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Notes

Synthesis of *ansa*-Dimethylsilanediyl−dicyclopentadienyl−zirconacyclopent-3-yne, $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$, and Its Reactions with Ni(0) and $B(C_6F_5)_3$[†]

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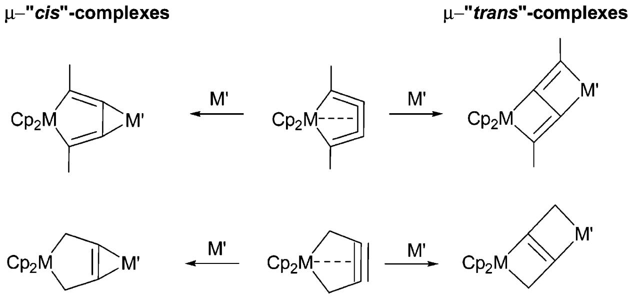
Summary: The synthesis and reactions of ansa-dimethylsilanediyl−dicyclopentadienyl−zirconacyclopent-3-yne, $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ *(**7**), are described. Complexation by Ni(0) complexes gives an external coordination of the triple bond and formation of the complex* $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]Ni(PPh_3)_2$ *(**8**), representing a μ-"cis"-complexation of 1,2,3-butatrienes, which is described and compared with the coordination of similar complexes. The reaction of complex **7** with* $B(C_6F_5)_3$ *results in ring opening of the 1-zirconacyclopent-3-yne and formation of the zwitterionic complex* $[Me_2Si(\eta^5\text{-}C_5H_4)_2Zr]^+{-}CH_2C{\equiv}CCH_2{-}[B^-(C_6F_5)_3]$ *(**9**), with the but-2-yne-1,4-diyl ligand bridging the zirconocenium center and the formed boranate. All complexes were characterized by X-ray analysis.*

Introduction

The recent chemistry of the 1-metallacyclopent-2,3,4-trienes (five-membered metallacyclocumulenes) and 1-metallacyclopent-3-ynes as related and small metallacyclic compounds has been the subject of several summarizing reviews.[1] In addition to these publications some recent selected papers describe experimental and theoretical details of such metallacycles.[2] It was calculated that the internal complexation of the unsaturated bonds C═C═C═C and C≡C by metals 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. In the structures of these compounds the central double or triple bond is elongated. This elongation is ascribed to the *intramolecular* interaction of the binding π-orbitals with empty d-orbitals at the metal.[3a,b] Another suggestion for the bonding situation in 1-zirconacyclopen-3-ynes 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 is 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 calculation approaches.[3]

Scheme 1



Metallacyclocumulenes and 1-metallacyclopent-3-ynes are also able to coordinate in an *intermolecular* manner with their unsaturated bonds to other metal fragments to form binuclear complexes (Scheme 1).[1]

By this complexation either metallacyclopentadienes or metallacyclopentenes in bridging *"cis"*-butadiyne and *"cis"*-butatriene complexes are formed, or alternatively *μ-"trans"*-butadiyne complexes and *μ-"trans"*-butatriene complexes (better described as dimetallabicycles 2,5-dimetallabicyclo[2.2.0]hex-1(4)-enes).[1,2]

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

[†] Dedicated to Professor Heinz Berke on the occasion of his 60th birthday.

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(1) (a) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456. (b) Rosenthal, U. *Angew. Chem.* **2004**, *116*, 3972; *Angew. Chem., Int. Ed.* **2004**, *43*, 3882. (c) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884. (d) Rosenthal, U.; Pellny, P.-M., Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119.

(2) (a) Suzuki, N.; Ahihara, N.; Takahara, H.; Watanabe, T.; Iwasaki, M.; Saburi, M.; Hashizume, D.; Chihara, T. *J. Am. Chem. Soc.* **2004**, *126*, 60. (b) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074. (c) Suzuki, N.; Watanabe, T.; Hirose, T.; Chihara, T. *Chem. Lett.* **2004**, *33*, 1488. (d) Suzuki, N.; Watanabe, N.; Iwasaki, M.; Chihara, T. *Organometallics* **2005**, *24*, 2065. (e) Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2005**, *24*, 3047. (f) Bach, M. A.; Beweries, T.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Bonrath, W. *Organometallics* **2005**, *24*, 5916. (g) Suzuki, N.; Watanabe, N.; Yoshida, H.; Iwasaki, M.; Saburi, M.; Tezuka, M.; Hirose, T.; Hashizume, D.; Chihara, T. *J. Organomet. Chem.* **2006**, *691*, 1175.

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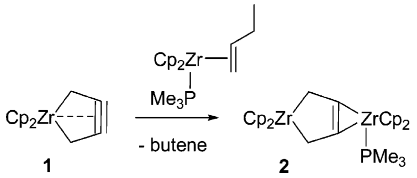
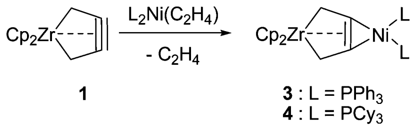
10.1021/om0608760 CCC: $37.00

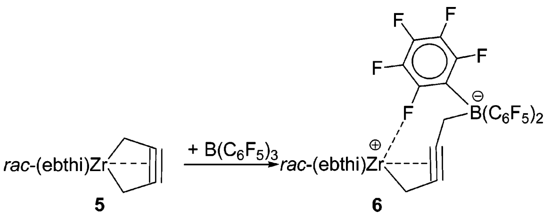
Scheme 2



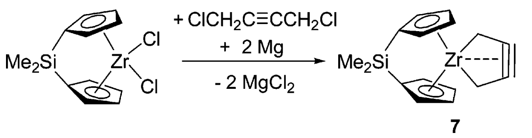
Scheme 3



Scheme 4



Scheme 5



Recently we reported that the unsubstituted 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**1**) reacts with equimolar amounts of the Ni(0) complexes $L_2Ni(\eta^2\text{-}C_2H_4)$ ($L = PPh_3$ or PCy_3) to give the binuclear complexes $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]NiL_2$ (**3**, $L = PPh_3$; **4**, PCy_3) (Scheme 3).[2e]

More recently we found that the reaction of the 1-zirconacyclopent-3-yne *rac*-(ebthi)Zr(η^4-$H_2C_4H_2$) (**5**) with the Lewis acid $B(C_6F_5)_3$, after ring-opening of the metallacycle, gives a zwitterionic complex, [*rac*-(ebthi)Zr]$^+$$-CH_2C{\equiv}CCH_2-$[$B^-$($C_6F_5$)$_3$] (**6**), that has the zirconocenium center and the negatively charged boranate bridged by a but-2-yne-1,4-diyl ligand (Scheme 4).[2f]

Nevertheless, the stoichiometric and catalytic chemistry of 1-metallacyclopent-3-ynes was relatively unspectacular with regard to expected insertion, coupling, trimerization, or oligomerization reactions.[1b] We were interested to see how the use of an *ansa*-bridged ligand such as the *ansa*-dimethylsilanediyl−dicyclopentadienyl ligand can alter and influence the structure and the reactivity of 1-zirconacyclopent-3-ynes.

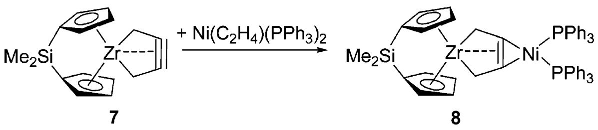
Results and Discussion

Ansa-Dimethylsilanediyl−dicyclopentadienyl−1-zirconacyclopent-3-yne, $Me_2Si(\eta^5C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**7**), was prepared by Suzuki's procedure for the preparation of 1-zirconacyclopent-3-ynes,[2] the reaction of $Me_2Si(\eta^5\text{-}C_5H_4)_2ZrCl_2$ with 1,4-dichlorobut-2-yne and magnesium in THF (Scheme 5).

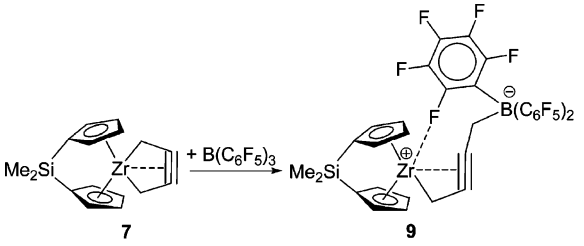
The IR spectrum of **7** shows ν(C≡C) at 2013 cm^{-1}, which is very close to the 2018 cm^{-1} absorption of complex **1**. Also the ^{13}C NMR signal of the coordinated triple bond of **7**, 101.2 ppm, essentially is the same as that of the unbridged 1-zirconacyclopent-3-yne, **1**: 102.5 ppm.[2]

External complexation of the triple bond of **7** to Ni(0) yielded the complex $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]Ni(PPh_3)_2$ (**8**) (Scheme 6).

Scheme 6



Scheme 7



The IR spectrum of **8** showed ν(C≡C) at 1645 cm^{-1}. This shift versus that of the umcomplexed C≡C bond of **7**, 368 cm^{-1}, is nearly the same as that observed when **1** was converted to the Ni(0) complexes **3**, 363 cm^{-1}, and **4**, 392 cm^{-1}.[2e] The larger shift for **4** was explained by the well-established better alkyne complexation for Ni(0) complexes containing stronger donor ligands.[4] The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic investigations confirmed the structure of **8** as a Ni(0) zirconacycloalkyne complex. Room-temperature spectra displayed equivalent η^5-C_5H_4 and α-CH_2 protons with C_{2v} symmetry. This is not consistent with the solid-state structure of **8** as discussed below. A similar difference between solution and solid-state structure was found for complexes **3** and **4**.[2e] The ^{13}C NMR signals of the coordinated triple bond (**8**: 116.3 ppm) appear *downfield* from the respective signals in the free 1-zirconacyclopent-3-yne (**7**: 101.2 ppm), as was found in the other cases (**3**: 114.4; **4**: 117.4 ppm), with a coordination shift $\Delta\delta$ of 15.1 for **8** (**4**: 11.9; **5**: 14.9 ppm).

Complex **7** on reaction with $B(C_6F_5)_3$ undergoes ring-opening of the 1-zirconacyclopent-3-yne, resulting in formation of **9**, a zwitterionic complex, $[Me_2Si(\eta^5\text{-}C_5H_4)_2Zr]^+{-}CH_2C{\equiv}CCH_2{-}[B^-(C_6F_5)_3]$, in which the but-2-yne-1,4-diyl ligand bridges the zirconocenium center and the boranate is incorporated into the complex (Scheme 7).

The ν(C≡C) absorption of 1-zirconacyclopent-3-yne **7** was not observed in the IR spectrum of **9**. This was also the case in the IR spectrum of the very similar complex **6**. The extremely low solubility of **9** prevents the acquisition of ^{13}C NMR data and detailed investigations of the molecular dynamics. ^{19}F NMR spectra in THF-d_8 solution gave no indication for a Zr−F interaction. Nevertheless, in toluene-d_8 some hints for the coordination of one C−F were found (see Supporting Information).

The solid-state structures of complexes **7**, **8**, and **9** were determined by X-ray crystallography; see Table 1 for crystallographic data and Figures 1, 2, and 3 for the respective molecular structures.

The molecular structure of complex **7** shows a planar metallacycle as a typical part of the 1-zirconacyclopent-3-yne (see Supporting Information).

Complex **8** displays a bent zirconocene together with an additional *cis*-bridging but-2-yne-1,4-diyl ligand whose C≡C

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(4) (a) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103. (b) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1988**, *348*, 135. (c) Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119. (d) Rosenthal, U.; Nauck, C.; Arndt, P.; Pulst, S.; Baumann, W.; Burlakov, V. V.; Görls, H. *J. Organomet. Chem.* **1994**, *484*, 81.

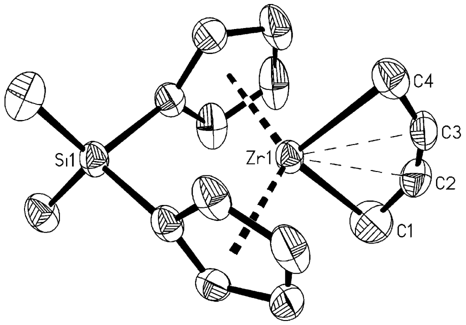

Figure 1. Molecular structure of one of the two molecules of the asymmetric unit of complex **7**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

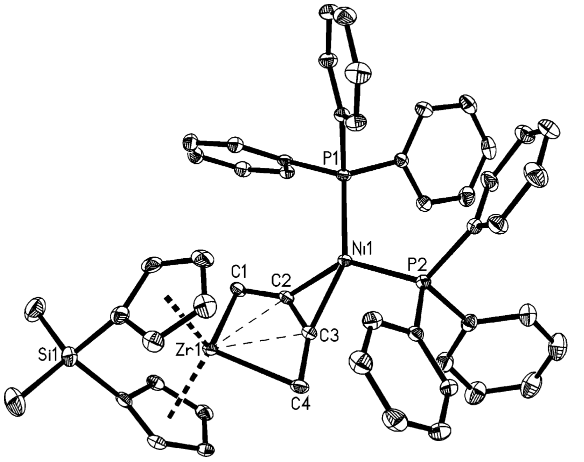

Figure 2. Molecular structure of complex **8**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C1 2.326(2), Zr1−C2 2.379(2), Zr1−C3 2.379(2), Zr1−C4 2.353(2), C1−C2 1.442(3), C2−C3 1.317(3), C3−C4 1.441(3), Ni1−C2 1.913(2), Ni1−C3 1.913(2), Ni−P1 2.1723(7), Ni−P2 2.163(1); Zr1−C1−C2 74.1(1), Zr1−C4−C3, 73.2(1), C1−C2−C3 141.4(2), C2−C3−C4 142.8(2), C1−Zr1−C4 100.34(8), C2−Ni1−C3 40.28(8), P1−Ni1−P2 112.84(4).

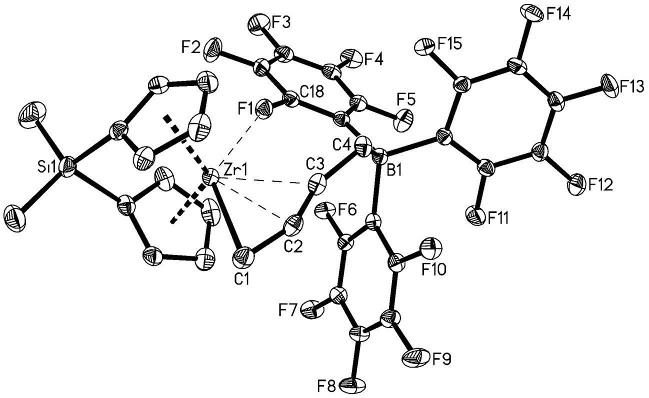

Figure 3. Molecular structure of complex **9**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C1 2.405(2), Zr1−C2 2.388(2), Zr1−C3 2.492(2), C1−C2 1.392(3), C2−C3 1.229(2), C3−C4 1.468(2), C4−B1 1.666(2), Zr1−F1 2.399(1) Å; Zr1−C1−C2 72.43(10), C1−C2−C3 153.8(2), C2−C3−C4 159.2(2)°.

Table 1. Crystallographic Data

	7	**8**	**9**
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	20.454(1)	10.983(2)	12.820(3)
b [Å]	6.9281(4)	15.046(3)	14.237(3)
c [Å]	21.020(1)	16.135(3)	21.049(4)
α [deg]	90.00	66.34(3)	90.0
β [deg]	94.416(4)	83.28(3)	100.52(3)
γ [deg]	90.00	81.07(3)	90.0
V [Å^3]	2969.8(3)	2408.2(8)	3777.4(13)
Z	8	2	4
density [g cm^{-3}]	1.474	1.358	1.642
μ(Mo Kα) [mm^{-1}]	0.801	0.738	0.429
T [K]	293(2)	200(2)	200(2)
no. of rflns (measd)	36 806	40 186	60 790
no. of rflns (indep)	5233	11 070	8681
no. of rflns (obsd)	3706	7943	7261
no. of params	265	569	548
R1 ($I > 2\sigma(I)$)	0.033	0.027	0.028
wR2 (all data)	0.077	0.056	0.072

bond is coordinated to a Ni(0) center in a slightly distorted trigonal planar arrangement. Similar complexes were recently calculated in detail by the Jemmis group.[5] One can regard complex **8** as a "1-zirconacyclopent-3-ene" with an additional interaction of the remaining double bond with the zirconium atom. The longer bond distance for the coordinated triple bond in **8** (1.317(3) Å) compared to the 1-zirconacyclopent-3-yne **7** is due to the interaction with the Ni(0) fragment (see Supporting Information).

The structural data of the zwitterionic complex [$Me_2Si(\eta^5$-$C_5H_4)_2Zr]^+$−$CH_2C{\equiv}CCH_2$−[$B^-(C_6F_5)_3$] (**9**) [Zr1−C1 2.405(2), Zr1−C2 2.388(2), Zr1−C3 2.492(2), C1−C2 1.392(3), C2−C3 1.229(2), C3−C4 1.468(2), Zr1−F1 2.399(1) Å; Zr1−C1−C2 72.43(10), C1−C2−C3 153.8(2), C2−C3−C4 159.2(2)°] are comparable with those of [*rac*-(ebthi)Zr]$^+$−$CH_2C{\equiv}CCH_2$−[$B^-(C_6F_5)_3$] (**6**): Zr1−C1 2.371(2), Zr1−C2 2.414(2), Zr1−C3 2.601(2), C1−C2 1.401(3), C2−C3 1.229(3), C3−C4 1.476(3), Zr1−F1 2.442(1) Å; Zr1−C1−C2 74.67(13), C1−C2−C3 155.5(2), C2−C3−C4 161.1(2)°.

Both complexes feature the typical bent *ansa*-metallocene parts $Me_2Si(\eta^5$-$C_5H_4)_2Zr$ and *rac*-(ebthi)Zr, which interact with the but-2-yne-1,4-diyl ligand. For **6** the short C2−C3 bond of 1.229(3) Å and long Zr1−C3 distances of 2.601(2) Å as well as C2−C3−C4 angles of 161.1(2)° indicate only a very weak interaction of the Zr with the triple bond, as expected for alkyne complexes of Zr in higher oxidation state. For **9** this interaction seems to be stronger, as reflected by the shorter Zr1−C3 distances of 2.492(2) Å and smaller C2−C3−C4 angle of 159.2(2)°. On the other hand both complexes possess the same short C2−C3 bond of 1.229 Å. Typical for these zwitterionic complexes is the interaction of an *ortho*-F atom of one of the pentafluorophenyl rings with the zirconocenium center. For complex **9** the corresponding distance, 2.399(1) Å, is shorter than for **6** (2.442(1) Å).

By using the *ansa*-dimethylsilanediyl−dicyclopentadienyl ligand in the $Me_2Si(\eta^5$-$C_5H_4)_2M$ core an enhancement of reactivity often is observed, when the two cyclopentadienyl ligands are "tied back" by a dimethylsilanediyl link.[6] The products, obtained in the reaction of $Me_2Si(\eta^5$-$C_5H_4)_2Zr(\eta^4$-$H_2C_4H_2)$ (**7**) with Ni(0) and $B(C_6F_5)_3$, namely, the cycloalkyne complex $Me_2Si(\eta^5$-$C_5H_4)_2Zr[\mu(\eta^4$-$H_2C_4H_2)]Ni(PPh_3)_2$ (**8**) and the zwitterionic complex [$Me_2Si(\eta^5$-$C_5H_4)_2Zr]^+$−$CH_2C{\equiv}CCH_2$−[$B^-(C_6F_5)_3$] (**9**), did not exhibit different structural features compared with the unbridged examples $Cp_2Zr[\mu$-$(\eta^4$-$H_2C_4H_2)]$-NiL_2 (**3**, L = PPh_3; **4**, PCy_3) and the zwitterionic complex [*rac*-

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(5) Jemmis, E. D.; Parameswaran, P.; Phukan, A. K. *Mol. Phys.* **2005**, *103*, 897, and references therein.

(6) Chapter by Okuda, J. In *Metallocenes, Synthesis−Reactivity−Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, p 415.

(ebthi)Zr]$^+$−$CH_2C{\equiv}CCH_2$−[$B^-(C_6F_5)_3$] (**6**) (see Supporting Information).

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, toluene-d_8 and 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 AV 300/AV 400. Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvents: C_6D_6 ($\delta_H = 7.16$, $\delta_C = 128.0$), toluene-d_8 ($\delta_H = 2.03$, $\delta_C = 20.4$); 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 $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ (7). Under argon $Me_2Si(C_5H_4)_2ZrCl_2$ (3.00 g, 8.6 mmol) and Mg turnings (0.418 g, 17.2 mmol) were suspended in 40 mL of THF. 1,4-dichlorobut-2-yne (0.84 mL, 8.6 mmol) was added, and the yellow suspension was stirred at room temperature for 16 h. During this time the color changed to red. 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-red powder remained, which was recrystallized from THF to give orange crystals. Yield: 2.10 g (74%), mp 121−124 °C under Ar (dec). Anal. Calcd for $C_{16}H_{18}SiZr$ (329.62 g·mol^{-1}): C, 58.30; H, 5.50. Found: C, 58.32; H, 5.90. MS (70 eV, *m/z*): *m/z* 328 [M]$^+$. ^{1}H NMR (298 K, C_6D_6): δ 0.38 (s, 6 H, $SiMe_2$), 2.79 (s, 4 H, CH_2), 4.44 (dd, 4 H, Cp), 6.05 (dd, 4 H, Cp) ppm. ^{13}C{^{1}H} NMR (298 K, C_6D_6): δ −5.3 (s, $SiMe_2$), 39.3 (s, CH_2), 101.2 (s, C≡C), 102.7 (s, Cp), 105.5 (s, Cp), 113.8 (s, Cp). IR (Nujol mull, cm^{-1}): 2013 cm^{-1} (C≡C).

Preparation of $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]Ni(PPh_3)_2$ (8). To a solution of $Me_2Si(C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**7**) (0.433 g, 1.31 mmol) in 15 mL of THF was added a solution of $(Ph_3P)_2Ni(\eta^2\text{-}C_2H_4)$[7] (0.796 g, 1.31 mmol) in 15 mL of THF. The mixture was stirred for 2 days at 60 °C, and the volatiles were removed from the yellow solution in vacuum. The yellow-brown residue was extracted with hot *n*-hexane (3 × 15 mL). After cooling, crystals had formed, which were filtered off and recrystallized from THF to give yellow crystals, which were washed with cold *n*-hexane and dried. Yield: 0.652 g (55%); mp 130 °C under Ar (dec). Anal. Calcd for $C_{52}H_{48}NiP_2SiZr$ (912.89 g·mol^{-1}): C, 68.42; H, 5.30. Found: C, 68.04; H, 5.49. MS (70 eV, *m/z*): 78 [Ph]$^+$, 183 [PPh_2]$^+$, 262 [PPh_3]$^+$, 276 [$Me_2Si(C_5H_4)_2Zr$]$^+$. ^{1}H NMR (298 K, C_6D_6): δ 0.38 (s, 6 H, Me_2Si), 2.01 (s, 4 H, CH_2), 4.88 (dd, 4 H, Cp), 5.88 (dd 4 H, Cp), 7.0 (m, 18 H, *m*-Ph, *p*-Ph), 7.68 (m, 12 H, *o*-Ph) ppm. ^{13}C{^{1}H} NMR (298 K, C_6D_6): δ −4.9 (s, Me_2Si), 33.1 (s, CH_2), 98.7 (s, Cp), 104.2 (s, Cp), 113.3 (s, Cp), 116.3 ("t", C═C), 128.1 ("t", *m*-Ph), 128.8 ("t", *p*-Ph), 134.4 ("t", *o*-Ph), 136.9 ("t", *i*-Ph). ^{31}P: $\delta = 38.5$ (PPh_3). IR (Nujol mull, cm^{-1}): 1645 cm^{-1} (C═C).

Preparation of [$Me_2Si(\eta^5\text{-}C_5H_4)_2Zr$]$^+$−$CH_2C{\equiv}CCH_2$−[$B^-(C_6F_5)_3$] (9). To a solution of $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(\eta^4\text{-}H_2C_4H_2)$ (**8**) (0.300 g, 0.91 mmol) in 10 mL of toluene was added dropwise a filtered solution of $B(C_6F_5)_3$ (0.466 g, 0.91 mmol) in 20 mL of toluene. The resulting red-brown solution gave, after standing at room temperature for some days, yellow crystals, which were washed with cold toluene and dried. Yield: 0.410 g (53%). mp: 150−153 °C under Ar (dec). Anal. Calcd for $C_{34}H_{18}BF_{15}SiZr$ (841.60 g·mol^{-1}): C, 48.52; H, 2.16. Found: C, 48.65; H, 2.69. MS (70 eV, m/z): *m/z* 276 [$Me_2Si(C_5H_4)_2$]$^+$, 512 [$B(C_6F_5)_3$]$^+$. ^{1}H NMR (298 K, THF-d_8): δ 0.59, 0.75 (6 H, $SiMe_2$), 2.40 (2 H, CH_2), 2.68 (2 H, CH_2), 5.64 (2 H, Cp), 5.89 (4 H, Cp), 6.43 (2 H, Cp) ppm. ^{19}F NMR (298 K, THF-d_8): δ −132.4 (d, *ortho*-F), −164.0 (t, *para*-F), −167.4 (t, *meta*-F). IR (Nujol mull, cm^{-1}): 1641 cm^{-1} (C_6F_5).

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: Sheldrick, G. M.; University Göttingen, 1997, and SIR 2004: Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381, resp.) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). XP (Bruker AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in cif file format, including bond lengths and angles of compound **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Preparation according to: (a) Herrmann, G. Ph.D. Thesis, TH Aachen, 1963. (b) Wilke, G.; Herrmann, G. *Angew. Chem.* **1962**, *74*, 693.