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Migratory Insertion of an Isocyanide into 1-Zirconacyclopent-3-ynes

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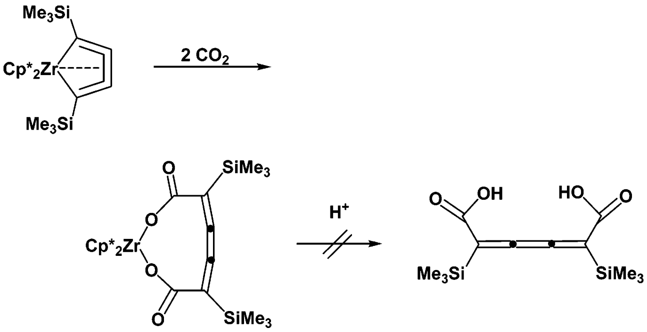
The reactions of the 1-zirconacyclopent-3-ynes $Cp'_2Zr(\eta^4\text{-}H_2C_4H_2)$ with $Cp'_2 = Cp_2$ (**1**), $(\eta^5\text{-}t\text{-}BuC_5H_4)_2$ (**2**), and $Me_2Si(\eta^5\text{-}C_5H_4)_2$ (**3**) and of the zirconacyclopropene $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8**) toward *t*-Bu-NC are described. In the case of the 1-zirconacyclopent-3-ynes 2 equiv of *t*-Bu-NC were inserted into the β-Zr−C bonds of the zirconacycle. After subsequent rearrangement the substituted 1-zircona-2,5-diazacyclopent-3-enes **4**, **5**, and **6**, possessing an anellated cyclobutene ring having two exocyclic double bonds, were obtained. In the protolysis of **6** with MeOH the metal-free cyclobutene **7** was formed. The alkyne complex **9** reacted with the isocyanide to give *end-on* complexation instead of an expected insertion, resulting in the alkyne complex $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^1\text{-}CN\text{-}t\text{-}Bu)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**11**).

Introduction

The chemistry of 1-metallacyclopenta-2,3,4-trienes (five-membered metallacyclocumulenes) and 1-metallacyclopent-3-ynes as structurally related and small metallacyclic compounds has been the subject of several summarizing reviews.[1] These results were complemented by theoretical calculations for such metallacycles that pointed out that the internal complexation of the unsaturated bonds C=C=C=C and C≡C by metal centers in these ring systems is the main stabilizing effect for the metallacyclocumulenes (1-metallacyclopenta-2,3,4-trienes) and the similar 1-metallacyclopent-3-ynes.[2] In the structures of these compounds the central double or triple bond is elongated. This effect was ascribed to the *intramolecular* interaction of the binding π molecular orbitals with empty d orbitals of the metal.[3a,b] Another approach for the bonding situation was made by Lin and co-workers, who proposed a resonance hybrid between the (η^2, σ, σ) and (η^2, π, π) coordination, in which the latter makes the major contribution for the stabilization of such compounds.[3c,d] This is in agreement with experimental electron density studies on 1-zirconacyclopent-3-ynes.[3d] The bonding situation in the metallacyclocumulenes and the 1-zirconacyclopent-3-ynes was compared by calculational approaches.[3]

Scheme 1. Insertions of Carbon Dioxide into a Zirconacyclocumulene



Unexpectedly, the current knowledge of the reactivity of these metallacycles with regard to insertion reactions into the metal−carbon bond is very poor. There are only a few examples of such reactions. The zirconacyclocumulene $Cp^*_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$ reacted with 2 equiv of carbon dioxide to form a cumulenic dicarboxylate by a formal 2-fold insertion into the η^4-complex.[1a] Acidolysis of the insertion product did not yield the corresponding [3]cumulenic dicarboxylic acids or esters (Scheme 1).

Very recently Liu and co-workers described an elegant approach to *cis*-^{3}cumulenic diols by the reaction of alkynylated zirconacyclopentenes with ketones for which zirconacyclocumulenes were assumed as intermediates (Scheme 2).[4] This reaction is clearly related to the carbon dioxide insertion mentioned above.

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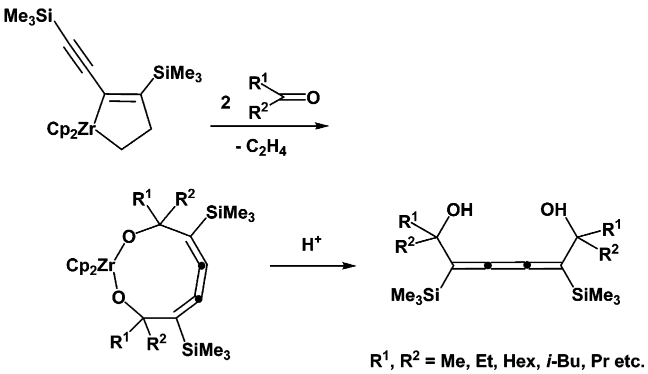
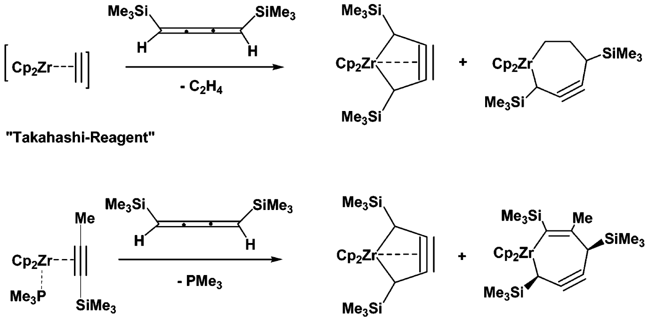
10.1021/om700324k CCC: $37.00

Scheme 2. Formal Insertions of Ketones into a Zirconacyclocumulene



Scheme 3. Formal Insertion of Ethylene and of an Alkyne into the 1-Zirconacyclopent-3-yne



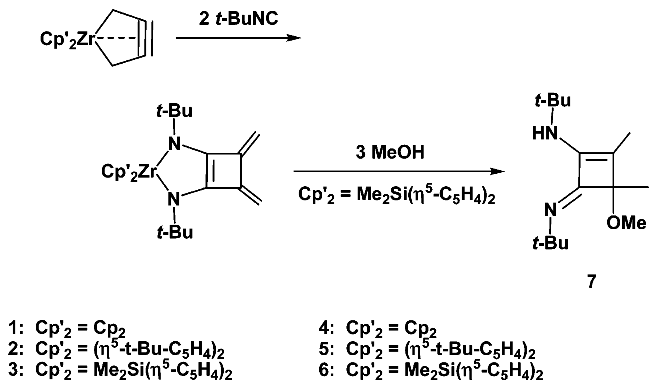
For the 1-metallacyclopent-3-ynes similar insertion reactions have not been described as yet. Nevertheless, the products of the reaction of the "Takahashi reagent"[5a] and of Cp$_2$Zr(η^2-Me$_3$SiC$_2$Me)(PMe$_3$) with butatrienes could indicate the presence of a 1-zirconacyclopent-3-yne and its insertion reaction (Scheme 3).[5b]

Our preliminary attempts with several 1-metallacyclopent-3-ynes gave no insertion products from the reactions with carbon dioxide and carbon monoxide. In this report we detail our investigations of the reactions of isocyanides with 1-zirconacyclopent-3-ynes.

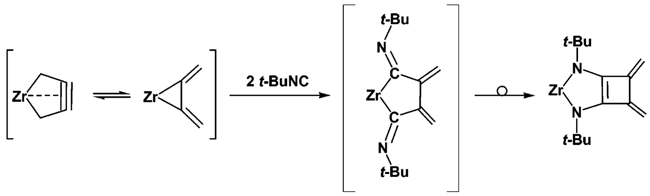
Results and Discussion

Synthesis. The 1-zirconacyclopent-3-ynes Cp′$_2$Zr(η^4-H$_2$C$_4$H$_2$) with Cp′$_2$ = Cp$_2$ (**1**), (η^5-*t*-Bu-C$_5$H$_4$)$_2$ (**2**), and Me$_2$Si(η^5-C$_5$H$_4$)$_2$ (**3**) undergo a migratory insertion of *t*-Bu-NC. In the first step 2 equiv of the isocyanide unexpectedly were inserted into the β-Zr−C bonds of the zirconacycle. After subsequent rearrangement the corresponding substituted 1-zircona-2,5-diazacyclopent-3-enes **4**, **5**, and **6** were formed, which may be considered as enediamido complexes (Scheme 4). We were unable to isolate analytically pure samples of complex **6**. Nevertheless, the spectroscopic and X-ray structural data establish the character of this complex without doubt. Methanolysis of complex **6** gave the cyclobutene **7** in very low isolated yield together with Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(OMe)$_2$, which was indicated by its NMR spectral data.

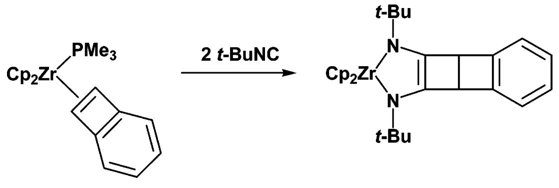
Scheme 4. Migratory Insertions of *t*-Bu-NC



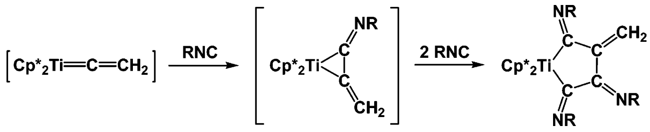
Scheme 5. Isocyanide Insertions into a (2−3η) Butatriene Complex (metallacyclopropane) and Subsequent Rearrangement



Scheme 6. Sharp's Isocyanide Insertions into a η^2-Cyclobutadiene Complex



Scheme 7. Isocyanide Insertions into a η^2-1-Monoaza-buta-2,3-triene Complex



Mechanistics. Three different possible explanations for the formation of these unusual products can be proposed. The first one could take place by insertion of the isocyanides into a (2−3η) butatriene complex (zirconacyclopropane) and subsequent stabilization of the intermediate by rearrangement (Scheme 5).

A similar reaction was first described for a coordinated double bond by Fischer and Buchwald in the case of a zirconocene η^2-cyclobutene complex leading to a saturated diiminozirconacyclopentane derivative.[6] Later Sharp and co-workers reported the insertion of 2 equiv of *t*-Bu-NC into a zirconocene η^2-cyclobutadiene complex to give a 1-zircona-2,5-diazacyclopent-3-ene[7a] with the typical enediamido (diazadiene) structure[7b,c] (Scheme 6).

Beckhaus and co-workers extended this chemistry systematically to 1-monoaza-buta-2,3-triene complexes [Cp*$_2$Ti(η^2-H$_2$C=C=C=NR)], which were formed as intermediates in the reaction of titanaallenes [Cp*$_2$Ti=C=CH$_2$] with isocyanides R-NC.[8] A 1-titana-2-azacyclopent-3-yne was not discussed for [Cp*$_2$Ti(η^2-H$_2$C=C=C=NR)], but insertion of 2 equiv of R-NC gave a five-membered metallacycle (Scheme 7), which is very similar to the assumed intermediate in Scheme 5.

The second approach to understand the formation of the 1-zircona-2,5-diazacyclopent-3-enes **4**, **5**, and **6** could be made

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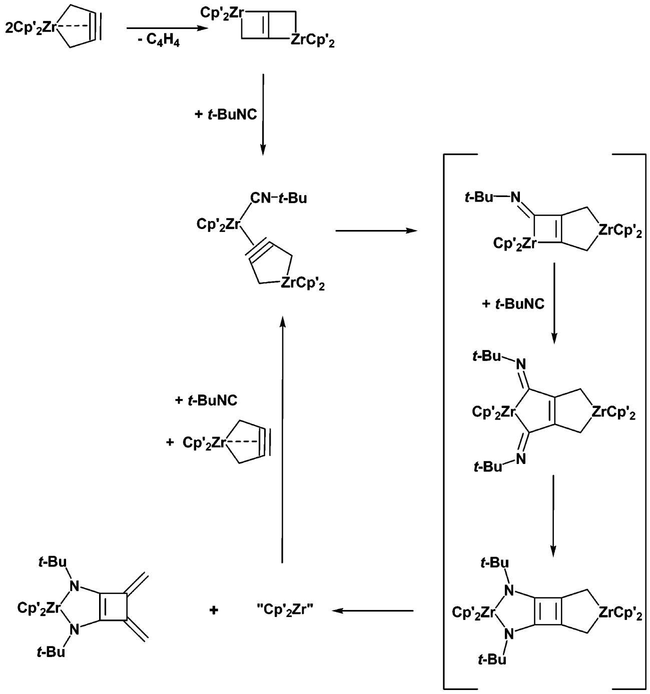
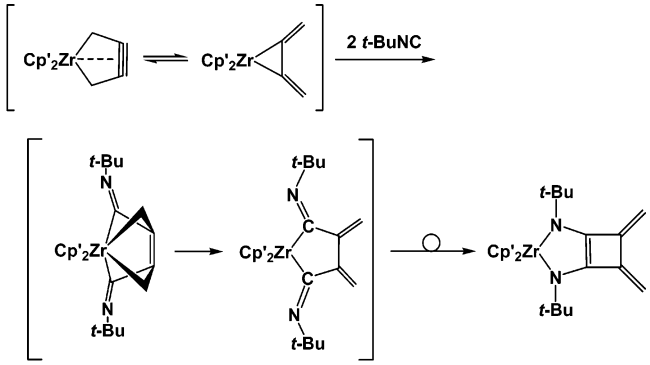
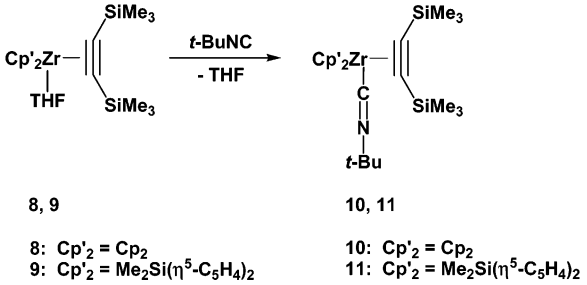
Scheme 8. Isocyanide Insertions into a 1-Zirconacyclopent-3-yne Formed from the Bis-zirconocene-μ-(*Z*)-1,2,3-butatriene Complex (2,5-dizircona-bicyclo[2.2.0]hex-1(4)-ene)



Scheme 9. Coupling of the Internal Coordinated Triple Bond of the Starting 1-Zirconacyclopent-3-yne



Scheme 10. Formation of Complexes 10 and 11 by Reaction of the Zirconacyclopropenes $Cp'_2Zr(THF)(\eta^2-Me_3SiC_2SiMe_3)$ (8, $Cp'_2 = Cp_2$; 9, $Cp'_2 = Me_2Si(\eta^5-C_5H_4)_2$) with *t*-Bu-NC



starting from dinuclear complexes, which are easily formed by dissociation of the butatriene (Scheme 8). Such species can coordinate isocyanide ligands, as shown before by Suzuki for PMe_3 as a ligand.[2a] Insertions of isocyanide molecules and dissociation of the "Cp'_2Zr" could directly result in the formation of the products.

On the other hand, the formation of diiminometallacyclopent-3-enes from direct alkyne−isocyanide coupling is known.[9] This leads to the suggestion to understand in a similar manner the isocyanide insertion as a coupling of the internal coordinated triple bond of the starting 1-zirconacyclopent-3-yne (Scheme 9).

It is not clear yet which of the proposed mechanisms may be applicable for the formation of the insertion products. Nevertheless, it must be noted that there is no hint for any insertion at the α-carbon atoms with formation of a seven-membered diimino-1-metallacyclohept-4-yne.

Many insertion reactions of isocyanides into zirconium carbon bonds are known,[9a] but there exists to the best of our knowledge no example in the case of zirconacyclopropenes (alkyne complexes). The reaction of silazirconacyclopentenes, formed from zirconium−silene complexes and diarylacetylenes, with *t*-Bu-NC afforded iminosilazirconacyclohexenes.[9b] Nevertheless, alkyne isocyanide coupling reactions leading to diiminometallacyclopentene complexes were described for other metals, e.g., for molybdenum.[9c]

To study the insertion reaction of the isocyanide into a zirconacyclopropene in detail, we tried to insert *t*-Bu-NC into the Zr−C bond of $Cp_2Zr(THF)(\eta^2-Me_3SiC_2SiMe_3)$ (**8**) and the *in situ* formed corresponding *ansa*-dimethylsilanediyl−dicyclopentadienyl complex $Me_2Si(\eta^5-C_5H_4)_2Zr(THF)(\eta^2-Me_3SiC_2SiMe_3)$ (**9**), which is stable only in solution.[10] Surprisingly we found instead of an insertion the *end-on* coordination of the isocyanide to give the complexes $Cp_2Zr(\eta^1$-CN-*t*-Bu$)(\eta^2-Me_3SiC_2SiMe_3)$ (**10**) and $Me_2Si(\eta^5-C_5H_4)_2Zr(\eta^1$-CN-*t*-Bu$)(\eta^2-Me_3SiC_2SiMe_3)$ (**11**) (Scheme 10). We could not isolate analytically pure samples of complex **11**. However, the spectroscopic and X-ray structural data unambiguously establish the molecular structure of this complex.

These complexes represent the first examples for zirconocene complexes that contain in addition to an alkyne an isocyanide without any coupling of both ligands.

Spectra. The spectroscopic data measured for the complexes **4**, **5**, and **6** can be compared to the $^{13}C\{^1H\}$ NMR data of the diazadiene complex obtained by Sharp et al. (Scheme 6), but the signals of the latter (δ = 149.3, 117.3, and 58.2 ppm) cannot definitely be assigned to the signals found for the new complexes (**4**, 128.9; **5**, 128.5; and **6**, 129.5 ppm). Additionally, these complexes show the typical behavior of group 4 metallocene complexes of 1,3-dienes, 1-aza-1,3-dienes, or 1,4-diaza-1,3-dienes being fluxional metallacycles with a "ring flipping" around the N1−N2 axis along which the ring is folded.[7d]

The $^{13}C\{^1H\}$ NMR signals for the alkyne carbon atoms in the *t*-Bu-NC complexes $Cp'_2Zr(\eta^1$-CN-*t*-Bu$)(\eta^2-Me_3SiC_2SiMe_3)$ (**10**, 182.0 and 166.9; **11**, 183.2 and 165.0 ppm) differ from those of the corresponding pyridine complexes $Cp'_2Zr(py)(\eta^2$-

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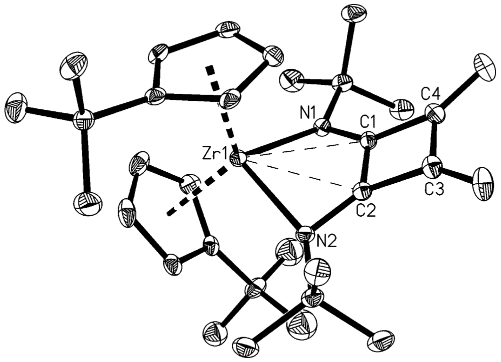

Figure 1. Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr−N1 2.176(2), Zr1−N2 2.158(2), Zr1−C1 2.579(3), Zr1−C2 2.570(2), N1−C1 1.367(4), N2−C2 1.364(3), C1−C2 1.421(4); N1−Zr1−N2 89.60(8), Zr1−N1−C1 90.5(2), Zr1−N2−C2 90.9(2).

Table 1. Crystallographic Data

	5	**6**	**7**	**11**
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$C2/m$	$P2_1/n$
a [Å]	20.632(4)	9.6079(19)	15.816(3)	12.166(2)
b [Å]	12.178(2)	24.719(5)	10.573(2)	12.236(2)
c [Å]	11.572(2)	11.812(2)	10.120(2)	20.316(4)
α [deg]	90.00	90.00	90.00	90.00
β [deg]	90.00	92.09(3)	109.70(3)	97.04(3)
γ [deg]	90.00	90.00	90.00	90.00
V [Å^3]	2907.6(10)	2803.5(10)	1593.3(6)	3001.5(10)
Z	4	4	4	4
density [g·cm^{-3}]	1.261	1.277	1.052	1.175
μ(Mo Kα) [mm^{-1}]	0.40	0.45	0.07	0.50
T [K]	200(2)	200(2)	200(2)	200(2)
no. of rflns (measd)	45 601	25 974	10 325	10 657
no. of rflns (indep)	6664	4916	1491	5840
no. of rflns (obsd)	5005	3189	1162	4145
no. of params	330	298	119	271
R1 ($I > 2\sigma(I)$)	0.032	0.045	0.051	0.027
wR2 (all data)	0.055	0.075	0.153	0.051

$Me_3SiC_2SiMe_3$) (**12**, $Cp'_2 = Me_2Si(\eta^5\text{-}C_5H_4)_2$; 193.0 and 218.5;[10] **13**, $Cp'_2 = Cp_2$, 195.3 and 220.5 ppm).[11] This indicates a weaker alkyne complexation in the isocyanide complexes **10** and **11** compared to the pyridine complexes **12** and **13**. The typical dynamics for ligand-stabilized group 4 metallocene alkyne complexes such as alkyne rotation and ligand exchange were not investigated here.[10,11]

From the CN stretching vibration at 2156 cm^{-1} for the cycloheptatrienyl−cyclopentadienyl−zirconium sandwich complex $(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)Zr(\eta^1\text{-CN-}t\text{-Bu})$ (**14**)[12] it can be concluded that for the here described complexes (**10**, 2124; **11**, 2116 cm^{-1}) a stronger zirconium−isocyanide interaction is evident.

Solid-State Structures. The solid-state structures of compounds **5**, **6**, **7**, and **11** were determined by X-ray crystallography; see Table 1 for crystallographic data and Figures 1, 2, 3, and 4 for the respective molecular structures.

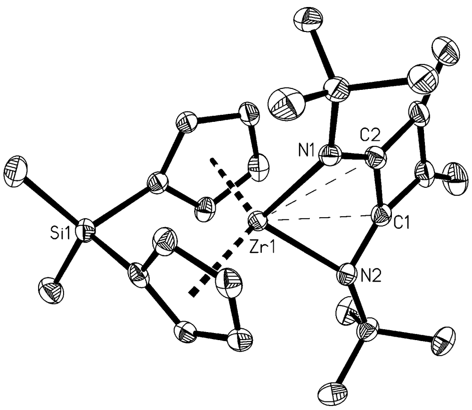

Figure 2. Molecular structure of complex **6**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−N2 2.159(3), Zr−N1 2.149(3), Zr1−C1 2.531(4), Zr1−C2 2.540(4), N2−C1 1.348(4), N1−C2 1.351(5), C1−C2 1.432(5), N1−Zr1−N2 87.70(11), Zr1−N2−C1 89.3(2), Zr1−N1−C2 90.1(2).

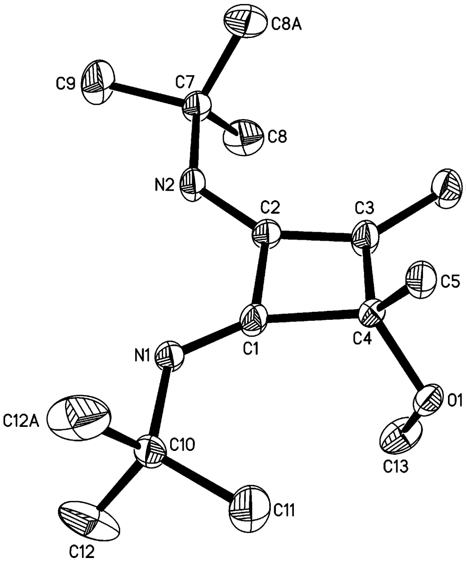

Figure 3. Molecular structure of compound **7**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: C1−C2 1.465(3), C2−C3 1.359(3), C1−N1 1.261(3), C2−N2 1.356(3). C4−C1−C2 88.4(2), C1−C2−C3 94.6(2), C2−C3−C4 92.6(2), C3−C4−C1 81.52(17).

The molecular structures of complexes **5** and **6** show a typical 1-zircona-2,5-diazacyclopent-3-ene, which can be compared to Sharp's product (Scheme 6: **4**, Zr−N1 2.130(6), Zr1−N2 2.152(7), Zr1−C9 2.470(7), Zr1−C10 2.479(8), N1−C9 1.375(10), C9−C10 1.402(11) Å; N1−Zr1−N2 89.1(3)°, Zr1−N1−C9 86.8(4)°; **5** and **6**, see Figures 1 and 2). Bond distances and angles indicate the structural relation of **5** and **6** with this compound. Moreover both complexes display the typical enediamido (diazadiene) unit with the 1-zircona-2,5-diazacyclopent-3-ene adopting an envelope conformation.[7b,c]

Complex **11** shows the typical structural features of several already described ligand-stabilized alkyne complexes. Compared to the well-known pyridine-stabilized alkyne complex $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**12**)[10] the C1−C2 bond distance [**12**, 1.297(6); **11**, 1.294(3) Å] is in the same range. With regard to the isocyanide interaction the significantly shorter Zr1−C3 distance of 2.293(2) Å for **11** indicates a stronger interaction of the isocyanide with the metal center compared to the cycloheptatrienyl−cyclopentadienyl−zirconium sandwich complex $(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)Zr(\eta^1\text{-CN-}t\text{-Bu})$ [**14**, Zr−C 2.376(3); C−N 1.150(4) Å].[12] This is in agreement with the abovementioned comparison of the IR data.

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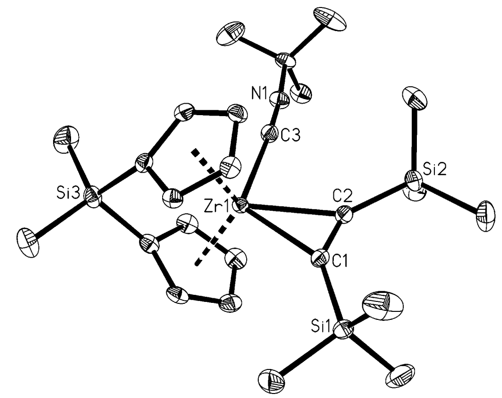

Figure 4. Molecular structure of complex **11**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C1 2.252(2), Zr1−C2 2.302(2), C1−C2 1.294(3), Zr1−C3 2.293(2), C3−N1 1.153(2); C1−Zr1−C2 32.98(7), Zr1−C3−N1 175.2(2), C3−N1−C10 173.8(2).

Conclusion

Following an unexpected insertion pattern into the β-Zr−C bonds, the isocyanide *t*-Bu-NC inserts into 1-zirconacyclopent-3-ynes to give substituted 1-zircona-2,5-diazacyclopent-3-enes with an anellated cyclobutene. With regard to the mechanism it is not clear if a 2−3η-butatriene complex (metallacyclopropane), a bis-zirconocene-μ-(*Z*)-1,2,3-butatriene complex (2,5-dizirconabicyclo[2.2.0]hex-1(4)-ene), or the internally η^2-complexed alkyne (zirconacyclopropene) is reacting directly. The fact that the here investigated typical zirconacyclopropenes do not insert isocyanide molecules into their Zr−C bonds is contradictory to the latter suggestion because ligand exchange reactions are favored, resulting in isocycanide-stabilized alkyne complexes.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvent (C_6D_6) was treated with sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: C_6D_6 ($\delta_H = 7.16$, $\delta_C = 128.0$). The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer. Due to decomposition, no accurate elemental analysis of the organometallic compounds **4**, **5**, **6**, **10**, and **11** could be obtained.

Preparation of 4. To a solution of $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**1**) (0.78 g, 2.9 mmol) in toluene (15 mL) was added *t*-Bu-NC (0.96 mL, 8.5 mmol), and the brownish mixture was stirred for 12 h at 50 °C. All volatiles were removed in vacuum, and the residue was dissolved in *n*-hexane (15 mL). The solution was cooled to −30 °C, yielding red crystals, which were isolated by decanting of the mother liquor and washed with cold *n*-hexane (1 mL, −78 °C) to give 1.10 g (85%) of complex **4**. HRMS (EI): calcd for $C_{24}H_{32}N_2Zr$ [M]$^+$ 438.1603, found 438.1607. ^{1}H NMR (C_6D_6, 297 K): δ 1.36 (s, 18H, *t*-Bu), 4.79 (d, 1.0 Hz, 2H, CH_2), 4.89 (d, 1.0 Hz, 2H, CH_2), 5.70 (s, 10H, Cp). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 32.9 (CH_3), 57.7 (*C*(CH_3)$_3$), 88.8 (CH_2), 107.3 (Cp), 128.9 (*t*-Bu-N*C*), 147.9 (*C*=CH_2). IR (Nujol mull, cm^{-1}): ν 1699, 1657, 1632, 1598, 1205, 835, 800, 791.

Preparation of 5. To a solution of (η^5-*t*-Bu-C_5H_4)$_2$Zr(η^4-$H_2C_4H_2$) (**2**) (0.50 g, 1.3 mmol) in toluene (15 mL) was added *t*-Bu-NC (0.3 mL, 2.6 mmol), and the gold-brownish mixture was stirred for 12 h at 50 °C. All volatiles were removed in vacuum, and the residue was dissolved in *n*-hexane (15 mL). The solution was cooled to −30 °C, yielding red crystals, which were isolated by decanting of the mother liquor and washed with cold *n*-hexane (1 mL, −78 °C) to give 0.32 g (44%) of complex **5**. HRMS (EI): calcd for $C_{32}H_{48}N_2Zr$ [M]$^+$ 550.2854, found 550.2859. ^{1}H NMR (C_6D_6, 297 K): δ 1.23 (s, 18H, *t*-Bu), 1.51 (s, 18H, *t*-Bu), 4.81 (d, 0.9 Hz, 2H, CH_2), 4.91 (d, 0.9 Hz, 2H, CH_2), 5.67 (dd, 2.8 Hz, 4H, C_5H_4), 6.09 (dd, 2.8 Hz, 4H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 32.5 (C(*C*H_3)$_3$), 32.8 (C_5H_4-*C*(CH_3)$_3$), 33.3 (C_5H_4)-C(*C*H_3)$_3$), 58.1 (N-*C*(CH)$_3$), 88.3 (CH_2), 103.0 (C_5H_4), 110.9 (C_5H_4), 125.6 (C_5H_4 quart.), 129.5 (*t*-Bu-N*C*), 148.1 (*C*=CH_2). IR (Nujol mull, cm^{-1}): ν 2963, 2924, 2854, 1709, 1629, 1189.

Preparation of 6. To a solution of $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**3**) (0.44 g, 1.3 mmol) in toluene (15 mL) was added *t*-Bu-NC (0.3 mL, 2.6 mmol), and the gold-brownish mixture was stirred for 12 h at 50 °C. All volatiles were removed in vacuum, and the residue was dissolved in *n*-hexane (15 mL). The solution was cooled to −30 °C, yielding red crystals, which were isolated by decanting of the mother liquor and washed with cold *n*-hexane (1 mL, −78 °C) to give 0.39 g (56%) of complex **6**, $C_{26}H_{36}N_2SiZr$ (495.89). HRMS (EI): calcd for $C_{36}H_{36}N_2SiZr$ [M]$^+$ 494.1692, found 494.1689. ^{1}H NMR (C_6D_6, 297 K): δ 0.46 (s, 6H, CH_3), 1.38 (s, 18H, *t*-Bu), 4.80 (d, 1.0 Hz, CH_2), 4.90 (d, 1.0 Hz, CH_2), 5.26−6.14 (br, 8H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ −5.3 (CH_3), 32.6 (CH_3), 57.7 (*C*(CH_3)$_3$), 88.8 (CH_2), C_5H_4 extremely broad, not detected, 129.2 (*t*-Bu-N*C*), 147.6 (*C*=CH_2). IR (Nujol mull, cm^{-1}): ν 2925, 1700, 1642, 1618, 1255, 827, 796.

Synthesis of *N,N′*-(4-Methoxy-3,4-dimethylcyclobut-2-en-2-yl-1-yliden)bis(2-methylpropane-2-amine) (7). Compound **6** (1.0 g, 2.27 mmol) was dissolved in methanol (15 mL) to give a deep red solution, which was stirred for 1 h at rt. During this time the color changed slowly to pale yellow. The reaction mixture was filtrated through a silica column (SiO_2, 3 cm × 1.5 cm). The volatiles were removed in vacuum (5 mbar, 0 °C) very slowly so that colorless crystals formed at the Schlenk-tube wall. Yield: <1% of compound **7**. Anal. Calcd for $C_{15}H_{28}N_2O$ (252.41): C, 71.38; H, 11.18; N, 11.10. Found: C, 70.94; H, 11.03; N, 10.87. MS (70 eV) *m/z*: 236 [M$^+$ − Me], 221 [M$^+$ − OMe], 57 [*t*-Bu]. ^{1}H NMR (C_6D_6, 297 K): δ 1.04 (s, 9H, C=NC(C*H*$_3$)$_3$), 1.43 (s, 9H, HNC-(C*H*$_3$)$_3$), 1.55 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 3.12 (s, 3H, OCH_3), 4.65 (s 1H, NH). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 11.5 (CH_3) 23.2 (CH_3), 30.2 (C(*C*H_3)$_3$), 31.1 (C(*C*H_3)$_3$), 49.0 (*C*(CH_3)$_3$), 51.1 (OCH_3), 55.1 (*C*(CH_3)$_3$), 92.8 (*C*OCH_3), 120.7 (C=*C*-CH_3), 143.6 (N*C*=C), 161.6 (N=*C*). IR (Nujol mull, cm^{-1}): ν 2923, 2854, 1677, 1632, 1260, 1222.

Preparation of 10. To a solution of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2\text{-}SiMe_3)$ (**8**) (0.44 g, 0.93 mmol) in THF (30 mL) was added *t*-Bu-NC (0.21 mL, 1.8 mmol, 2 equiv). Stirring of the reaction mixture at rt for 3 h resulted in a color change from brownish to red-orange. All volatiles were removed in vacuum, and the remaining residue was dissolved in *n*-hexane (8 mL). Crystallization at −78 °C yielded bright orange crystals (0.42 g, 88%), from which the mother liquor was decanted at low temperatures. MS (70 eV) *m/z*: 390 [M$^+$ − *t*-Bu-NC], 303 [M$^+$ − btmsa], 220 [Cp_2Zr], 155 [CpZr]. ^{1}H NMR (C_6D_6, 297 K): δ 0.40 (s, 9H, $SiMe_3$), 0.48 (s, 9H, $SiMe_3$), 1.03 (s, 9H, *t*-Bu), 5.27 (s, 10H, Cp). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ 1.5 ($SiMe_3$), 2.1 ($SiMe_3$), 30.0 (C(*C*H_3)$_3$), 56.8 (*C*(CH_3)$_3$), 101.4 (Cp) 166.9 (C≡C), 182.0 (C≡C), 184.4 (NC). IR (Nujol mull, cm^{-1}): ν 2950, 2854, 2124, 1460, 1377, 1235, 1016, 858, 828.

Preparation of 11 via *in Situ* Prepared $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (9). To a suspension of $Me_2Si(\eta^5\text{-}C_5H_4)_2ZrCl_2$ (1.0 g, 2.86 mmol) and bis(trimethylsilyl)acetylene (0.63 mL, 2.86 mmol) in THF (30 mL) was added Mg powder (0.1 g, 4.11 mmol). Upon stirring at rt the color of the reaction mixture changed to deep purple. *t*-Bu-NC (0.32 mL, 2.86 mmol) was added dropwise to yield a reddish suspension, which was stirred for another 12 h at rt. Volatiles were removed in vacuum, and the residue was extracted with *n*-hexane at 50 °C (5 × 15 mL). After removing the solvent from the mother liquor in vacuum an orange powder remained, which was recrystallized from *n*-hexane to give 0.18 g (12%) of orange crystals of **11**. HRMS (EI): calcd for $C_{25}H_{41}NSi_3$-Zr $[M]^+$ 529.1577, found 529.1588 ^1H NMR (C_6D_6, 297 K): δ 0.38 (s, 3H, $SiMe_2$), 0.40 (s, 9H, $SiMe_3$), 0.50 (s, 9H, $SiMe_3$), 0.57 (s, 3H, $SiMe_2$), 1.06 (s, 9H, *t*-Bu), 4.94 (m, 2H, C_5H_4), 5.28 (m, 2H, C_5H_4), 5.48 (m, 2H, C_5H_4), 6.36 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ −5.2 ($SiMe_2$), −4.8 ($SiMe_2$), 1.5 ($SiMe_3$), 2.1 ($SiMe_3$), 30.0 (*t*-Bu), 57.0 (*t*-Bu), 98.3 (C_5H_4), 98.4 (C_5H_4), 101.0 (C_5H_4), 103.5 (C_5H_4), 118.2 (C_5H_4), 165.0($C\equiv C$), 183.2 ($C\equiv C$), CN not found. IR (Nujol mull, cm^{-1}): ν 2957, 2854, 2116, 1683, 1644, 1240.

X-ray diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97[13] and SIR 2004,[14] respectively) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[15]). XP (Bruker AXS) was used for structural representations.

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Supporting Information Available: Copies of NMR spectra of complexes **6**, **7**, and **11** and tables of crystallographic data in cif file format, including bond lengths and angles of compounds **5**, **6**, **7**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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