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Reactions of Group 4 Metallocene Complexes with Mono- and Diphenylacetonitrile: Formation of Unusual Four- and Six-Membered Metallacycles

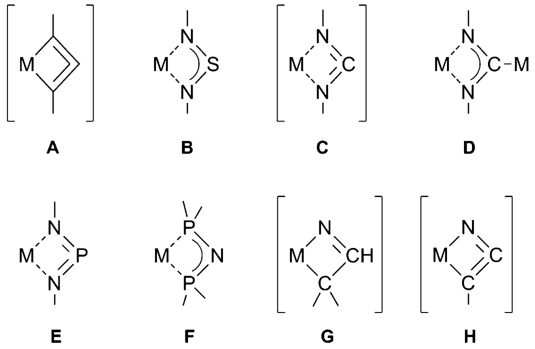
Lisanne Becker,[a] Vladimir V. Burlakov,[a, b] Perdita Arndt,[a] Anke Spannenberg,[a] Wolfgang Baumann,[a] Haijun Jiao,[a] and Uwe Rosenthal*[a]

Abstract: Reactions of Group 4 metallocene alkyne complexes $[Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**: M = Zr, Cp′ = Cp* = η^5-pentamethylcyclopentadienyl; **2a**: M = Ti, Cp′ = Cp*, and **2b**: M = Ti, Cp'_2 = *rac*-(ebthi) = *rac*-1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with diphenylacetonitrile (Ph_2CHCN) and of the seven-membered zirconacyclocumulene **3** with phenylacetonitrile ($PhCH_2CN$) were investigated. Different compounds were obtained depending on the metal, the cyclopentadienyl ligand and the reaction temperature. In the first step, Ph_2CHCN coordinated to **1** to form $[Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)(NCCHPh_2)]$ (**4**). Higher temperatures led to elimination of the alkyne, coordination of a second Ph_2CHCN and transformation of the nitriles to a keteniminate and an imine ligand in $[Cp^*_2Zr(NC_2Ph_2)(NCHCHPh_2)]$ (**5**). The conversion of **4** to **5** was monitored by using ^1H NMR spectroscopy. The analogue titanocene complex **2a** eliminated the alkyne first, which led directly to $[Cp^*_2Ti(NC_2Ph_2)_2]$ (**6**) with two keteniminate ligands. In contrast, the reaction of **2b** with diphenylacetonitrile involved a formal coupling of the nitriles to obtain the unusual four-membered titanacycle **7**. An unexpected six-membered fused zirconaheterocycle (**8**) resulted from the reaction of **3** with $PhCH_2CN$. The molecular structures of complexes **4**, **5**, **6**, **7** and **8** were determined by X-ray crystallography.

Keywords: metallacycles · N ligands · titanium · zirconium

Introduction

During the last decades, low-membered metallacycles of Group 4 metallocenes have attracted great interest because of their stability and reactivity. In particular, the three- and five-membered all-carbon metallacycles, metallacyclopropenes, 1-metallacyclopent-3-ynes (metallacyclopentynes), 1-metallacyclopenta-2,3,4-trienes (metallacyclocumulenes) and 1-metallacyclopenta-2,3-dienes (metallacycloallenes) were synthesised to study their reaction behaviour.[1] The analogue all-carbon four-membered metallacyclobuta-2,3-diene of Group 4 metallocenes (**A**, Scheme 1) has not been successfully prepared to date, but theoretical studies have predicted its existence.[2] In most cases, the stabilisation of strained ring systems has been realised by incorporating heteroatoms.[1b,3] Therefore, we were interested in the synthesis of four-membered heterometallacycles of Group 4 metallocenes. The reactions of $[Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (M = Ti, no L; M = Zr, L = pyridine; Cp = η^5-cyclopentadienyl) with the sulfur diimide $Me_3SiN{=}S{=}NSiMe_3$ gave the four-membered metallacycles $[Cp_2M(\kappa^2\text{-}N,N\text{-}Me_3SiNSNSiMe_3)]$ (M = Ti, Zr; **B**).[4] Additionally, the reaction of $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ with the carbodiimide $CyN{=}C{=}NCy$ (DCC) formed a dimetallic complex, with coordination of the metal fragments to the two nitrogen atoms and to the central carbon atom of the substrate (**D**).[5]



Scheme 1. Different four-membered metallacycles.

In the reaction of $[Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (py = pyridine) with the same carbodiimide, the five-membered

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[a] L. Becker, Dr. V. V. Burlakov, Dr. P. Arndt, Dr. A. Spannenberg, Dr. W. Baumann, Dr. H. Jiao, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Straße 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51176
E-mail: uwe.rosenthal@catalysis.de

[b] Dr. V. V. Burlakov
A. N. Nesmeyanov Institute of Organoelement Compounds
Russian Academy of Sciences
Vavilov St. 28, 119991, Moscow (Russia)

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heterometallacycloallene complex [$Cp_2Zr(Me_3SiC{=}C{=}C\{N(SiMe_3)(Cy)\}N(Cy))$] was obtained.[6] In a very recent study of the coordination chemistry of the bis(diphenylphosphino)amide ligand [Ph_2P-*N*-PPh_2] in Group 4 metallocenes, the highly strained four-membered heterometallacycles [$Cp_2M(\kappa^2$-*P,P*-$Ph_2PNPPh_2)$] (M = Ti, Zr; **F**) were formed.[7]

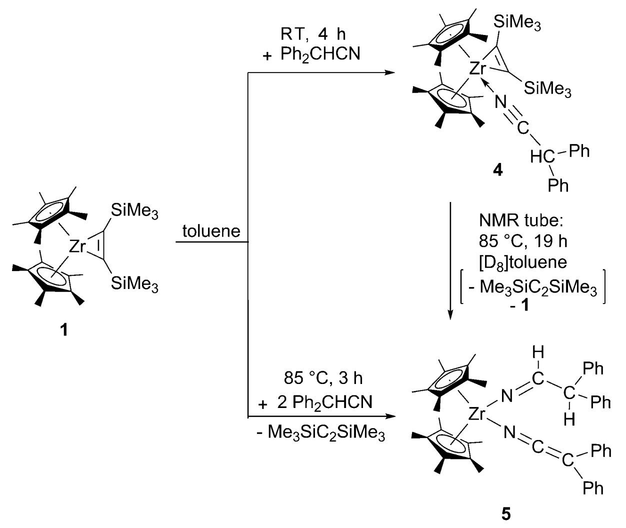
Due to these results, we were interested in the reactions of Group 4 metallocenes with nitriles. These substrates are known for insertion reactions in Group 4 organometallic chemistry.[8] In the presence of an acidic α-proton, a deprotonation of the nitrile and the formation of keteniminate species can take place.[9] Notably, the total deprotonation of monophenylacetonitrile ($PhCH_2CN$) or the complexation of diphenylacetonitrile (Ph_2CHCN) can occur to give as yet unknown four-membered metallacycles that contain only one nitrogen atom, for example, [$Cp'_2M(\kappa^2$-*N,C*-$N{=}CHCPh_2)$] (**G**) or [$Cp'_2M(\kappa^2$-*N,C*-$N{=}C{=}CPh)$] (**H**). Xi and co-workers investigated the reactions of diphenylacetonitrile with zirconocene complexes to obtain five-membered heterometallacycles by alkyne nitrile coupling. This involved deprotonation of a second nitrile and its conversion to a keteniminate ligand due to the need to stabilise the formed azazirconacyclopentadiene intermediate.[10] Other examples of isolated products of alkyne nitrile coupling at Group 4 metallocene complexes are also stabilised by, for example, transfer of H, but they are few in number.[11]

Herein, we describe reactions of different alkyne complexes [$Cp'_2M(\eta^2$-$Me_3SiC_2SiMe_3)$] **1** (M = Zr, Cp′ = Cp* = η^5-pentamethylcyclopentadienyl); **2a** (M = Ti, Cp′ = Cp*) and **2b** (M = Ti, Cp'_2 = *rac*-(ebthi) = *rac*-1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with diphenylacetonitrile and of the seven-membered zirconacyclocumulene **3** with $PhCH_2CN$. Unfortunately, we could not obtain the predicted and very attractive four-membered metallacycles [$Cp'_2M(\kappa^2$-*N,C*-$N{=}CHCPh_2)$] (**G**) and [$Cp'_2M(\kappa^2$-*N,C*-$N{=}C{=}CPh)$] (**H**).

Results and Discussion

Treatment of a solution of [$Cp^*_2Zr(\eta^2$-$Me_3SiC_2SiMe_3)$] (**1**)[12] in toluene with one equivalent of diphenylacetonitrile at ambient temperature led to complex **4**, which could be isolated as yellow crystals in 77 % yield (Scheme 2).

In addition to the signals of the Cp* ligand, ^1H and ^{13}C NMR spectra of **4** revealed characteristic resonances of the alkyne (^1H: $\delta = 0.49$ ppm, ^{13}C: $\delta = 232.7$ ppm ($C{\equiv}C$)) and the coordinated nitrile (^1H: $\delta = 5.02$ ppm (CH), ^{13}C: $\delta = 117.8$ ppm ($C{\equiv}N$)). These values are in the same range as those observed for the corresponding zirconocene complexes (**1**: ^{13}C: $\delta = 260.5$ ($C{\equiv}C$),[12] [$Cp_2Zr(py)(\eta^2$-$Me_3SiC_2SiMe_3)$]: ^{13}C: $\delta = 220.5$ ppm ($C{\equiv}C$)[13]). The typical IR resonance of the C−N triple bond is shifted from 2240 to 2214 cm^{-1}. This slight change reveals the coordination as an η^1-ligand. The molecular structure of **4** (Figure 1) consists of a zirconocene with a coordinated alkyne and nitrile. In comparison with starting complex **1**, it shows a very similar $C{-}C_{alkyne}$ bond length (**1**: C1−C2 1.320(3), **4**: C1−C2 1.312(2) Å) of the alkyne. The C−N bond lengths in **4** and in the uncomplexed diphenylacetonitrile are the same (**4**: N1−C9 1.147(2) Å, Ph_2CHCN: N1−C9 1.147(2) Å).[9b] The structural motif is also known for a zirconacyclopropene complex, stabilised by $N{\equiv}C{-}t$Bu, ($C{-}C_{alkyne}$ 1.322(8) Å, C−N 1.150(9) Å).[8b]



Scheme 2. Reaction of complex **1** with Ph_2CHCN.

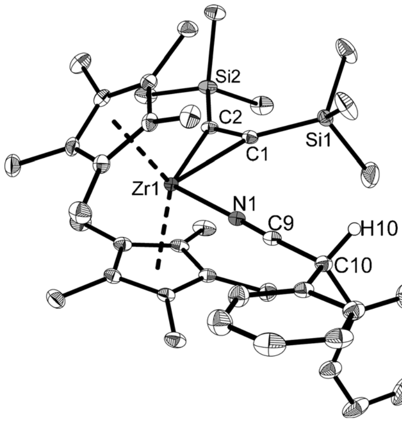


Figure 1. Molecular structure of **4** with thermal ellipsoids set at the 30 % probability level. All hydrogen atoms (except H10) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1−N1 2.309(1), C1−C2 1.312(2), N1−C9 1.147(2), C9−C10 1.479(2); N1-C9-C10 175.0(2).

The reaction of **1** with two equivalents of Ph_2CHCN at 85 °C gives, after elimination of the alkyne and a hydrogen transfer, red crystals of complex **5** (yield 85 %) with a keteniminate and an imine ligand (Scheme 2). The diphenylacetonitrile acts as a protonation agent due to its acidic α-proton and also as a proton acceptor. The resonances of the two different protons of the imine ligand appear in the ^1H NMR spectra at $\delta = 4.70$ ($CHPh_2$) and 9.12 ppm ($CH{=}N$). The strong shift of the second signal is caused by the neighbouring nitrogen. The signal of the Cp* ligand is shifted upfield ($\delta = 1.65$ ppm) in comparison with the corresponding complexes ($\delta = 1.76$[12] (**1**) and 1.75 ppm (**4**)). Furthermore, complex **5** was characterised by IR spectroscopy. The strong infrared band at 2048 cm^{-1} was assigned to the N=C=C stretching mode, as observed for lithium[9b] and barium keteniminate complexes.[9c] In contrast to **4**, this is a shift of nearly 200 cm^{-1} in comparison to diphenylacetonitrile (2240 cm^{-1} (N≡C)). This illustrates the conversion of the triple bond to a C–N double bond.

Complex **5** was characterised by using X-ray diffraction (Figure 2), which revealed it as a zirconocene with a keteniminate and an imine ligand. The bonding situation of the keteniminate unit (N2–C15 1.170(3), C15–C16 1.366(4) Å) corresponds to that of the already described [$Cp_2Zr(C(SiMe_3)=C(Me)C(CHPh_2)=NH)(N=C=CPh_2)$] complex (N–C 1.159(5), C–C 1.386(6) Å).[10] The N2-C15-C16 angle (176.7(3)°) confirms the almost linear nature. In contrast, the second ligand in **5** is an imine species (N1–C1 1.232(3), C1–C2 1.521(4) Å; N1-C1-C2 125.5(3), C1-C2-C3 114.2(2), C1-C2-C9 109.7(2), Zr1-N1-C1 164.6(2)°), which is comparable with the molecular structure of the known zirconocene complex [$Cp_2ClZr(N=CHPh)$][14] (N–C 1.259(7) Å; Zr-N-C 170.5(5)°). A titanocene complex with such an imine ligand was also described (N–C 1.258(6), C–C 1.487(6) Å).[15] Several examples with similar imine ligands are known in the literature for elements such as niobium,[16] aluminium,[17] iron[18] and samarium.[19]

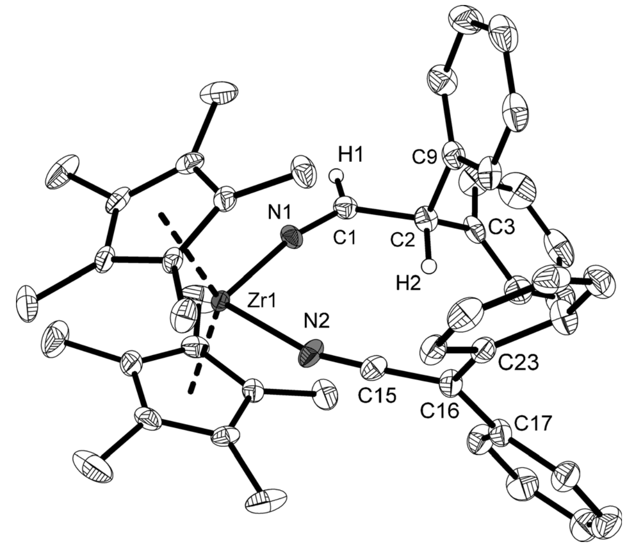
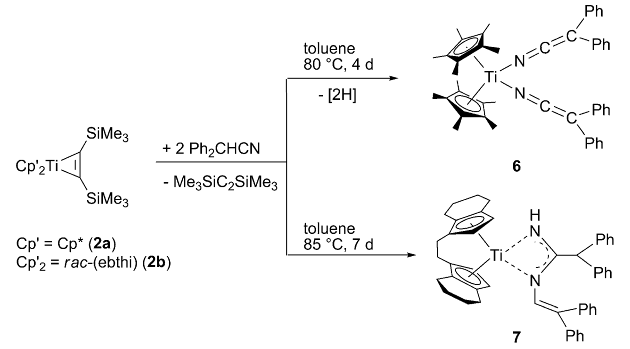


Figure 2. Molecular structure of **5** with thermal ellipsoids set at the 30% probability level. All hydrogen atoms (except H1 and H2) and the second molecule of the asymmetric unit have been omitted for clarity. Selected bond lengths [Å] and angles [°], corresponding values of the second molecule in the asymmetric unit are given in square brackets: Zr1–N1 2.036(2) [Zr2–N3 2.026(2)], Zr1–N2 2.177(2) [Zr2–N4 2.184(2)], N1–C1 1.232(3) [N3–C49 1.243(3)], N2–C15 1.170(3) [N4–C63 1.169(3)], C1–C2 1.521(4) [C49–C50 1.526(3)], C15–C16 1.366(4) [C63–C64 1.367(4)]; N1-C1-C2 125.5(3) [N3-C49-C50 123.1(3)], N2-C15-C16 176.7(3) [N4-C63-C64 178.9(3)], Zr1-N1-C1 164.6(2) [Zr2-N3-C49 171.6(2)].

In regard to a possible formation pathway, we considered complex **4** to be an intermediate of the reaction from **1** to **5**. This was corroborated by heating the solution of **4** in [D$_8$]toluene to 85 °C. The ^{1}H NMR spectra of the solution were recorded before heating and after 19 h at 85 °C. After heating, the signals of complex **4** ($\delta = 0.32$ (SiMe_3), 1.69 (C_5Me_5), 4.86 ppm ($CH_{nitrile}$)) disappeared. This implies that two molecules of **4** were converted into one molecule of **5** ($\delta = 1.59$ (C_5Me_5), 4.56 ($C_\beta H$), 9.03 ppm ($C_\alpha H$)), one molecule of **1** ($\delta = 0.11$ (SiMe_3), 1.71 ppm (C_5Me_5)) and one free $Me_3SiC_2SiMe_3$ molecule ($\delta = 0.09$ ppm (SiMe_3)).

The reaction of the analogous titanocene alkyne complex [$Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**2a**)[20] with diphenylacetonitrile in toluene was completed after 4 d at 80 °C and gave the bis-keteniminate complex **6** (Scheme 3). Its molecular ion peak in the mass spectrum can be found at *m*/*z* 702. The IR resonances of the N=C=C bonds are located at 2060 and 2025 cm^{-1} and are thus in the same region as for complex **5**. A decisive characterisation of complex **6** by NMR spectroscopy was not possible due to the formation of mixtures in solution. The molecular structure of **6** was confirmed by using X-ray analysis and is depicted in Figure 3. It shows two keteniminate units (N1–C1 1.179(3), C1–C2 1.360(3) Å) bonded to titanocene. The bond lengths and angles of these ligands are comparable to those of the keteniminate moiety in complex **5** and to similar complexes of zirconium,[10] iridium,[9a] indium,[9b] gallium,[9b] lithium,[9b,d] barium,[9c] magnesium[9c,g] and strontium.[9c]



Scheme 3. Reaction of titanocene complexes **2a** and **2b** with Ph_2CHCN.

Changing the cyclopentadienyl ligand from Cp* to *rac*-(ebthi) provokes a different kind of reaction. Whereas the nitriles were deprotonated and converted to keteniminate species in the reaction with **2a**, a coupling occurred when [Ti(*rac*-(ebthi))(η^2-$Me_3SiC_2SiMe_3$] (**2b**)[21] was applied. This was accompanied by a formal reduction of the metal from Ti^{IV} to Ti^{III}, and the unusual paramagnetic four-membered titanaheterocycle **7** is formed (Scheme 3). It is supposed that the origin of the additional hydrogen atom is either the solvent or a deprotonation of Ph_2CHCN.

Complex **7** was characterised by using mass spectrometry; its molecular ion peak can be found at *m*/*z* 699. The typical

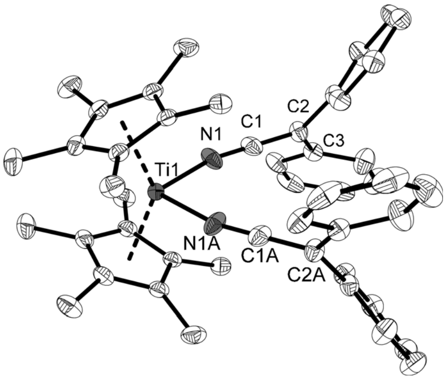


Figure 3. Molecular structure of **6** with thermal ellipsoids set at the 30% probability level. All hydrogen atoms and the second molecule of the asymmetric unit have been omitted for clarity. Selected bond lengths [Å] and angles [°], corresponding values of the second molecule in the asymmetric unit are given in square brackets: Ti1−N1 1.996(2) [Ti2−N2 2.002(2)], N1−C1 1.179(3) [N2−C25 1.177(3)], C1−C2 1.360(3) [C25−C26 1.359(3)]; N1-C1-C2 175.6(3) [N2-C25-C26 176.5(2)].

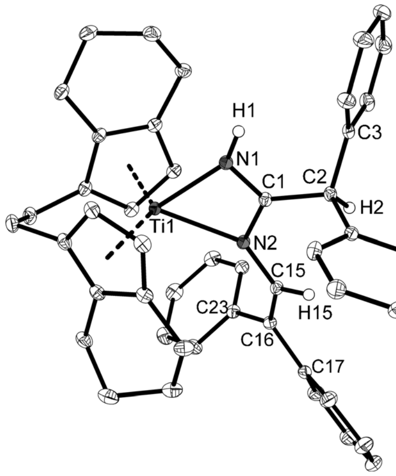
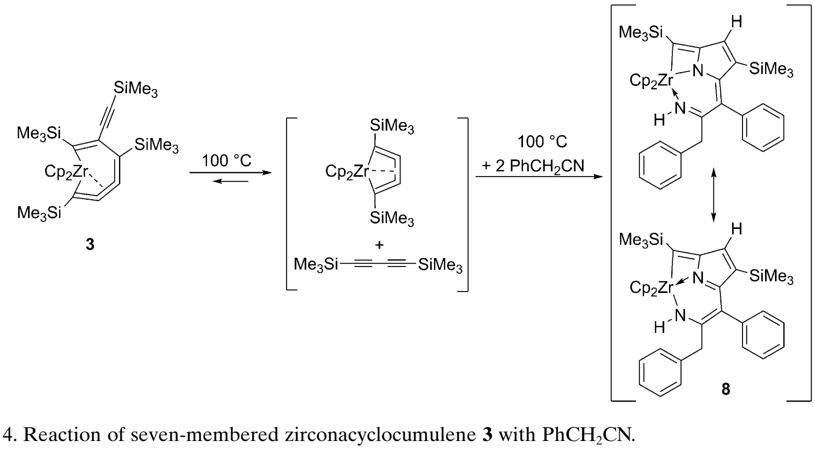


Figure 4. Molecular structure of **7** with thermal ellipsoids set at the 30% probability level. All hydrogen atoms (except H1, H2 and H15) and the solvent molecule (*n*-hexane) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1−N1 2.148(1), Ti1−N2 2.254(1), N1−C1 1.311(1), N2−C1 1.345(1), N2−C15 1.388(1), C1−C2 1.533(2); C1-N1-Ti1 96.32(7), C1-N2-Ti1 90.56(6), N1-Ti1-N2 60.27(3), N1-C1-N2 112.74(10), N1-C1-C2 124.42(10), N2-C1-C2 122.83(9).

IR resonances of the C−N bonds at 1489, 1502 and 1592 cm^{-1} are comparable to those of analogue four-membered metallacycles of other metals.[22,23] The molecular structure of **7** is depicted in Figure 4. Similar complexes with metals such as samarium,[22] molybdenum,[23] yttrium[24] or aluminium[25] were obtained in reactions of metal complexes of the appropriate elements with carbodiimides. Analogue four-membered paramagnetic titanaheterocycles were presumed to be intermediates in the reactions of [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] with carbodiimides. These need to be stabilised by complexation, dimerisation or substitution of the carbon atom in the ring system.[26] Compound **7** is comparable to the complexes of titanium and zirconium with guanidinate ligands, which consist of substituents at the ring carbon atom as well.[27] The coupling product of two nitriles with an yttrium complex was published very recently.[28]

The difference between complex **7** and the known structures, except the yttrium complex,[28] is the substitution of the nitrogen atoms. N1 carries a hydrogen atom, whereas an organic residue is found at N2. Therefore, the bond lengths and angles in the ring system differ (Ti1−N1 2.148(1), Ti1−N2 2.254(1), N1−C1 1.311(1), N2−C1 1.345(1) Å; C1-N1-Ti1 96.32(7), C1-N2-Ti1 90.56(6)°). This structural feature can also be found in the yttrium compound [CpY(N(H)C(Ph)-NC(Ph)=CHPh)(Tp^{Me_2})] (Y1−N1 2.371(3), Y1−N2 2.430(3), N1−C1 1.312(5), N2−C1 1.332(5) Å; C1-N1-Y1 96.4(2), C1-N2-Y1 93.2(2)°).[28] The titanacycle reveals two relatively short N−C bonds (see N1−C1, N2−C1 above), which indicates a partial N−C double-bond character.[5] Additionally, the angles of N1-C1-C2 (124.42(10)°), N2-C1-C2 (122.83(9)°) and N1-C1-N2 (112.74(10)°) illustrate the sp^2 hybridisation of carbon atom C1.

Additionally, coupling of two nitriles is observed in the reaction of seven-membered zirconacyclocumulene **3**[29] with two equivalents of phenylacetonitrile. It is presumed that one butadiyne molecule is eliminated and a five-membered zirconacyclocumulene is formed as an intermediate in the first step of the reaction. Consequently, four- and five-membered cycles are obtained by coupling of one nitrile with the diyne in addition to insertion of $PhCH_2CN$. The coupling of the nitriles leads to a six-membered zirconaheterocycle **8** (Scheme 4), in contrast to complex **7**. Similar reactions of the alkyne complexes [$Cp_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (M = Ti, Zr) with phenylacetonitrile and with diphenylacetonitrile produced complex mixtures that have not been separated yet.



Scheme 4. Reaction of seven-membered zirconacyclocumulene **3** with $PhCH_2CN$.

The assumed reaction steps to form **8** from **3** are accompanied by shifts of the acidic α-protons of one of the nitriles. These protons show resonances in the ^{1}H NMR spectra at $\delta = 5.10$ and 6.99 ppm. The first signal is assigned to the proton at the nitrogen atom and the second proton is located at the former cumulene in the five-membered cycle. Furthermore, the ^{1}H NMR spectra shows two different signals for the $SiMe_3$ groups ($\delta = -0.09$, 0.43 ppm) and the resonance of the Cp at $\delta = 5.72$ ppm.

Single crystals of **8** for X-ray analysis were obtained from a solution in C_6D_6. The molecular structure, depicted in Figure 5, shows three different cycles. The four-membered metallacycle was formed by a formal N−C coupling of one nitrile and the diyne. The bond lengths of C1−C2 (1.360(3) Å) and C2−N1 (1.392(3) Å) correspond to a double bond and to a single bond, respectively. The Zr−N bond (Zr1−N1 2.162(2) Å) is also assigned to a single bond. In contrast, the bond between Zr and N2 is somewhat longer (Zr1−N2 2.282(2) Å), which is caused by the different substitution of the nitrogen atoms.

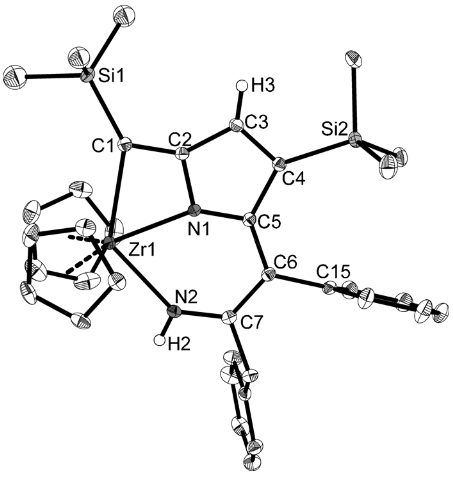


Figure 5. Molecular structure of **8** with thermal ellipsoids set at the 30% probability level. All hydrogen atoms (except H2 and H3) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1−N1 2.162(2), Zr1−N2 2.282(2), C1−C2 1.360(3), N1−C2 1.392(3), N1−C5 1.327(3), N2−C7 1.331(3), C3−C4 1.368(3), C4−C5 1.507(3), C5−C6 1.412(3), C6−C7 1.412(3); C2-C1-Zr1 89.76(15), C2-N1-Zr1 98.71(14), C5-N1-Zr1 149.27(17), C7-N2-Zr1 138.59(17), C5-C6-C7 119.0(2), C5-C6-C15 122.5(2), C7-C6-C15 118.6(2).

The N−C bond lengths of the planar six-membered zirconacycle, which is formed by coupling of the nitriles, are equal (N1−C5 1.327(3), N2−C7 1.331(3) Å). The same was observed for the C−C linkages (C5−C6 1.412(3), C6−C7 1.412(3) Å). This fact implies two possible resonance forms of **8** (Scheme 4). The angles of C5-C6-C7 (119.0(2)°), C5-C6-C15 (122.5(2)°) and C7-C6-C15 (118.6(2)°) highlight the proposed sp^2 hybridisation of the carbon atom C6.

It is presumed that the first step in the formation of complex **8** is an insertion of one nitrile into the M−C bond of the zirconacyclocumulene. As a result, a new C4−C5 bond (1.507(3) Å) is created. Such insertion reactions have already been established in zirconium-mediated multi-component reactions of butadiynes with nitriles[8] or carbamoyl cyanides.[30] The subsequent coupling of N1 and C2 leads to the formation of the five-membered cycle in **8**. In this ring system, the C3−C4 bond (1.368(3) Å) corresponds to a double bond. Due to the planarity of the six-membered zirconacycle, it could be considered as an aromatic system; theoretical calculations should lead to a better understanding.

Due to the interaction of the metal centre and the unsaturated carbon atoms on the metallacycle, metallacyclopropenes,[31] 1-metallacyclopent-3-ynes and 1-metallacyclopenta-2,3,4-trienes[32] have been characterised as aromatic on the basis of their geometric, (equalised C−C lengths), energetic (extra stabilisation energy) and magnetic (negative nucleus-independent chemical shifts (NICS) and downfield chemical shifts[33]) properties. The aromatic stabilisation is the governing factor for the stability of these low-membered metallacycles. To understand the possible aromatic nature of complex **8**, we calculated the NICS values for the four- (Zr1-N1-C2-C1), five- (N1-C2-C3-C4-C5) and six- (Zr1-N2-C7-C6-C5-N1) membered rings at 1 Å over the ring centres. As given in the Supporting Information, the computed structural parameters are in very good agreement with the data from X-ray analysis. The NICS(1) value is $\delta = -0.89$ ppm for the six-membered ring, $\delta = -4.97$ ppm for the five-membered ring and $\delta = -1.39$ ppm for the four-membered ring. The small NICS difference for six- and five-membered rings ($\delta = -4.97$ vs. -1.39 ppm) is in agreement with the difference in the observed ^{1}H NMR signals of H-C3 ($\delta = 6.99$ ppm) and H-N2 ($\delta = 5.10$ ppm). However, these rather small NICS values reveal the non-aromatic character of complex **8**.

Conclusion

Herein, we present a detailed experimental study of the reaction of phenylated nitriles with Group 4 metallocene alkyne complexes and a zirconacyclocumulene. Different compounds were obtained depending on the metal, the cyclopentadienyl ligand and the reaction temperature. The reactions of pentamethylcyclopentadienyl-substituted complexes **1** and **2a** with diphenylacetonitrile led to the formation of **4**, **5** and **6**, which contain the nitrile coordinated as an η^1-ligand, as either a keteniminate or an imine ligand. Replacement of the Cp ligand with *rac*-(ebthi) in **2b** resulted in a coupling of two nitriles and the four-membered metallacycle **7** is obtained. This ring system is stabilised by the substitution of the ring carbon atom. Another coupling of two nitriles was observed in the reaction of **3** with phenylacetonitrile to form **8**. This was accompanied by the formation of a four-membered metallacycle by coupling of the butadiyne and the nitrile. These results clearly show the different functions of nitriles in organometallic chemistry. Nitriles can behave as a coordination agent in complex **4**. Due to the acidic α-proton, nitriles act as protonation agents and also as proton acceptors, which promote the formation of compounds **5**–**8**. It is supposed that this behaviour influences the coupling reactions that lead to **7** and **8**. Studies on the reaction behaviour of the established complexes and of the reactions with differently substituted nitriles are still ongoing and will be published in due course.

Experimental Section

General information: All manipulations were carried out under an oxygen- and moisture-free argon atmosphere by using standard Schlenk and dry-box techniques. Non-halogenated solvents were dried over sodium/benzophenone and freshly distilled prior to use. Diphenylacetonitrile is commercially available and was dried in vacuum prior to use. Metallocene complexes **1**,[12] **2**,[20] **2b**[21] and **3**[29] were synthesised as described previously in the literature. NMR spectra were recorded by using Bruker AV300 and AV400 spectrometers. ^{1}H and ^{13}C chemical shifts were referenced to the solvent signals of [D$_6$]benzene (δ_H=7.16 ppm, δ_C=128.0 ppm) and [D$_8$]toluene (δ_H=2.03 ppm, δ_C=20.4 ppm). ^{29}Si chemical shifts are given relative to $SiMe_4$, ^{15}N chemical shifts are relative to nitromethane (Ξ=10.136767 MHz). Detailed NMR data of **4**, **5** and **8** are given in Supporting Information. IR spectra were recorded by using a Nicolet 6700 FT-IR spectrometer equipped with a smart endurance attenuated total reflection (ATR) device and a Bruker Alpha FT-IR spectrometer. MS data were recorded by using a Finnigan MAT 95-XP instrument (Thermo-Electron). Elemental analyses were recorded by using a Leco Tru Spec elemental analyser. Melting points were recorded by using an *E*/*Z*-Melt instrument (Stanford Research Systems). Melting points are uncorrected and were measured in sealed capillaries.

Computational details: Structure optimisation (**8**) has been carried out at the BP86[34] density functional level of theory with the TZVP basis set[35] for C, H, N, Si and the LANL2DZ basis set with the effective core potentials of Hay and Wadt for Zr[36] by using Gaussian 09 program package.[37] The optimized geometries are characterised as energy minima 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, whereas transition-state structures have only one imaginary frequency. To judge the extent of cyclic delocalisation of electrons in complex **8**, nucleus-independent chemical shifts (NICS) were calculated at the geometrical centre point of the ring. This gives an insight into the possible interaction between the Zr centre and the unsaturated carbon atoms in the metallacycle (see the Supporting Information).

Crystallographic data: Diffraction data for **4**, **5**, **6**, **7** and **8** were collected by using a Bruker Kappa APEX II Duo diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved by using direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[38] Diamond was used for graphical representations.[39]

Crystal data for **4**: $C_{42}H_{59}NSi_2Zr$; M_r=725.30; monoclinic; a=14.4529(2), b=16.2004(2), c=17.1335(3) Å; β=96.943(1)°; V=3982.27(10) Å^3; T=150(2) K; space group $P2_1/c$; Z=4; 99901 reflections measured, 8782 independent reflections (R_{int}=0.0362), final R values ($I>2\sigma(I)$): R_1=0.0271, wR_2=0.0656, final R values (all data): R_1=0.0353, wR_2=0.0709, 431 parameters.

Crystal data for **5**: $C_{48}H_{52}N_2Zr$; M_r=748.14; triclinic; a=14.9276(3), b=17.4124(4), c=18.0249(5) Å; α=65.159(1), β=68.119(1), γ=89.989(1)°; V=3876.74(16) Å^3; T=150(2) K; space group $P\bar{1}$; Z=4; 72384 reflections measured, 18482 independent reflections (R_{int}=0.0512), final R values ($I>2\sigma(I)$): R_1=0.0418, wR_2=0.0973, final R values (all data): R_1=0.0720, wR_2=0.1075, 903 parameters.

Crystal data for **6**: $C_{48}H_{50}N_2Ti$; M_r=702.80; monoclinic; a=17.9736(4), b=11.3581(2), c=19.2637(4) Å; β=95.665(1)°; V=3913.40(14) Å^3; T=150(2) K; space group $P2/c$; Z=4; 74831 reflections measured, 8396 independent reflections (R_{int}=0.0584), final R values ($I>2\sigma(I)$): R_1=0.0504, wR_2=0.1188, final R values (all data): R_1=0.0757, wR_2=0.1318, 447 parameters.

Crystal data for **7**: $C_{51}H_{54}N_2Ti$; M_r=742.86; triclinic; a=12.0263(3), b=12.5669(3), c=15.3150(3) Å; α=70.552(1), β=69.230(1), γ=89.308(1)°; V=2025.90(8) Å^3; T=150(2) K; space group $P\bar{1}$; Z=2; 98562 reflections measured, 10466 independent reflections (R_{int}=0.0387), final R values ($I>2\sigma(I)$): R_1=0.0334, wR_2=0.0836, final R values (all data): R_1=0.0417, wR_2=0.0892, 492 parameters.

Crystal data for **8**: $C_{36}H_{42}N_2Si_2Zr$; M_r=650.12; monoclinic; a=15.3032(4), b=10.3810(3), c=20.4205(6) Å; β=92.446(2)°; V=3241.10(16) Å^3; T=150(2) K; space group $P2_1/n$; Z=4; 81921 reflections measured, 7450 independent reflections (R_{int}=0.0523), final R values ($I>2\sigma(I)$): R_1=0.0375, wR_2=0.0883, final R values (all data): R_1=0.0501, wR_2=0.0951, 340 parameters.

CCDC-907143 (**4**), CCDC-907146 (**5**), CCDC-907144 (**6**), CCDC-907145 (**7**) and CCDC-907147 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of complex 4: A solution of Ph_2CHCN (0.193 g, 1.00 mmol) in toluene (10 mL) was added with stirring to a solution of **1** (0.530 g, 1.00 mmol) in toluene (5 mL). The orange solution was stirred 4 h at room temperature. The solvent was removed under vacuum and the residue washed with cold *n*-hexane. The resulting yellow crystals were dried under vacuum (yield: 0.556 g, 0.77 mmol, 77%). M.p: 112 °C (decomp.) under Ar; ^{1}H NMR (300 MHz, [D$_6$]benzene, 297 K): δ=0.49 (s, 18H, SiMe_3), 1.77 (s, 30H, C_5Me_5), 5.02 (s, 1H, C$H_{nitrile}$), 6.98 (m, 2H, CH_{Ph}), 7.04 (m, 4H, CH_{Ph}), 7.17 ppm (m, 4H, CH_{Ph}); ^{13}C NMR (75 MHz, [D$_6$]benzene, 297 K): δ=4.8 (SiMe_3), 12.3 (C_5Me_5), 44.9 ($CH_{nitrile}$), 113.9 (C_5Me$_5$), 117.8 (C≡N), 128.5, 128.7, 129.3 (CH-Ph), 135.5 (*i*-*C*-Ph), 232.7 ppm (C≡C); IR (ATR): $\tilde{\nu}$=2894 (w), 2214 (vw), 1491 (w), 1239 (m), 825 (vs), 738(s), 696 (vs), 650 (m), 624 (m), 542 (m), 459 cm^{-1} (m); MS (CI): *m*/*z* (%): 532 (12) [*M*-NCCHPh$_2$]$^+$, 360 (100) [Cp*$_2$Zr]$^+$, 194 (30) [Ph$_2$CHCN+H]$^+$; elemental analysis calcd (%) for $C_{42}H_{59}NSi_2Zr$: C 69.55, H 8.20, N 1.93; found: C 69.64, H 8.07, N 1.83.

Preparation of complex 5: To a stirred solution of **1** (0.530 g, 1.00 mmol) in toluene (5 mL) was added a solution of Ph_2CHCN (0.385 g, 2.00 mmol) in toluene (10 mL). The solution was stirred for 2 h at room temperature and subsequently for 4 h at 85 °C; the colour of the solution turned deep red. All volatiles were removed under vacuum and the residue was dissolved in *n*-hexane. After filtration, the solution was allowed to stand at room temperature. Red crystals of **5** formed within 3 d (yield: 0.633 g, 0.85 mmol 85%). M.p: 165 °C (decomp.) under Ar; ^{1}H NMR (300 MHz, [D$_6$]benzene, 297 K): δ=1.65 (s, 30H, C_5Me_5), 4.70 (d, ^3J=7.3 Hz, 1H, C$_\beta$*H*), 7.02 (m, 8H, CH_{Ph}), 7.39 (m, 8H, CH_{Ph}), 7.80 (m, 4H, CH_{Ph}), 9.12 ppm (d, ^3J=7.3 Hz, 1H, C$_\alpha$*H*); ^{13}C NMR (75 MHz, [D$_6$]benzene, 297 K): δ=11.3 (C_5Me_5), 55.9 (N=C=CPh$_2$), 62.7 (N=CHCHPh$_2$), 118.4 (C_5Me$_5$), 141.9, 142.4 (*i*-C_{Ph}), 160.4 (N=C=CPh$_2$), 165.0 (N=CHCHPh$_2$), 121.2, 125.9, 127.0, 128.6, 128.8, 129.1 ppm (CH$_{Ph}$); IR (ATR): $\tilde{\nu}$=2902 (w), 2048 (s), 1675 (w), 1588 (m), 1486 (m), 693 cm^{-1} (vs); MS (EI): *m*/*z* (%): 746 (73) [*M*]$^+$, 554 (69) [*M*-NC$_2$Ph$_2$]$^+$, 552 (18) [*M*-NCHCHPh$_2$]$^+$.

^{1}H NMR investigation of the conversion of complex 4 to 5: Complex **4** was dissolved in [D$_8$]toluene in a Young tube. Initially, ^{1}H NMR (300 MHz, [D$_8$]toluene, 297 K): δ=0.32 (SiMe_3), 1.69 (C_5Me_5), 4.86 ppm (C$H_{nitrile}$). Subsequently it was warmed to 85 °C for 19 h, ^{1}H NMR (300 MHz, [D$_8$]toluene, 297 K): δ=0.11 (Si$Me_{3\,free\,alkyne}$), 1.71 (C_5Me_5, **1**), 1.59 (C_5Me_5, **5**), 9.04 ppm (C$_\alpha$*H*, **5**). For the spectra, see the Supporting Information.

Preparation of complex 6: Ph_2CHCN (0.387 g, 2.00 mmol) was dissolved in toluene (10 mL) and subsequently added with stirring to a solution of complex **2a** (0.490 g, 1.00 mmol) in toluene (5 mL). The solution was stirred at 80 °C for 4 days and the colour turned from green to brown. All volatiles were removed from the brown solution under vacuum, followed by addition of *n*-hexane to the oily residue. The solution was filtered, concentrated and allowed to stand at room temperature. Brown crystals started to form within 30 min. The crystals were separated from the mother liquor by decanting, washed with cold *n*-hexane and dried under vacuum to give complex **6** (yield: 0.177 g, 0.252 mmol, 25 %). M.p: 219–221 °C (decomp.) under Ar; IR (ATR): $\tilde{\nu}=2921$ (w), 2845 (w), 1502 (s), 1489 (s), 1259 (m), 761 (m), 698 (vs), 644 (s), 554 (m), 468 cm^{-1} (m); MS (EI): *m*/*z* (%): 702 (8) [*M*]$^+$, 510 (2) [*M*-NC$_2$Ph$_2$]$^+$, 318 (4) [Cp*$_2$Ti]$^+$, 388 (6) [2×NCCHPh$_2$]$^+$, 312 (39) [ebthi-Ti]$^+$; elemental analysis calcd (%) for $C_{48}H_{50}N_2Ti$: C 82.03, H 7.17, N 3.99; found: C 82.11, H 7.11, N 3.99.

Preparation of complex 7: To a stirred solution of **2b** (0.483 g, 1.00 mmol) in toluene (5 mL) was added a solution of Ph_2CHCN (0.387 g, 2.00 mmol) in toluene (10 mL). The solution was stirred for 7 d at 85 °C. The solvent was removed under vacuum and the dark residue dissolved in *n*-hexane and filtered. After 1 h green crystals had formed, which were separated by decanting, washed with cold *n*-hexane and dried under vacuum to give complex **7** (0.423 g). Concentration of the mother liquor resulted in an additional amount of **7** (0.082 g) to give the total yield of compound **7** (0.505 g, 0.72 mmol, 72 %). M.p: 124–127 °C (decomp.) under Ar; IR (ATR): $\tilde{\nu}=2921$ (w), 2845 (w), 1592 (w), 1502 (s), 1489 (s), 1259 (m), 761 (m), 698 (vs), 644 (s), 554 (m), 468 cm^{-1} (m); MS (EI): *m*/*z* (%): 699 (63) [*M*]$^+$, 506 (3) [*M*-NCCHPh$_2$]$^+$, 388 (6) [2×NCCHPh$_2$]$^+$, 312 (39) [ebthi-Ti]$^+$; elemental analysis calcd (%) for $C_{48}H_{47}N_2Ti$: C 82.40, H 7.06, N 3.85; found: C 82.52, H 6.97, N 3.74.

Preparation of complex 8: Complex **3** (1.156 g, 1.89 mmol) was dissolved in toluene (15 mL) and $PhCH_2CN$ (0.55 mL, 4.76 mmol) was added to the obtained solution. The yellow-orange solution was warmed at 100 °C for 24 h, then the resulting red-brown solution was evaporated to dryness. The residue was extracted with warm *n*-hexane (20 mL, 60 °C). The dark-red solution was filtered and allowed to stand at −78 °C. After 1 day, the dark red crystals were separated from the mother liquor, washed with *n*-hexane and dried in vacuum to give complex **8** (yield: 0.298 g, 24.2 %). M.p: 233–234 °C under Ar; ^{1}H NMR (300/400 MHz, [D$_6$]benzene, 297 K): $\delta=-0.09$, 0.43 (2×s, 2×9 H, Si*Me*$_3$), 3.33 (s, 2 H, C*H*$_2$), 5.10 (s, 1 H, N2*H*), 5.72 (s, 10 H, Cp), 6.97 (m, 2 H, *o*-C*H*$_{\mathrm{Bn}}$), 6.99 (s, 1 H, C3*H*), 7.06 (m, 1 H, *p*-C*H*$_{\mathrm{Bn}}$), 7.14 ppm (m, 2 H, *m*-C*H*$_{\mathrm{Bn}}$); ^{13}C NMR (75 MHz, [D$_6$]benzene, 297 K): $\delta=0.7$ (^1J(C,H) = 119 Hz, Si*Me*$_3$), 2.4 (^1J(C,H) = 118 Hz, Si*Me*$_3$), 45.4 (*C*H$_2$), 103.5 (C6), 110.6 (^1J(C,H) = 173 Hz, Cp), 127.0 (*p*-*C*H$_{\mathrm{Bn}}$), 127.1 (*p*-*C*H$_{\mathrm{Ph}}$), 128.7 (*m*-*C*H$_{\mathrm{Ph}}$), 128.9 (*m*-*C*H$_{\mathrm{Bn}}$), 129.7 (^1J(C,H) = 127 Hz, *o*-*C*H$_{\mathrm{Bn}}$), 134.5 (^1J(C,H) = 157 Hz, *o*-*C*H$_{\mathrm{Ph}}$), 139.3 (*i*-*C*$_{\mathrm{Bn}}$), 139.6 (^1J(C,H) = 168 Hz, C3), 141.4 (*i*-*C*$_{\mathrm{Ph}}$), 144.7 (C4), 159.4 (C5), 163.1 (C2), 165.1 (C7), 205.0 ppm (C1); ^{29}Si NMR (74.5 MHz, [D$_6$]benzene, 297 K): $\delta=-10.1$ (^2J(Si,H) = 6.4 Hz, SiMe$_3$), −8.8 ppm (^2J-(Si,H) = 6.7 Hz, ^3J(Si,H) = 4 Hz, SiMe$_3$); ^{15}N NMR (40.5 MHz, [D$_6$]benzene, 297 K): δ −193.2, −182.6 (^1J(N,H) = 62 Hz). IR (ATR): $\tilde{\nu}=2962$ (w), 1343 (vw), 1260 (s), 1089 (m), 1017 (s), 797 (vs), 697 cm^{-1} (w); MS (EI): *m*/*z* (%): 648 (100) [*M*]$^+$, 575 (58) [*M*-SiMe$_3$]$^+$, 220 (26) [Cp$_2$Zr]$^+$; elemental analysis calcd (%) for $C_{36}H_{42}N_2Si_2Zr$: C 66.51, H 6.51, N 4.31; found: C 66.13, H 6.21, N 4.09.

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