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Articles

Nickel(0) Complexes of a 1-Zirconacyclopent-3-yne

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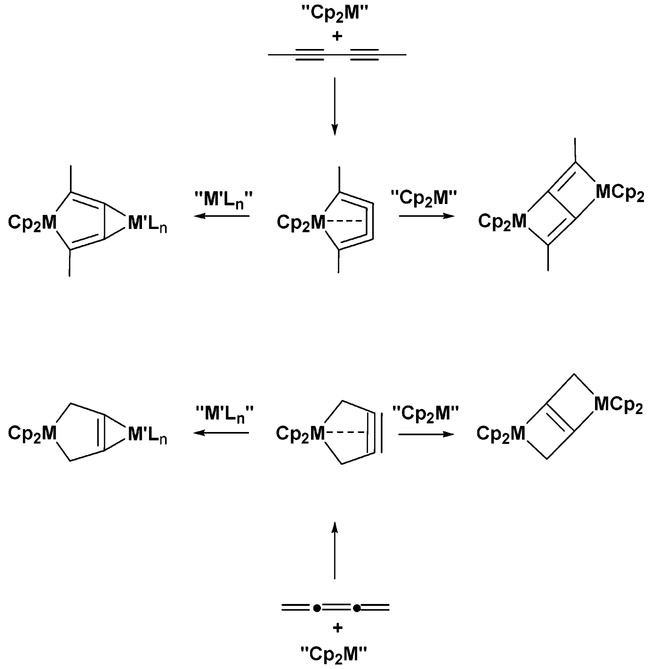
The complexation of the uncommon 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4-H_2C_4H_2)$ by Ni(0) complexes is described and compared to the coordination of similar 1-metallacyclopenta-2,3,4-trienes $Cp_2M(\eta^4-PhC_4Ph)$ of titanium and zirconium, both showing μ-"*cis*"-complexation of 1,2,3-butatrienes and 1,3-butadiynes in addition to the well-known μ-"*trans*"-complexation.

Introduction

Very recently, in some reviews[1] the chemistry of rather exotic and uncommon five-membered metallacyclocumulenes[2] and metallacyclopentynes[3] as small cyclic compounds was summarized. Internal complexation of the unsaturated bonds C=C=C=C and C≡C by metals in these rings was considered as the main stabilizing effect for the metallacyclocumulenes (1-metallacyclopenta-2,3,4-trienes) and the similar 1-metallacyclopent-3-ynes.[1] For example, the structures of titana- and zirconacyclocumulenes show an almost planar arrangement of the metallacycle with three C−C double bonds, of which the central one is more elongated in comparison to the other two. This elongation is ascribed to the intramolecular interaction of the central C=C bond with the metal. The bonding situation in the metallacyclocumulenes and the zirconacyclopentynes was compared by some calculations.[4] Metallacyclocumulenes and metallacyclopentynes coordinate with their unsaturated bonds to other metals to form binuclear complexes (Scheme 1).[1−5]

Scheme 1



These complexes are compounds with either "*cis*"-butatriene or "*cis*"-butadiyne bridging ligands. Thus, metallacyclo*pentynes* form metallacyclo*pentene* complexes and metallacyclo*pentatrienes* yield metallacyclo-

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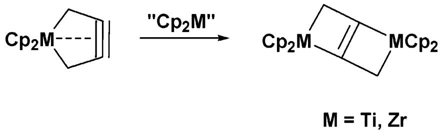
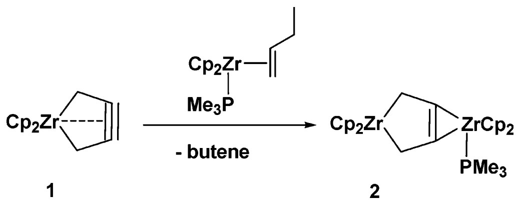
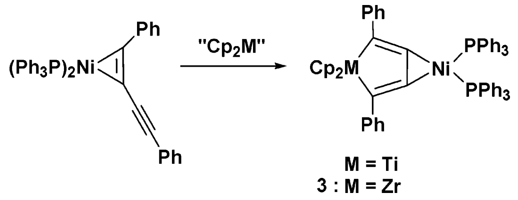
Scheme 2



Scheme 3



Scheme 4



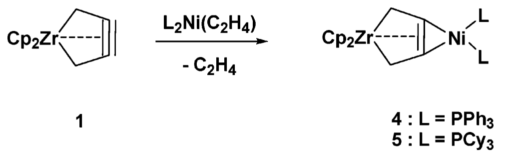
pentadienes. Two "titanocenes" and diverse butadiynes yield binuclear complexes with intact C_4 units between the two metals.[5e] The former "*cis*"-complexed diynes of the metallacyclocumulenes are transformed to "zigzag-butadiene ligands" or μ−(1−3),η(2−4)-*trans,trans*-tetradehydrobutadiene moieties between two metallocene centers. Such complexes are unknown for M = Zr, although calculations predict that they should exist for certain substitution patterns, e.g., CN and F.[4b] The 1-metallacyclopent-3-ynes react with metallocene "Cp_2M" to form μ-"*trans*"-butatriene complexes, which are better described as dimetallabicycles (2,5-dimetallabicyclo-[2.2.0]hex-1(4)-enes)[3c,e] in analogy with the above-mentioned μ-"*trans*"-butadiyne complexes (Scheme 2).

The unsubstituted 1-zirconacyclopent-3-yne forms with "$Cp_2Zr(PMe_3)$" the cycloalkyne complex **2**, containing a C_4 unit between the metals, described as a "flat" 1-zirconacyclopent-3-ene (Scheme 3).[3b]

Reactions of Ni(0) butadiyne complexes with metallocenes gave compounds that can be considered as complexes of 1-metallacyclopenta-2,3,4-trienes with "$Ni(PPh_3)_2$" (Scheme 4).[5a]

Depending on the nature of the metals and the substituents, only certain metallacyclocumulenes gave such stable complexes. For example, π-complexes of metallacyclocumulenes were isolated for M = Ti and Zr (**3**) only with two phenyl substituents, which can be regarded as Ni(0) complexes of the type $(Ph_3P)_2$Ni(cycloolefin). Interestingly, these compounds represent stable complexes of η^2-metallacyclopentatrienes. Such complexes are not stable with two Me_3Si substituents or one Ph together with one Me_3Si substituent.[5a,b]

Scheme 5



Meanwhile, other π-complexes of metallacyclocumulenes with Ph substituents were reported, and for other elements such complexes were assumed to be intermediates in the C−C single bond cleavage reaction of butadiynes.[5] Complexes of other cyclocumulenes with "$[Cp_2V]$",[5c,d,f−h] "[R−P]",[5i,j] and "$[R_2Si]$"[5k−m] are examples of this.

Here we describe first heterobimetallic complexes $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]NiL_2$ of the unsubstituted 1-zirconacyclopent-3-yne with "$Ni(PPh_3)_2$" and "$Ni(PCy_3)_2$".

Results and Discussion

The unsubstituted 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**1**) reacts with equimolar amounts of the nickel(0) complexes $L_2Ni(\eta^2\text{-}C_2H_4)$ (L = PPh_3 or PCy_3) in THF at room temperature to give the binuclear complexes $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]NiL_2$ (**4**, L = PPh_3; **5**, PCy_3) (Scheme 5).

Complexes **4** and **5** are golden-yellow crystals, stable at room temperature. The spectroscopic and structural data indicate that the internal interaction of the triple bond in the starting complex **1** is reduced by an external complexation to the nickel center.[6] For example, IR spectroscopic measurements gave shifts $\Delta\nu$ (**4**, 363; **5**, 392 cm^{-1}) of the absorption ν(C≡C) of 2018 cm^{-1} in complex **1** to 1655 cm^{-1} in **4** and 1626 cm^{-1} in **5**. The larger shift for **5** is according to the well-established better alkyne complexation for Ni(0) complexes with stronger donor ligands.[6c,d] The ^1H, ^{13}C, and ^{31}P NMR spectroscopic investigations characterize the structures of **4** and **5** as Ni(0) zirconacycloalkyne complexes. Room-temperature spectra displayed equivalent Cp and α-CH_2 protons (apparent C_{2v} symmetry, which is not consistent with the below discussed structure of the solid). Even at −80 °C the ^1H and ^{13}C signals of the Cp ligand in **4** remained sharp, whereas the CH_2 signals started broadening. Obviously, there is a dynamic process comparable to the well-known automerization of *s-cis*-butadiene complexes of early transition metallocenes (folded metallacyclopent-3-enes).[7a] This "ring-flip" seems

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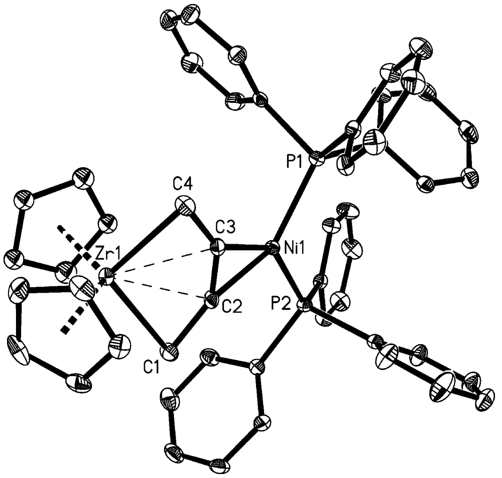


Figure 1. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C1 2.318(3), Zr1−C2 2.397(3), Zr1−C3 2.392(3), Zr1−C4 2.323(3), C1−C2 1.452(4), C2−C3 1.305(4), C3−C4 1.452(4), Ni1−C2 1.917(3), Ni1−C3 1.922(3), Ni1−P1 2.165(1), Ni1−P2 2.180(1); Zr1C1C2 75.0(2), Zr1C4C3, 74.7(2), C1C2C3 141.7(3), C2C3C4 142.5(3), C1Zr1C4 101.6(1), C2Ni1C3 39.7(1), P1Ni1P2 115.58(3).

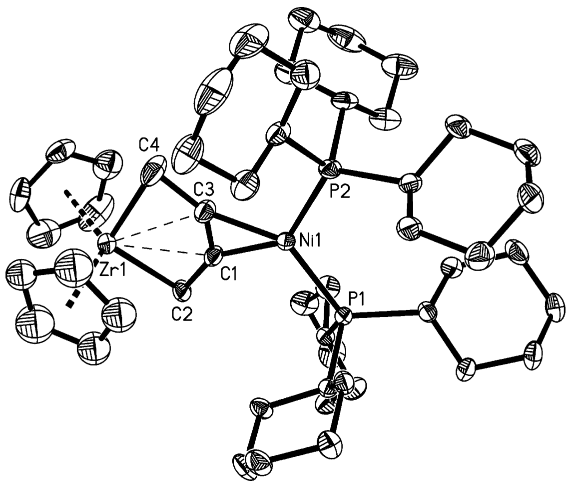


Figure 2. Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C4 2.217(5), Zr1−C3 2.396(7), Zr1−C1 2.409(7), Zr1−C2 2.285(7), C1−C2 1.455(9), C1−C3 1.294(9), C3−C4 1.493(8), Ni1−C1 1.908(7), Ni1−C3 1.905(7), Ni1−P1 2.218(2), Ni1−P2 2.204(2); Zr1C4C3 77.8(3), Zr1C2C1, 76.7(4), C1C3C4 139.0(7), C3C1C2 140.2(7), C2Zr1C4 103.6(2), C1Ni1C3 39.7(3), P1Ni1P2 116.85(8).

Table 1. Crystallographic Data

	4	**5**
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a [Å]	16.976(3)	18.253(4)
b [Å]	12.365(2)	14.993(3)
c [Å]	21.226(4)	19.523(4)
β [deg]	94.61(3)	104.23(3)
V [Å^3]	4441(1)	5179(2)
Z	4	4
density [g·cm^{-3}]	1.389	1.192
μ(Mo Kα) [mm^{-1}]	0.770	0.659
T [K]	200	293
no. of rflns (measd)	15 892	12 746
no. of rflns (indep)	8465	6556
no. of rflns (obsd)	5591	3803
no. of params	527	457
R1 ($I > 2\sigma(I)$)	0.034	0.057
wR2 (all data)	0.066	0.167

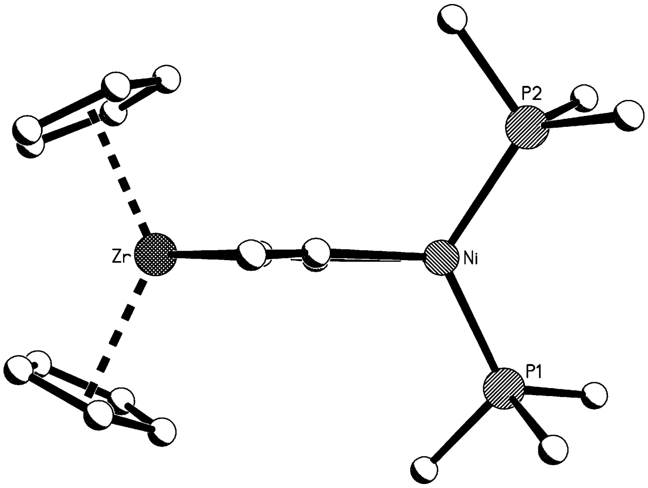


Figure 3. Side view of the molecular structure of complex **3**. All phenyl groups (except *ipso* C atoms at phosphorus) and the hydrogen atoms are omitted for clarity.

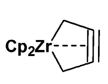
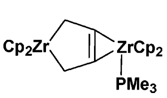
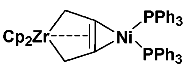
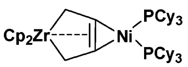
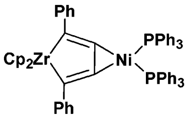
to have a very low activation barrier and was therefore not frozen out. It would generate an additional mirror plane (defined by Zr, Ni, and the metallacyclic carbon atoms), which would cause the zirconacycle to appear "flat". The ^{13}C NMR signals of the coordinated triple bond (**4**, 114.4; **5**, 117.4 ppm) are not affected by this process; they appear *downfield* from the respective signals in the free zirconacyclopentyne (**1**, 102.5 ppm[3b]) with coordination shifts $\Delta\delta$ of 11.9 and 14.9 ppm for **4** and **5**, respectively, which is in accord with the abovementioned difference in complexation strength.

Complexes **4** and **5** were investigated by X-ray crystallography. The crystallographic data are shown in Table 1 and the molecular structures in Figures 1 and 2. Both complexes display a bent zirconocene together with an additional butyne-1,4-diyl ligand, which coordinates with its triple bond a Ni(0) center in a slightly distorted trigonal planar arrangement.

The formed 1-zirconacyclopent-3-ene unit in these complexes is not planar and the coordinated triple bond is elongated as expected for Ni(0) alkyne complexes (1-zirconacyclopent-3-yne (**1**), 1.237(5); **4**, 1.305(4); and **5**, 1.294(9) Å).[6] In principle one would expect for complex **5** a longer C−C bond distance due to the abovementioned better complexation, but no significant differences were found. This is again an example that the expected bonding situation of alkyne complexation is not very well reflected by X-ray parameters of the complexed triple bonds.[6c] Additionally, the nickel carbon bond distances NiCβ and NiCβ′ as well as the "bending back" angles CαCβCβ′ and CβCβ′Cα are not significantly different for a discussion (Table 2).

Nevertheless, it is worth comparing complexes **4** and **5** with the Ni(0) complex of the zirconacyclocumulene $Cp_2Zr[\mu(\eta^4\text{-}PhC_4Ph)]Ni(PPh_3)_2$, **3** (Scheme 4). The data for this comparison are listed in Table 2. The CαCβ and the Cα′Cβ′ in complex **3** show double-bond character, whereas the corresponding bonds in complexes **4** and **5** are single bonds. On the other side the CβCβ′ bond length in complex **3** is longer, as found in complexes **4**

Table 2. Comparison of Structural Data of Five-Membered Zirconacycles

Compounds					
	1	**2**	**4**	**5**	**3**
References	[3b]	[3b]	this work	this work	[5a]
Bond distances [Å]					
CαCβ	1.406(4)	1.490(4)	1.452(4)	1.493(8)	1.322(5)
Cβ'Cα'	1.408(5)	1.480(4)	1.452(4)	1.455(9)	1.331(5)
CβCβ'	1.237(5)	1.336(4)	1.305(4)	1.294(9)	1.410(5)
ZrCα	2.415(3)	2.279(4)	2.318(3)	2.217(5)	2.238(4)
ZrCα'	2.428(3)	2.270(3)	2.323(3)	2.285(7)	2.223(4)
ZrCβ	2.314 (3)	2.495(3)	2.397(3)	2.396(7)	2.390(3)
ZrCβ'	2.320(3)	2.461(3)	2.392(3)	2.409(7)	2.379(3)
NiCβ	No	No	1.917(3)	1.905(7)	1.928(4)
NiCβ'	No	No	1.922(3)	1.908(7)	1.911(3)
NiP1	No	No	2.165(1)	2.218(2)	2.215(1)
NiP2	No	No	2.180(1)	2.204(2)	2.223(1)
Angles [°]					
ZrCαCβ	68.8(2)	79.9	75.0(2)	77.8(3)	79.8(2)
Cβ'Cα'Zr	68.6(2)	79.0	74.7(2)	76.7(4)	79.7(2)
CαCβCβ'	151.5(3)	136.7(3)	141.7(3)	139.0(7)	139.4(3)
CβCβ'Cα'	151.3(3)	140.6(3)	142.5(3)	140.2(7)	139.8(4)

and **5**, typical in **3** for Ni(0) olefin complexes and in **4** and **5** for Ni(0) alkyne complexes.[6] Interestingly, all the central ZrC distances are similar in the complexes **3**, **4**, and **5**. The most important difference between the complexes of the metallacyclocumulene and the metallacyclopentyne complexes is shown in a side view of the molecules **3** and **4** (Figures 3 and 4). From this point of view one can study the angle in the coordinated metallacyclocumulene and metallacyclopentyne at the axes CαCα′ (between ZrCαCα′ and CαCβCβ′Cα′) and the planes defined by CβCβ′Ni and P1P2Ni.

In complex **3** the coordinated cyclopentatriene is together with the nickel atom nearly planar (mean deviation from the best plane defined by ZrCαCβCβ′Cα′Ni is 0.019 Å).[5a] In complex **4** the angle between the plane ZrCαCα′ and CαCβCβ′Cα is 25.6° (mean deviation in the latter from the best plane 0.001 Å). For complex **5** the angle between the planes defined by ZrCαCα′ and CαCβCβ′Cα is 19.5° (mean deviation in the latter from the best plane 0.005 Å). This is an argument to understand complexes **4** and **5** as "metallacyclopentenes" with a typical additional interaction of the remaining double bond with the zirconium, which is not planar,[7] in contrast to the "metallacyclopentadiene" in complex **3**. Nevertheless, in the metallacyclopentyne complex $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2C_4H_2)]ZrCp_2(PMe_3)$ (**2**) the formed "metallacyclopentene" was reported to be "flat".[3b] To explain this difference between complexes **4** and **5** on one side and **2** on the other, one can discuss a stronger interaction of the triple bond with the second zirconium center in complex **2** compared to a weaker interaction with nickel in the case of **4** and **5**.[6c,d] That is why the "metallacyclopentene" unit in **4** and **5** shows the tendency to interact additionally with the zirconium center. Longer ZrCβ and ZrCβ′ bond distances and a more elongated CβCβ′ distance in **2** are in agreement with these suggestions. This stronger complexation of alkynes in case of titanocene and zirconocene in comparison to nickel(0) is a well-established fact and the basis to understand these structural differences in the zirconacyclopentyne complexes of Zr(II) and Ni(0).[6c,d]

Another interesting feature is the difference in the

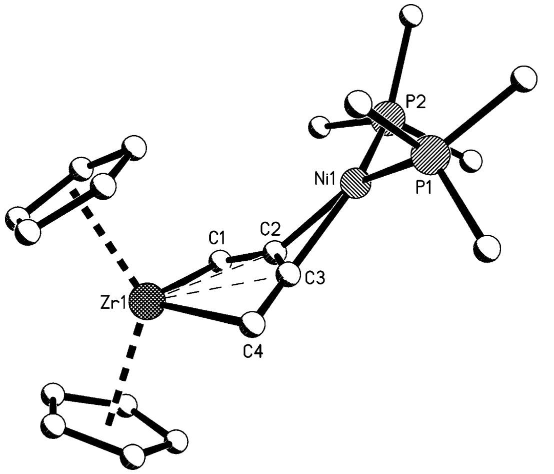


Figure 4. Side view of the molecular structure of complex **4**. The phenyl groups (except *ipso* C atoms) and the hydrogen atoms are omitted for clarity.

coordination geometry at the nickel atom. The coordinated metallacycloalkyne is nearly in the same plane, and the metallacyclotriene forms an angle to this plane (angle between P1P2Ni and CβCβ'Ni for **3**, 70.0°; for **4**, 6.2°). For bis-ligand Ni(0) alkyne complexes, e.g., the complex (η^2-cyclohexyne)Ni($Cy_2PCH_2CH_2PCy_2$), a corresponding angle of 3.7° was found.[8] To the best of our knowledge, structures for Ni(0) complexes with all carbon cyclopenta-1,2,3-trienes were not described, but in the structure of the complex $[Mo(CO)_3]$(μ-cycloheptatriene)$[Pt(PPh_3)_2]$ the corresponding angle at Pt was found to be 8.9°.[9]

In the zirconacyclocumulene the π-electrons of the central double bond are located in the same plane as the metallacycle.[4e−g] If the "internal" complexation with Zr in the ring is displaced by an "external" interaction with Ni, the NiL_2 fragment must be in the same plane where enough electron density is available. In the zirconacyclopentyne two orthogonal π-systems exist for the triple bond.[4e−g] If one of these is used for the "internal" complexation with Zr in the ring, the NiL_2 fragment interacts "externally", giving an angle to the ring plane similar to that found in typical complexes with alkynes as bridging ligands between two metals.[10a,b] This model explains the different coordination of zirconacyclocumulenes and zirconacyclopentynes with Ni(0). Following these suggestions, the different complexation of zirconacyclopentynes by Zr(II) and Ni(0) also becomes clear by the competition of both metals in the coordination with the unsaturated bond.

The interaction of the double bond (as a part of the bridged butatriene with respect to the formed metallacyclopentene) in the complex $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2C_4H_2)]ZrCp_2(PMe_3)$ (**2**) is comparable to the side-on-bridged μ-η^2-ethylene complex $Cp_2Zr(Me)[\mu\text{-}(\eta^2\text{-}C_2H_4)]Zr(Me)Cp_2$, in which an ethylene ligand is simultaneously coordinating to two zirconocene moieties. Interestingly, this molecule is planar, too.[10c]

The 1-titanacyclopent-3-yne $Cp_2Ti(\eta^4\text{-}H_2C_4H_2)$ did not show a complexation with $(Ph_3P)_2Ni(\eta^2\text{-}C_2H_4)$ and $(Cy_3P)_2Ni(\eta^2\text{-}C_2H_4)$, comparable to the formation of **4** and **5**. After 2 days' reaction time at 50 °C only the 2,5-dititanabicyclo[2.2.0]hex-1(4)-ene (Scheme 2) as the μ-*trans*-butatriene complex was detected in the reaction mixtures by NMR. Because this complex also is formed more slowly without nickel complex, it is reasonable to assume that Ni(0) consumes a part of butatriene (eventually formed by dissociation) and sets the titanocene free to form with the 1-titanacyclopent-3-yne the binuclear complex.

Conclusion

The complexation of the 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ by Ni(0) complexes with formation of $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2C_4H_2)]NiL_2$ (L = PPh_3, PCy_3) indicates that in the different bonding descriptions of the starting zirconacycle a genuine metallacyclopentyne is involved. For this the intramolecular interaction of the triple bond with the zirconium is reduced by an intermolecular one with the nickel(0) center. A different behavior was found for the 1-metallacyclopenta-2,3,4-trienes $Cp_2M(\eta^4\text{-}PhC_4Ph)$ of titanium and zirconium, in which the intramolecular interaction of the double bond with titanium and zirconium is replaced by an intermolecular complexation.

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 (THF-d_8) was treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker ARX 400. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvents, THF-d_8 ($\delta_H = 1.73$, $\delta_C = 25.2$); chemical shifts (^{31}P) are given relative to H_3PO_4 (85%). Signals designated "t" are apparent triplets due to coupling with the magnetically inequivalent P atoms. The spectra were assigned with the help of DEPT. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 4. $(Ph_3P)_2Ni(\eta^2\text{-}C_2H_4)$[11] (1.94 g, 3.2 mmol) was dissolved in THF (60 mL) under Ar, and $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$[3b] (**1**) (0.84 g, 3.0 mmol) was added to the resulting solution. The resulting yellow solution was stirred under an argon atmosphere at room temperature. After 3 days all volatiles were removed in a vacuum, and the yellow-brown residue was washed three times with *n*-hexane (15 mL). The remaining solvate-free yellow powder was used for NMR measurements. It was recrystallized from hot THF to yield golden-yellow crystals, which were separated from the mother liquor by decanting. Yield: 1.74 g (67%), mp 170 °C under Ar (60 °C loss of THF). Anal. Calcd for $C_{50}H_{44}NiP_2Zr(THF)$ (928.6): C, 69.83; H, 5.64. Found: C, 69.17; H, 5.58 (loss of THF as the reason for poor analysis). MS (70 eV, *m/z*): 262 $[PPh_3]^+$, 220 $[Cp_2Zr]^+$, 183 $[PPh_2]^+$, 108 $[PPh]^+$, 77 $[Ph]^+$. ^{1}H NMR (THF-d_8, 297 K): δ 1.58 (t, 1.3 Hz, 4H, CH_2), 5.10 (s, 10H, Cp), 7.14 (m, 12H, *m*-Ph), 7.22 (m, 6H, *p*-Ph), 7.40 ppm (m, 12H, *o*-Ph). ^{1}H NMR (THF-d_8, 193 K): δ 1.58 (br, 4H, CH_2),

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[9] Klosin, J.; Abboud, K. A.; Jones, W. M. *Organometallics* **1996**, *15*, 596.

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5.08 (s, 10H, Cp), 7.20 (m, 12H, *m*-Ph), 7.28 (m, 6H, *p*-Ph), 7.38 ppm (m, 12H, *o*-Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K): δ 32.5 (t, 2.7 Hz, CH_2), 103.5 (s, Cp), 114.4 (t, 10.1 Hz, complexed C≡C), 128.3 (t, 4.4 Hz, *m*-Ph), 129.1 (s, *p*-Ph), 134.7 (t, 6.9 Hz, *o*-Ph), 137.3 ppm (t, 16/17 Hz, *i*-Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 193 K): δ 33.1 (br, CH_2), 103.2 (s, Cp), 113.0 (t, 10.2 Hz, complexed C≡C), 128.5 (t, *m*-Ph), 129.4 (s, *p*-Ph), 134.5 (t, 6.4 Hz, *o*-Ph), 136.8 ppm (t, 17 Hz, *i*-Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 297 K): δ 38.3 ppm, at 193 K 37.6 ppm. IR (Nujol mull, cm^{-1}): 1655 (ν C≡C).

Preparation of Complex 5. As described before for complex **2**, starting from $(Cy_3P)_2Ni(\eta^2\text{-}C_2H_4)$[11] (0.47 g, 0.73 mmol) in THF (30 mL) with $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**1**) (0.20 g, 0.74 mmol) golden-yellow crystals were isolated. Yield: 0.46 g (62%), mp 120 °C under Ar. Anal. Calcd for $C_{50}H_{80}NiP_2Zr\text{-}(THF)_{0.5}$ (929.06): C, 67.22; H, 9.11. Found: C, 67.02; H, 9.05. MS (70 eV, *m/z*): 280 $[PCy_3]^+$, 272 $[Cp_2Zr(\eta^4\text{-}H_2C_4H_2)]^+$, 220 $[Cp_2Zr]$, 198 $[PCy_2]^+$, 83 $[Cy]^+$. ^1H NMR (THF-d_8, 297 K): δ 1.2−2.3 (m, 66H, Cy), 1.93 (4H, CH_2), 5.33 ppm (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K): δ 27.7 (s, Cy), 28.9 (t, Cy), 30.6 (CH_2), 31.2 (s, Cy), 35.9 (br, Cy), 103.9 ppm (s, Cp); 117.4 (t, complexed C≡C). $^{31}P\{^1H\}$ NMR (THF-d_8, 297 K): δ 40.3 ppm. IR (Nujol mull, cm^{-1}): 1626 (ν C≡C).

X-ray data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). XP (Bruker AXS) was used for structure representations. Crystals of **5** contain a half molecule of THF as solvent, which is disordered in addition to one of the Cp ligands. The high residual electron density (0.99 e·Å^{-3}) in **5** is located in the THF molecule. In **4** also one of the Cp ligands is disordered.

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Supporting Information Available: Tables of crystallographic data in cif file format, including bond lengths and angles of compound **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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