a red solid. After warming to ambient temperature the red solution was filtered off the now brownish solid. The residue was washed twice with cold toluene and dried in vacuum. NMR spectra revealed that it consisted of **13** and **15b**. (Attempts to separate this mixture were unsuccessful due to similar solubility and the subsequent reaction.) The brownish solid was dissolved in toluene and the brown solution was warmed to 60 °C for 7 d. NMR spectra were measured before and after the heating. They revealed the conversion of **13** and **15b** to **16b**, decamethylfulvalene (Cp^*_2), tetramethylfulvene and the formal [Cp*Ti] species.

Analytical data of 15b: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.47$ (m, 2H, py), 6.58 (m, 2H, py), 7.22 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 116.3$ ($\mathit{C}{\equiv}N$), 127.2, 129.4, 137.8 (C_{py}), 132.3 ($\mathit{ipsoC}_{py-C{\equiv}N}$), 150.4 ($\mathit{ipsoC}_{py}$), 164.9 ppm ($\mathit{C}$=N); MS: m/z (CI): 307 (49) $[M+H]^+$.

Analytical data of 16b: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.53$ (m, 2H, py), 6.65 (m, 2H, py), 7.40 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 117.0$ ($\mathit{C}{\equiv}\mathit{N}$), 126.5, 129.3, 137.3 ($C_{py}$), 132.8 ($\mathit{ipsoC}_{py-C{\equiv}N}$), 152.9, 158.7 ppm ($\mathit{ipsoC}_{py}$ or C=N). MS: m/z (CI): 291 (100) $[M+H]^+$.

Preparation of 15c and 16c: A toluene solution of $Cp^*_2Ti(N{=}C(2\text{-Br-5-py}){-}C(2\text{-Br-5-py}){=}N)$ (**14**; 0.360 g, 0.5 mmol) was cooled to −78 °C and then a 0.2 M toluene solution of $SOCl_2$ (2.5 mL, 0.5 mmol) was added. After warming to ambient temperature the mixture consisted of **13**, **15c** and **16c**. (Attempts to separate **15c** from these compounds were unsuccessful due to similar solubility.) After 2 weeks at ambient temperature the mixture contained **13**, **15c** (minor concentration), **16c**, the formal [Cp*Ti] species and [Cp*]. Crystals of **16c** formed by cooling a THF solution of this mixture to −78 °C.

Analytical data for 15c: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.53$ (m, 2H, py), 6.61 (m, 2H, py), 7.90 ppm (m, 2H, py); ^{1}H NMR (400 MHz, 300 K, $[D_8]$THF): $\delta = 7.70$ (m, 2H, py), 7.82 (m, 2H, py), 8.60 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 124.1$, 139.3, 150.4 (C_{py}), 137.3, 155.7 (ipsoC_{py}), 164.4 ppm (C=N); ^{13}C NMR (100 MHz, 300 K, $[D_8]$THF): $\delta = 128.7$, 140.4, 151.7 ppm (C_{py}). The signals of the quaternary C atoms could not be detected. MS: m/z (ESI-TOF): 436.9 $[M+Na]^+$.

Analytical data for 16c: ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.75$ (m, 4H, py), 8.24 (m, 2H, py); ^{1}H NMR (300 MHz, 300 K, $[D_8]$THF): $\delta = 7.63$ (m, 2H, py), 7.77 (m, 2H, py), 8.54 ppm (m, 2H, py); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 127.9$, 137.8, 150.0 (C_{py}), 149.7, 155.8 ppm (ipsoC_{py} or C=N); ^{13}C NMR (100 MHz, 300 K, $[D_8]$THF): $\delta =$ 128.8, 139.3, 150.7 ppm (C_{py}). The remaining signals could not be detected in neither solvent. MS: m/z (ESI-TOF): 398.9 $[M+H]^+$; elemental analysis calcd (%) for $C_{12}H_6N_4Br_2S$ (398.08 g mol^{-1}): C 36.21, H 1.52, N 14.07, S 8.05; found: C 36.24, H 1.40, N 13.94, S 8.23.

Preparation of 16d: $Cp^*_2Ti(N{=}C(Ph){-}C(Ph){=}N)$ (**1b**) was synthesised in situ from $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (0.244 g, 0.5 mmol) and Ph−C≡N (0.10 mL, 1.0 mmol) as described in the published procedure.[15a] Then, the toluene solution was cooled to −78 °C and a 0.2 M toluene solution of $SOCl_2$ (2.5 mL, 0.5 mmol) was added. The mixture was warmed to ambient temperature and all volatiles were removed in vacuum. The remaining solid, consisting of **13** and **16 d** was separated by column chromatography (cyclohexane/ethyl acetate 8:1). Yield: 0.049 g (0.197 mmol, 39 %); ^{1}H NMR (300 MHz, 297 K, C_6D_6): $\delta = 6.82$ (m, 4 H, Ph), 6.97 (m, 2 H, Ph), 7.11 ppm (m, 4 H, Ph); ^{13}C NMR (75 MHz, 297 K, C_6D_6): $\delta = 128.3$, 130.3, 132.0 (C_{Ph}), 130.9 ($ipsoC_{Ph}$), 168.3 ppm ($C{=}N$). (For the comparison of the NMR data with the literature known the ^{1}H NMR spectrum was also measured in $CDCl_3$[36a] and the ^{13}C NMR in $[D_6]$DMSO[36b]). MS: m/z (CI): 239 (100) $[M+H]^+$.

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Keywords: exchange reaction · metallacycles · metallocenes · reactivity · small molecules

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FULL PAPER

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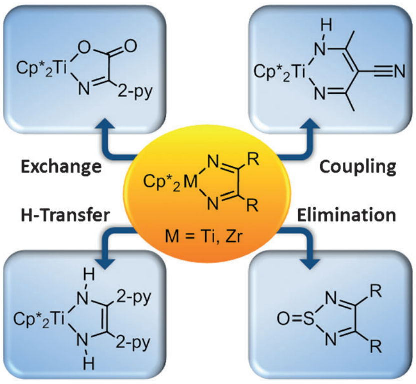
Reactivity Study of Pyridyl-Substituted 1-Metalla-2,5-diaza-cyclopenta-2,4-dienes of Group 4 Metallocenes



How nitrile cycles react: The reactions of pyridyl-substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes of group 4 metallocenes towards small molecules were investigated. In case of the addition of H_2, CO_2 and different nitriles exchange products were obtained. A C–C coupling and an H-transfer were observed in the reaction with $CH_3{-}C{\equiv}N$. The addition of $SOCl_2$ resulted in the formation of $Cp^*_2MCl_2$ and in thiadiazole oxides.

Group 4 Metallocenes

The picture highlights the central role of the symmetrically pyridyl substituted 1-metalla-2,5-diaza-cyclopenta-2,4-dienes $Cp^*_2M(N{=}C(2\text{-py}){-}C(2\text{-py}){=}N)$, the youngest members of the group 4 metallocene (M = Ti, Zr) family. The mystic tree and its reflection on the water surface connects these substrates with the unsymmetrically and fascinating molecules gained from their reactions with small molecules like H_2, CO_2, $CH_3{-}C{\equiv}N$, and $SOCl_2$. For example, for the zirconium complex a reversible coordination of CO_2 to the five-membered cycle was observed. In case of the titanium compound and $CH_3{-}C{\equiv}N$ a coupling product of three acetonitrile molecules was obtained. For more details, see the Full Paper by U. Rosenthal et al. on page ■■ff.