Carbon–Carbon Bond Formation versus Hydrogen Transfer in the Reaction of Alkynes with Mono(cyclopentadienyl)zirconium(II) Complexes: Regioselective Dimerization, Cocyclotrimerization, and Catalytic Cyclotrimerization. The Preparation and X-ray Structures of Cp(dmpe)XZr[(R)C=C(R′)C(R)=C(R′)] [R = CH₃; R′ = H, CH₃; X = Cl, CH₃; dmpe = 1,2-Bis(dimethylphosphino)ethane] and of CpZr(dmpe)Cl[C≡C(*t*-Bu)][CH=CH(*t*-Bu)]

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Under mild conditions, the reaction between CpZr(dmpe)₂X [X = Cl (**1**), Me (**2**); dmpe = 1,2-bis(dimethylphosphino)ethane] and aliphatic alkynes yields the crystalline CpZr[(R)C=C(R′)C(R)=C(R′)]-(dmpe)X [R = R′ = Me, X = Cl (**3**), Me (**4**); R′ = H, R = Me, X = Cl (**5**)]. In the case of **5**, the zirconacyclopentadiene ring has been formed regiospecifically via a quantitative head-to-tail dimerization reaction. Steric factors are probably the origin of the regioselectivity. The structures of the complexes have been demonstrated by X-ray analyses. Crystal data are as follows. **3**: monoclinic, *C2/c, a* = 16.807 (1) Å, *b* = 9.291 (1) Å, *c* = 27.557 (1) Å, *β* = 96.906 (4)°, *V* = 4271.9 (5) Å³, *Z* = 8. **4**: triclinic, *P1̄, a* = 9.252 (1) Å, *b* = 9.416 (1) Å, *c* = 14.104 (1) Å, *α* = 91.822 (8)°, *β* = 98.948 (9)°, *γ* = 118.09 (1)°, *V* = 1063.0 (2) Å³, *Z* = 2. **5**: monoclinic, *P2₁/n, a* = 9.699 (2) Å, *b* = 13.563 (5) Å, *c* = 15.361 (4) Å, *β* = 91.36 (2)°, *V* = 2020.1 (9) Å³, *Z* = 4. Hydrogen transfer between two molecules of alkyne has been observed with the bulky HC≡C(*t*-Bu). The structure of the resulting CpZr(dmpe)Cl[C≡C(*t*-Bu)][CH=CH(*t*-Bu)] (**6**) has been demonstrated by X-ray analysis. Crystal data for **6**: monoclinic, *P2₁/a, a* = 11.333 (3) Å, *b* = 15.655 (7) Å, *c* = 16.051 (3) Å, *β* = 100.08 (2)°, *V* = 2804 (1) Å³, *Z* = 4. Stoichiometric cyclotrimerization reactions and cocyclotrimerization can be achieved by further reaction of complexes **3**, **4**, and **5** with small alkynes (propyne, acetylene) and acetonitrile, forming random mixtures of isomeric arenes and substituted pyridine (collidine). Catalytic cyclotrimerization has been observed in the case of acetylene (−20 °C) and propyne (room temperature) with formation of benzene and a mixture of 1,3,5- and 1,2,4-mesitylene, respectively.

Introduction

The acetylenes are versatile and interesting targets for studying metal-promoted organic reactions. A number of transformations (insertions into the M–H and M–C bond,[1] cyclodimerization to η⁴-cyclobutadienes,[2] intramolecular dimerization,[3] oxidative coupling,[4] catalytic cyclotrimerization to arenes,[5] poly-/oligomerization,[6] cyclotrimerization,[7] metal-promoted organic synthesis,[8] are possible depending on the nature and the oxidation state of the transition metal used. In this wide field of interest, understanding the formation of metallacyclopentadienes is central to the role played by these functionalities as intermediates in most of the afore-mentioned transformations. The regioselective *oxidative coupling* is especially desirable when unsymmetric acetylenes are employed, the key step being the spontaneous cyclization reaction of intermediate bis(acetylene) transition-metal complexes. In a following step in fact, ring closure can be achieved by several reactions[9] (including Diels–Alder type),[10] in principle allowing the stereocontrolled elaboration into cyclic and even polycyclic structures. On the basis of theoretical analysis, Stockis and Hoffmann[11] proposed that, in the

Chart I
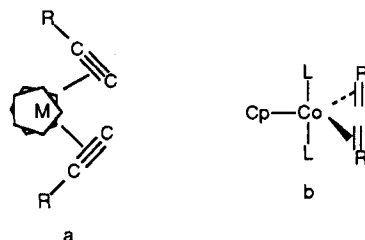
cases of metallocenic derivatives, the two acetylene molecules and the metal center should lie on the same mo-

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lecular plane (Chart Ia). The electron-donating properties of the substituents determine which pair of carbon atoms will be engaged in the formation of the C–C bond.

In agreement with this analysis, the regiospecificity in the formation of cycloimines, lactones, and oxacyclopentanes[8b] is quite satisfactory. However, the regiochemical control remains problematic for the formation of metallacyclopentadienes, and the utilization of sterically demanding molecules remains the most successful strategy for increasing the selectivity. For example, in the acetylene dimerization promoted by mono(cyclopentadienyl)cobalt systems the steric effects appear to be the major factors. In order to explain the observed isomer distribution, an "upright" orientation of the two coordinated acetylenes in the intermediate bis(acetylene) complex has been suggested.[12] The regioselectivity in this case is caused by the orientation of the two unsymmetric alkynes ("parallel" or "antiparallel") in respect to the bulky substituents (Chart Ib). Steric factors have also been adduced to explain the high regiospecificity observed in the Zr-promoted cyclization of diacetylenes to *E,E*-exocyclic dienes[13] as well as in the cyclotrimerization of *tert*-butylacetylene observed during the reaction with a Mo=C double bond of a molybdenum–carbene complex.[14]

Group IV low-valent bis(cyclopentadienyl) complexes have been shown to be versatile reagents for the acetylene oxidative coupling.[8b–d,g] Several synthetic pathways have been developed to bypass the difficulties in obtaining d[2] metallocenic species. Photolysis or thermolysis of metallocene dialkyls[15] and reduction with Mg[16] as well as RH

elimination from hydrido–alkyl complexes[17] have been used for in situ reactions with several acetylenes. In all cases, the reactions with unsymmetric alkynes lead to mixtures of the three possible isomers with a preference for the α,α'-disubstituted metallacycle.

We wish to report in this paper two sterically controlled *regioselective* and *quantitative* transformations of unsymmetric acetylenes promoted by Zr(II) complexes together with a study on the chemical behavior.

Experimental Section

All the operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB 200). CpZrCl(dmpe)$_2$ and CpZrMe(dmpe)$_2$ have been prepared according to published methods.[18,19] Solvents and organic reagents were purified and dried according to standard procedures. Dmpe has been synthesized as published (Caution: danger of serious explosions).[20] Acetylene, propyne (Matheson), 2-butyne, and *tert*-butylacetylene (Aldrich) have been used without further purification. Solvents used for nuclear magnetic resonance experiments (benzene-d_6, thf-d_8) were vacuum transferred from Na–K alloy. [1]H and ^{13}C spectra were recorded on a Varian VXR 300 or Bruker WH 90 spectrometer. Chemical shifts are reported in units of δ, referenced to the tetramethylsilane and calculated from the position of the solvent absorption. Infrared (IR) spectra were obtained on a Unicam SP3-300 instrument; Nujol mulls were prepared in the drybox. Gas chromatograms were obtained on a Hewlett-Packard 5890 A gas chromatograph equipped with a 50-m capillary column filled with CP-Sil-5-CB fused silica. Elemental analyses were performed at the Chemistry Department of the University of Groningen. Gas volumetric measurements have been carried out by using a Töpler pump.

Preparation of CpZr[(Me)C=C(Me)C(Me)=C(Me)]-(dmpe)Cl (3). A solution (50 mL) of CpZr(dmpe)$_2$Cl (0.65 g, 1.32 mmol) in ether (50 mL) was reacted with 3 equiv of 2-butyne. The color turned light orange within 8 h, and the resulting solution was concentrated to a small volume. Orange crystals precipitated upon cooling at −30 °C (0.45 g, 1.00 mmol, 75% yield).

Anal. Calcd for C$_{19}$H$_{33}$P$_2$ClZr (Found): C, 50.70 (50.86); H, 7.39 (7.40); Zr, 20.26 (20.32); Cl, 7.88 (8.09). ^{1}H NMR (300 MHz, C$_6$D$_6$, 27 °C): δ 6.27 (s, 5 H, Cp), 2.23 (br s, 3 H, Me$_{ring}$), 1.88 (d, J_{P-H} = 3.3 Hz, 3 H, Me$_{ring}$), 1.80 (d, J_{P-H} = 3.3 Hz, 3 H, Me$_{ring}$), 1.65 (s, 3 H, Me$_{ring}$), 1.40 (d, J_{P-H} = 7.0 Hz, 3 H, Me$_{dmpe}$), 1.31 (m, 2 H, (CH$_2$)$_{dmpe}$), 0.93 (m, 2 H, (CH$_2$)$_{dmpe}$), 0.83 (d, J_{P-H} = 6.0 Hz, 3 H, Me$_{dmpe}$), 0.70 (d, J_{P-H} = 5.4 Hz, 3 H, Me$_{dmpe}$), 0.63 (d, J_{P-H} = 8.4 Hz, 3 H, Me$_{dmpe}$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 27 °C): δ 188.0 (dd, J_{P-C} = 14.9 Hz, J_{P-C} = 2.7 Hz, C$_{ring}$), 186.4 (dd, J_{P-C} = 19.3 Hz, J_{P-C} = 6.9 Hz, C$_{ring}$), 144.0 (s, C$_{ring}$), 111.2 (d, J_{C-H} = 170.3 Hz, Cp), 27.0 (t, J_{C-H} = 129.8 Hz, (CH$_2$)$_{dmpe}$), 26.3 (t, J_{C-H} = 130.0 Hz, (CH$_2$)$_{dmpe}$), 22.9 (q, J_{C-H} = 123.1 Hz, Me$_{ring}$), 22.2 (q, J_{C-H} = 124.0 Hz, Me$_{ring}$), 15.7 (q, J_{C-H} = 131.0 Hz, Me$_{ring}$), 14.9 (q, J_{C-H} = 130.0 Hz, Me$_{ring}$), 14.6 (q, J_{C-H} = 129.5 Hz, Me$_{dmpe}$), 14.5 (q, J_{C-H} = 129.0 Hz, Me$_{dmpe}$), 13.3 (q, J_{C-H} = 129.6 Hz, Me$_{dmpe}$), 12.2 (q, J_{C-H} = 130.2 Hz, Me$_{dmpe}$).

Preparation of CpZr[(Me)C=C(Me)C(Me)=C(Me)]-(dmpe)Me (4). A solution of CpZr(dmpe)$_2$Me (1.20 g, 2.55 mmol) in pentane (50 mL) was reacted with 3 equiv of 2-butyne. The color turned light orange within 8 h, and the resulting solution was concentrated to a small volume. Orange crystals separated upon cooling at −30 °C (0.36 g, 0.84 mmol, 33% yield).

Anal. Calcd for C$_{20}$H$_{36}$P$_2$Zr (Found): C, 55.91 (55.48); H, 8.45 (8.47); Zr, 21.23 (21.21). ^{1}H NMR (300 MHz, C$_6$D$_6$, 27 °C): δ 6.17 (s, 5 H, Cp), 2.00 (s, 3 H, Me$_{ring}$), 1.94 (s, 3 H, Me$_{ring}$), 1.93 (s, 3 H, Me$_{ring}$), 1.88 (s, 3 H, Me$_{ring}$), 1.46 (br m, 4 H, (CH$_2$)$_{dmpe}$), 1.10

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Table I. Crystal Data and Structural Analysis Results

	3	4	5	6
formula	$C_{19}H_{33}P_2ClZr$	$C_{20}H_{36}P_2Zr$	$C_{17}H_{29}P_2ClZr$	$C_{23}H_{41}P_2ClZr$
fw, g mol^{-1}	450.09	429.67	422.04	506.20
cryst system	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/a$
Z	8	2	4	4
a, Å	16.807 (1)	9.252 (1)	9.699 (2)	11.333 (3)
b, Å	9.291 (1)	9.416 (1)	13.563 (5)	15.655 (7)
c, Å	27.577 (1)	14.104 (1)	15.361 (4)	16.051 (3)
α, deg		91.822 (8)		
β, deg	96.906 (4)	98.948 (9)	91.36 (2)	100.08 (2)
γ, deg		118.09 (1)		
V, Å^3	4271.9 (5)	1063.0 (2)	2020.1 (9)	2804 (1)
D_{calcd}, g cm^{-3}	1.400	1.342	1.39	1.199
$F(000)$	1872	452	872	1064
μ(Mo Kα), cm^{-1}	7.8	6.6	8.2	6.0
diffractometer	CAD-4F	CAD-4F	Nicolet R3m	CAD-4F
radiation	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)
T, K	100	100	293	293
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.72 ($2\theta_{max}$ = 62.0)	0.62 ($2\theta_{max}$ = 52.0)	0.64 ($2\theta_{max}$ = 55)	0.62 ($2\theta_{max}$ = 52.0)
range of hkl	-1, 24; 0, 13; -39, 39	-11, 11; -11, 11; -17, 1	-12, 12; 0, 17; 0, 19	-13, 5; -19, 0; -19, 19
no. of reflctns	7809	4720	4998	8662
no. of unique reflctns	6785	4179	4624	5486
no. of reflctns used	5681	3610	3554	3381
no. of parameters	341	353	196	266
R	0.031	0.025	0.029	0.085
R_w	0.038	0.028	0.031	0.083
GOF	2.004	1.322	1.079	2.992
largest shift/esd	0.777	0.024	0.015	0.320
largest residual peak	0.726	0.380	0.538	1.19

(d, J_{P-H} = 5.8 Hz, 3 H, Me$_{dmpe}$), 0.72 (d, J_{P-H} = 7.3 Hz, 3 H, Me$_{dmpe}$), 0.67 (d, J_{P-H} = 4.4 Hz, 3 H, Me$_{dmpe}$), 0.49 (d, J_{P-H} = 5.8 Hz, 3 H, Me$_{dmpe}$), -0.49 (dd, J_{P-H} = 10.3/3.0 Hz, 3 H, Me). ^{13}C NMR (75 MHz, C$_6$D$_6$, 27 °C): δ 188.0, 185.3, 142.7 (s, C$_{ring}$), 109.7 (d, J_{C-H} = 169.2 Hz, Cp), 30.0 (q, J_{C-H} = 115.0 Hz, Me), 27.7 (t, J_{C-H} = 130.0 Hz, (CH$_2$)$_{dmpe}$), 27.5 (t, J_{C-H} = 129.1 Hz, (CH$_2$)$_{dmpe}$), 25.0 (q, J_{C-H} = 122.0 Hz, Me$_{ring}$), 22.1 (q, J_{C-H} = 122.0 Hz, Me$_{ring}$), 15.8 (q, J_{C-H} = 122.0 Hz, Me$_{ring}$), 15.1 (q, J_{C-H} = 122.0 Hz, Me$_{ring}$), 14.1 (q, J_{C-H} = 130.0 Hz, Me$_{dmpe}$), 13.9 (q, J_{C-H} = 130.0 Hz, Me$_{dmpe}$), 13.5 (q, J_{C-H} = 130.0 Hz, Me$_{dmpe}$), 13.1 (q, J_{C-H} = 129.5 Hz, Me$_{dmpe}$).

Preparation of CpZr[(Me)C=CHC(Me)=CH](dmpe)Cl (5). A solution of CpZr(dmpe)$_2$Cl (0.750 g, 1.52 mmol) in ether (50 mL) was saturated with propyne. The color turned light yellow within few hours. The resulting solution separated light yellow crystals (0.47 g, 1.1 mmol, 72% yield) on cooling at -30 °C.

Anal. Calcd for C$_{17}$H$_{29}$P$_2$ZrCl (Found) C, 48.38 (48.24); H, 6.93 (7.05); Zr, 21.61 (21.87); Cl, 8.40 (8.57). ^{1}H NMR (300 MHz, C$_6$D$_6$, 27 °C): δ 6.75 (br s, 1 H, CH), 6.23 (br s, 1 H, CH), 6.21 (d, J_{P-H} = 5.5 Hz, 5 H, Cp), 2.41 (s, 3 H, Me$_{ring}$), 2.04 (dd, J_{P-H} = 4.4 Hz, J_{H-H} = 1.5 Hz, 3 H, Me$_{ring}$), 1.33 (d, J_{P-H} = 7.2 Hz, 3 H, Me$_{dmpe}$), 1.28 (m, 2 H, (CH$_2$)$_{dmpe}$), 0.78 (m, 2 H, (CH$_2$)$_{dmpe}$), 0.76 (d, J_{P-H} = 6.1 Hz, 3 H, Me$_{dmpe}$), 0.75 (d, J_{P-H} = 3.3 Hz, 3 H, Me$_{dmpe}$), 0.67 (d, J_{P-H} = 6.0 Hz, 3 H, Me$_{dmpe}$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 27 °C): δ 178.8 (d, J_{C-H} = 170.3 Hz, CH), 139.3 (d, J_{C-H} = 133.5 Hz, CH), 111.1 (d, J_{C-H} = 170.3 Hz, Cp), 27.8 (m, Me$_{ring}$), 26.5 (m, Me$_{ring}$), 26.2-26.6 (m, (CH$_2$)$_{dmpe}$), 13.5-12.6-12.5-11.2 (m, Me$_{dmpe}$). No determination of J_{C-H} and J_{P-H} was possible. No singlets attributable to the C$_{ring}$ atoms have been located.

Preparation of CpZr(dmpe)Cl[C≡C(t-Bu)][CH=CH(t-Bu)] (6). Neat *tert*-Butylacetylene (0.70 g, 8.5 mmol) was added to a solution of 1 (0.90 g, 1.8 mmol) in ether (70 mL). The resulting yellow solution obtained upon standing overnight at room temperature was evaporated to dryness and the residual solid recrystallized from pentane (0.76 g, 1.50 mmol, 83% yield).

Anal. Calcd for C$_{23}$H$_{41}$P$_2$ZrCl (Found): C, 54.65 (54.48); H, 8.12 (8.40); Cl, 7.02 (6.99), Zr, 18.02 (18.08). ^{1}H NMR (300 MHz, C$_6$D$_6$, 27 °C): δ 6.53 (dd, J_{H-H} = 18.7 Hz, J_{P-H} = 3.0 Hz, 1 H, CH), 6.41 (s, 5 H, Cp), 6.05 (dd, J_{H-H} = 18.7, J_{P-H} = 4.4 Hz, 1 H, CH), 1.54 (m, 4 H, (CH$_2$)$_{dmpe}$), 1.35 (d, J_{P-H} = 8.1 Hz, 3 H, Me$_{dmpe}$) 1.33 (d, J_{P-H} = 7.3 Hz, 3 H, Me$_{dmpe}$), 1.15 (s, 9 H, Me$_{t-Bu}$), 1.13 (s, 9 H, Me$_{t-Bu}$), 0.98 (d, J_{P-H} = 6.5 Hz, 3 H, Me$_{dmpe}$), 0.88 (d, J_{P-H} = 6.6 Hz, 3 H, Me$_{dmpe}$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 27 °C): δ 167.4 (dd, J_{C-H} = 117.0 Hz, J_{P-C} = 9.2 Hz, CH), 153.1 (dd, J_{C-H} = 148.6,

J_{P-C} = 4.6 Hz, CH), 124.5 (s, C$_{C=C}$), 113.6 (d, J_{C-H} = 172.3 Hz, Cp), 110.5 (s, C$_{C=C}$), 35.8 (s, C$_{t-Bu}$), 31.8 (q, J_{C-H} = 125.5 Hz, Me$_{t-Bu}$), 30.2 (q, J_{C-H} = 125.0 Hz, Me$_{t-Bu}$), 28.5 (s, C$_{t-Bu}$), 26.1 (dt, J_{C-H} = 132.4 Hz, (CH$_2$)$_{dmpe}$), 13.2 (q, J_{C-H} = 136.1 Hz, Me$_{dmpe}$), 13.1 (q, J_{C-H} = 129.5, Me$_{dmpe}$), 12.1 (q, J_{C-H} = 127.0 Hz, Me$_{dmpe}$), 11.3 (q, J_{C-H} = 129.2 Hz, Me$_{dmpe}$).

Cyclization Experiments. Acetylenes. In a standard procedure, a specially designed NMR tube was connected to a Töpler pump. Alkyne (10 equiv) was condensed into a frozen solution of 0.1 mmol of 1 and 2 in C$_6$D$_6$. The tube was sealed and NMR spectra were recorded at regular times. The formation of the organic product was observed simultaneously with the disappearance of the alkyne resonances. When all the acetylene was consumed, the organic products were identified by NMR and GC. No traces of decomposition were observed with the organometallic complex.

Acetonitrile. In a specially designed NMR tube connected with a Töpler pump, 4 equiv of acetonitrile was vacuum transferred into a frozen solution of 0.1 mmol of the complex in C$_6$D$_6$. A fast reaction occurred with separation of an insoluble white solid. After centrifugation, the organic product was identified by NMR and GC. Attempts to characterize the organometallic product failed. The results are summarized in the Table II.

X-ray Crystallography. The crystals used for this study were selected in a drybox equipped with a locally modified microscope. Suitable crystals were either sealed in thin-walled glass capillaries or glued on the top of a glass fiber and mounted on a diffractometer. Crystal and/or instrumental instability was monitored by measuring the intensities of three reference reflections collected every 3 h of X-ray exposure time. No significant decay has been observed during data collection. The net intensities were corrected for the scale variation and Lorentz and polarization effects, but not for absorption. All the relevant crystallographic data are summarized in Table I. Tables of hydrogen atom positions and thermal parameters, comprehensive lists of bond distances and angles, and tables of (F_o), (F_c), and $\sigma(F)$ are available as supplementary material. Scattering factors were from Cromer and Mann[21] and anomalous dispersion factors from Cromer and Liberman.[22] All calculations were carried out on the CDC-Cyber 170/760 computer at the University of Groningen with the program packages XTAL[23] and EUCLID[24] (calculation of geometric data)

(21) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(22) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

and a locally modified version of the program PLUTO[25] (preparation of illustrations).

CpZr[(Me)C=C(Me)C(Me)=C(Me)](dmpe)Cl (3). Data were obtained at 100 K by using an on-line liquid-nitrogen cooling system. Unit cell dimensions and their standard deviations were determined from the angle setting of 22 reflections in the range $30.09° < \theta < 31.49°$ in four alternate settings.[26] Reduced cell calculations did not indicate any higher lattice symmetry.[27] The choice of $C2/c$ as a possible space group was suggested by systematic extinctions and confirmed by successful refinement. A 360° Ψ-scan for the reflection (62$\bar{2}$) close to the axial showed an intensity variation up to 3% about the mean value. Standard deviations in the intensities based on counting statistics were increased according to the analysis of the excess variance[28] of three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.024I)^2$. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[29] Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of all the hydrogen atoms. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged to $R_F = 0.031$ ($R_\omega = 0.038$). Eleven reflections with $(w||F_o| - |F_c||) > 15$ were excluded from the final refinement cycle; a final difference Fourier map did not show any significant residual features. The final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given as supplementary material.

CpZr[(Me)C=C(Me)C(Me)=C(Me)](dmpe)Me (4). Data were obtained at 100 K by using an on-line liquid-nitrogen cooling system. Unit cell dimensions and their standard deviations were determined from the settings angles of 17 reflections in the range $20.23° < \theta < 21.62°$ in four alternate settings.[26] The unit cell was identified as triclinic, space group $P\bar{1}$. Reduced cell calculations did not indicate any higher lattice symmetry.[27] A 360° Ψ-scan for the reflection (10$\bar{7}$) close to the axial showed less than 1% variation in intensity about the mean value. Standard deviations in the intensities based on counting statistics were increased according to the analysis of excess variance[28] of three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.0268I)^2$. The resulting 3610 reflections satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[29] Refinement using anisotropic thermal parameters followed by a difference Fourier synthesis resulted in the location of all the hydrogen atoms. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms converged to $R_F = 0.025$ ($R_\omega = 0.028$). A final difference Fourier map did not show any significant residual features. The final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given as supplementary material.

CpZr[(Me)C=CHC(Me)=CH](dmpe)Cl (5). Selected crystals of **5** were mounted in capillaries and transferred onto a Nicolet R3m diffractometer. The crystal quality was tested by ω scans on some data points. Twenty-five centered reflections gave a monoclinic cell. The structure amplitudes were obtained after the empirical absorption correction and the usual Lorentz and polarization correction. Data reduction, structure solution,

and refinement were carried out on a Data General NOVA 4 computer using SHELXTL program system.[29] The Zr position was determined by Patterson method. The P and Cl atoms were located from the different Fourier map after the Zr position was refined. Subsequent map based on these atomic positions revealed all the non-hydrogen atoms. Anisotropic refinements were applied to all the non-hydrogen atoms. All the hydrogen atom positions have been found in the difference Fourier map. Each hydrogen atom was assigned with a temperature factor (U) 1.2 times that of the carbon attached. The final residual for 196 variables refined against the 3554 data for which $I > 3\sigma(I)$ were $R = 0.0293$, $R_\omega = 0.0309$, and GOF = 1.079. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$. In the final least-squares refinement all shifts are less than 0.0015 esd. However, four large false peaks (≤ 0.538 e/Å³) can still be found near the Zr atom within 1.14 Å. Their occurrence is presumably due to insufficient amount of high angle data in the data set. Scattering factors for neutral atoms were used. The positional and equivalent thermal parameters of non-hydrogen atoms are given as supplementary material.

CpZr(dmpe)Cl[C≡C(t-Bu)][CH=CH(t-Bu)] (6). Data were obtained at room temperature. Unit cell parameters and their standard deviations (esd's) were derived from the setting angles of 22 reflections in the range $19.92° < \theta < 22.00°$. Reduced cell calculations did not indicate any higher lattice symmetry.[27] Monoclinic space group $P2_1/a$ was determined from the systematic extinctions: $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$. Standard deviations in the intensities based on counting statistics were increased according to the analysis of the excess variance of three reference reflections:[28] $\sigma^2(I) = \sigma^2_{cs}(I) + (0.036I)^2$, resulting in 3381 reflections with $I \geq 2.5\sigma(I)$ with a consistency index of $\sum\sigma/\sum I = 0.061$. The molecular structure was solved by using Patterson methods (SHELXS86)[29] and completed by Fourier techniques. High thermal motions have been found for C(9), C(17), C(15), and C(4). Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of all the non-methyl hydrogen atoms and at least one hydrogen of each methyl group. The remaining hydrogen atoms were initially introduced at their idealized positions (C–H = 1.0 Å). In the final calculation all the H atoms with the exception of H(1)–H(5), H(18), and H(19) were refined in the riding mode with a fixed C–H bond length of 1.0 Å. Final refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged to $R_F = 0.085$ ($R_\omega = 0.083$). A final difference Fourier map did not show residual peaks outside –0.70 and 1.19 e/Å³, except one ghost peak of 3.36 e/Å³ between Zr(1) and P(2) (distance from P(2) is 1 Å). The details of the final refinements are included in Table I. Final fractional atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given as supplementary material.

Results

The ability of electronically and coordinatively saturated Zr(II) complexes CpZr(dmpe)$_2$X [X = Cl (**1**), Me (**2**); dmpe = 1,2-(dimethylphosphino)ethane] to dissociate one of the two chelating phosphine easily opened quite broad synthetic perspectives in the chemistry of low-valent zirconium. Substitution reactions have been achieved by using several ligands, including CO and butadiene under mild conditions,[30] while the reaction with ethylene allowed complicated transformations toward butadiene derivatives.[19,31]

Solutions of **1** and **2** react smoothly with 2 equiv (or excess) of 2-butyne forming light orange solutions from which orange crystals of CpZr[(Me)C=C(Me)C(Me)=C(Me)](dmpe)Cl [X = Cl (**3**), Me (**4**)] can be isolated in good yield on cooling at –30 °C (eq 1).

(23) Hall, S. R., Stewart, J. H., Eds. *XTAL2.2 User's Manual*; Universities of Western Australia (Australia) and Maryland (College Park, MD), 1987.

(24) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; D. Sayre, D., Ed.; Clarendon press: Oxfor 1982; p 528.
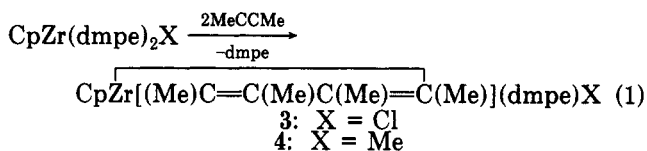
(25) (a) Meetsma, A. Extended version of the program PLUTO, University of Groningen, Groningen, The Netherlands (unpublished). (b) Motherwell, W. D. S.; Clegg, W. PLUTO, program for plotting molecular and crystal structures; University of Cambridge, Cambridge, England, 1978.

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(29) Sheldrick, G. M. SHELX86, program for crystal structure solution; University of Göttingen, Gottingen FRG, 1986.

(30) Wielstra, Y.; Gambarotta, S.; Roedelof, H.; Chiang, M. Y. N. *Organometallics* **1988**, *7*, 2177.

(31) Wielstra, Y.; Gambarotta, S.; Meetsma, A. *Organometallics*, in press.

$$CpZr(dmpe)_2X \xrightarrow[-dmpe]{2MeCCMe}$$

$$CpZr[(Me)C{=}C(Me)C(Me){=}C(Me)](dmpe)X \quad (1)$$
$$\textbf{3: } X = Cl$$
$$\textbf{4: } X = Me$$

The structures of the two complexes **3** and **4** have been determined by X-ray analysis. In both cases the structures can be described in terms of the same distorted pseudooctahedral geometry, with the Cp ring on the apical vertices and the metallacycle occupying two equatorial coordination sites (Figures 1 and 2). The chelating phosphine occupies one equatorial and one axial site while the X group lies on the fourth equatorial position. The strong steric interaction of the Cp ring with the equatorial ligands, which is a common feature for these zirconium pseudooctahedral complexes,[18,19] enforces a severe distortion in the coordination geometry. As a result, the metal is extruded from the equatorial plane (average distance from the plane 0.693 (7) Å). All the bond distances and angles compare well in the two complexes. The Zr–Cl and Zr–Me distances observed in **3** and **4** [2.531 (1) and 2.372 (3) Å, respectively] are significantly shorter than those in **1** and **2** [2.629 (2) and 2.47 (2) Å, respectively]. The close similarity between the structures of the two complexes **3** and **4** suggests the same formation pathway in both cases. The equatorial–axial arrangement of the remaining dmpe molecule is quite unusual. It has been previously observed only in the case of Cp*Hf(dmpe)(CO)$_2$Cl,[32] probably as a result of the prohibitive steric congestion. Conversely, in a series of complexes of formula CpZr(dmpe)(L)$_2$X [L = CO, butadiene; X = Cl, H][30,31] both the P atoms of dmpe are invariably placed on the equatorial plane of the molecule.

Spectroscopic data are in agreement with the structure shown in Figures 1 and 2. The IR stretching mode $\nu_{C=C}$ frequencies have been observed at 1410 and 1415 cm^{-1} for **3** and **4**, respectively. The ^{1}H NMR spectra reflect the asymmetricity of the two complexes. In both cases four distinct signals can be observed for the four Me substituents of the zirconacyclopentadiene moiety as well as for the four Me groups of dmpe.

The formation of complexes **3** and **4** is a quantitative reaction. In fact a surprisingly selective formation is observed alongside the release of 1 equiv of dmpe, during NMR tube experiments. In the case of the alkyl species **4** this is quite surprising because further insertion of alkyne into the Zr–Me bond with formation of more complicated products can be in principle expected for this 16-electron species.

More striking results have been obtained with terminal alkynes. The reactions with propyne proceed regiospecifically under mild conditions (room temperature, 1 atm.) leading to the alkyne *quantitative* head-to-tail dimerization. The resulting CpZr[(Me)C=CHC(Me)=CH]-(dmpe)Cl (**5**) is obtained within a few hours as light yellow crystalline solids (eq 2). The possible formation of isom-

$$CpZr(dmpe)_2X \xrightarrow[-dmpe]{2HCCMe}$$

$$CpZr[(Me)C{=}CHC(Me){=}CH](dmpe)Cl \quad (2)$$
$$\textbf{5}$$
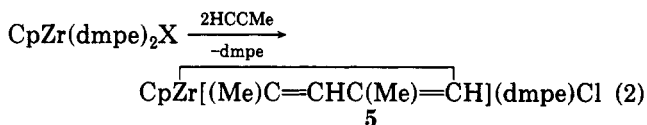
eric byproducts (e.g. 3,5-dialkylzirconacyclopentadiene) is excluded by NMR tube experiments, the only observed co-product being 1 equiv of dmpe. The location of the
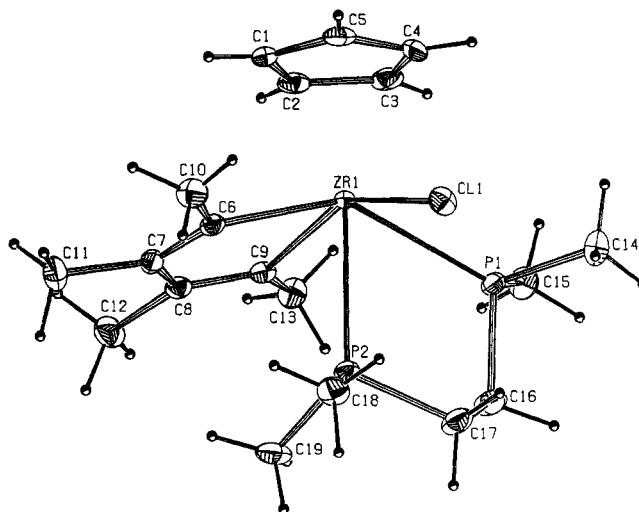
(32) Stein, B. K.; Frerichs, S. R.; Ellis, J. E. *Organometallics* **1987**, *6*, 2017.

Figure 1. ORTEP view of **3** with thrmal ellipsoids drawn at the 50% probability level.
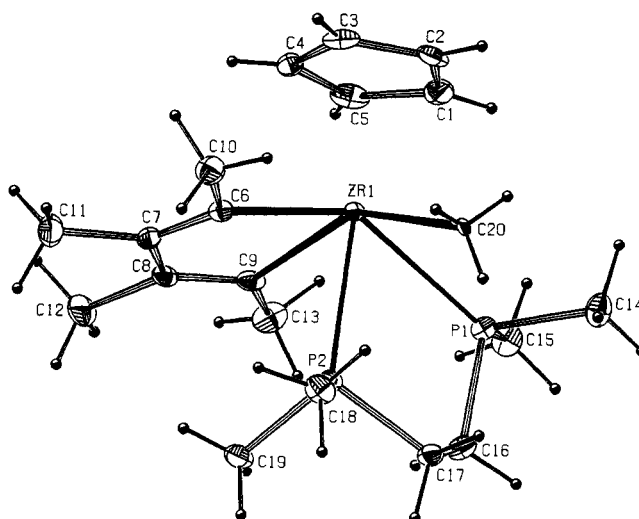

Figure 2. ORTEP view of **4** with thermal ellipsoids drawn at the 50% probability level.
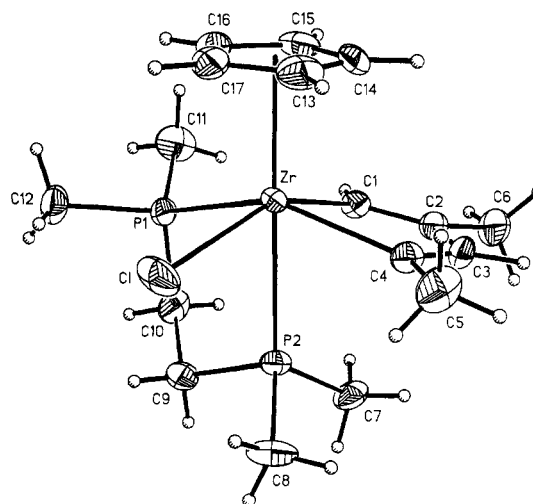

Figure 3. ORTEP view of **5** with thermal ellipsoids drawn at the 50% probability level.

substituents in positions 2 and 4 of the metallacyclopentadienyl ring has been demonstrated by an X-ray analysis carried out on a single crystal of **5**. The molecule showed the same arrangement already observed in the case of complexes **3** and **4** with the two methyl substituents
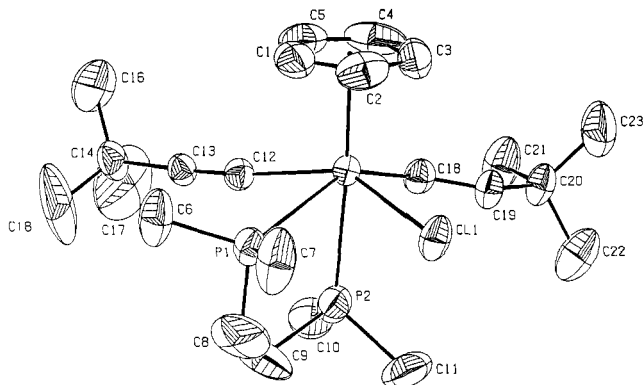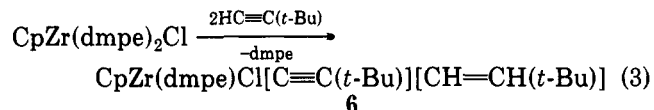
Figure 4. ORTEP view of **6** with thermal ellipsoids drawn at the 30% probability level.

Table II. Alkyne Cyclotrimerization Results

complex	alkyne	product	T, °C	
1, 2	acetylene	benzene	-20	cat.
3, 4	propyne	1,2,3,4,5-Me$_5$C$_6$H	25	stoich
3, 4	acetylene	1,2,3,4-Me$_4$C$_6$H$_2$	25	stoich
5	acetylene	m-xylene/benzene	-20	stoich
5	propyne	1,3,5-/1,2,4-mesitylene	25	cat.
5	acetonitrile	2,4,6-Me$_3$C$_5$H$_2$N	25	stoich

placed in positions 2 and 4 of the metallacycle ring (Figure 3). All the bond distances and angles compare well with those observed in the other two isostructural complexes. In the three structures, the angles subtended at the C_{ring} atoms are quite compatible and in all cases close to the ideal value of 120°. The spectroscopic data are consistent with the structure as described by the X-ray analysis. The reaction follows an unexpected pathway when the bulky HC≡C(*t*-Bu) is used. A hydrogen-transfer reaction is promoted between two molecules of alkyne, instead of the usual oxidative coupling, and the new complex CpZr-(dmpe)Cl[C≡C(*t*-Bu)][CH=CH(*t*-Bu)] (**6**) is quantitatively formed (eq 3). The presence of the -C≡C(*t*-Bu)

$$\text{CpZr(dmpe)}_2\text{Cl} \xrightarrow[\text{-dmpe}]{2\text{HC}≡\text{C}(t\text{-Bu})}$$

$$\text{CpZr(dmpe)Cl[C≡C(}t\text{-Bu)][CH=CH(}t\text{-Bu)]} \quad (3)$$
$$\mathbf{6}$$

group is diagnosed by the intense resonance at 2070 cm^{-1} of the IR spectrum. Another intense absorption at 1550 cm^{-1} is tentatively assigned to the $\nu_{C=C}$ stretching mode of the vinyl group. The structure of **6** has been demonstrated by X-ray analysis. The frame of the fragment CpZr(dmpe)Cl is identical with those previously observed for **3-5** (Figure 4). The two coordination sites usually occupied by the metallacycle have been replaced in complex **6** by the -C≡C(*t*-Bu) and the *trans* [-CH=CH(*t*-Bu)] groups. The acetylide moiety is almost linear [C(12)-C-(13)-C(14) = 177.0 (1)°; Zr(1)-C(12)-C(13) = 173.8 (8)°], and the vinyl group has the usual bent geometry [Zr(1)-C(18)-C(19) = 131.2 (7); C(18)-C(19)-C(20) = 133.1 (9)] bearing the two hydrogen atoms in trans positions.

Catalytic Cyclotrimerization Reactions. Fast catalytic reaction has been observed with acetylene. A vigorous reaction took place within few minutes when solution of **1** and **2** were saturated with acetylene. A deeply colored insoluble solid (probably polyacetylene) separated, and formation of large amounts of benzene was observed in NMR tube experiments. The organometallic residue exhibited a very complicated spectrum probably due to the presence of a mixture of several complexes. However, the reaction is more clean and selective when carried out at -20 °C. In this case, large amounts of benzene were formed

Table III. Bond Distances (Å) and Angles (deg)

	3 (X = Cl)	4 (X = CH$_3$)
	Bond Distances	
Zr-X	2.5308 (7)	2.372 (3)
Zr-P(1)	2.8422 (6)	2.8404 (7)
Zr-P(2)	2.7526 (6)	2.7278 (7)
Zr-C(6)	2.272 (2)	2.272 (3)
Zr-C(9)	2.309 (2)	2.324 (3)
	Bond Angles	
X-Zr-P(1)	82.04 (2)	78.58 (5)
X-Zr-P(2)	74.65 (2)	73.84 (5)
P(1)-Zr-P(2)	72.07 (2)	72.02 (2)
C(6)-Zr-P(2)	73.12 (5)	72.41 (5)
C(9)-Zr-P(2)	76.26 (5)	75.16 (5)

5

	Bond Distances			
Zr-Cl	2.512 (1)	Zr-P(1)	2.774 (1)
Zr-C(1)	2.301 (3)	Zr-P(2)	2.769 (1)
Zr-C(4)	2.290 (3)		
	Bond Angles		
P(1)-Zr-Cl	87.2 (1)	P(1)-Zr-P(2)	72.6 (1)
Cl-Zr-C(4)	103.8 (1)	C(1)-Zr-P(2)	73.3 (1)
C(1)-Zr-C(4)	74.9 (1)	C(4)-Zr-P2	75.0 (1)

6

	Bond Distances		
Zr-Cl	2.514 (3)	Zr-P(2)	2.692 (3)
Zr-C(18)	2.28 (1)	C(18)-C(19)	1.29 (1)
Zr-C(12)	2.273 (9)	C(12)-C(13)	1.20 (1)
Zr-P(1)	2.799 (3)		
	Bond Angles		
P(1)-Zr-Cl	78.5 (1)	C(12)-Zr-P(2)	72.4 (3)
C(12)-Zr-P(1)	74.9 (2)	Zr-C(18)-C(19)	131.2 (7)
P(1)-Zr-P(2)	72.0 (1)	Zr-C(12)-C(13)	173.8 (8)

within a few hours and no traces of polyacetylene were observed. Regrettably, all attempts to isolate and fully characterize the organometallic complex have so far failed.

These results prompted us to test the ability of complexes **3**, **4**, and **5** to catalyze cyclotrimerization reactions. A slow catalytic reaction has been observed in the case of propyne (ca. 1 turnover/day) with formation of a mixture of 1,3,5- and 1,2,4-mesytilene in comparable amounts (eq 4). No such catalytic feature has been observed in the case


(4)
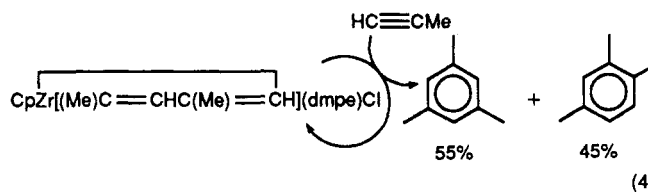
of more bulky alkynes like *tert*-butylacetylene or 2-butyne. However, stoichiometric ring closure to arenes was possible when propyne or acetylene was reacted with complexes **3** and **4**. Finally stoichiometric formation of substituted pyridine (collidine) has been obtained upon ring closure with acetonitrile. The results are summarized in Table II. It is remarkable that the very high selectivity exhibited in the formation of the metallacyclopentadiene rings is completely lost during the ring closure step to arenes. Complexes **3-6** are formally 16-electron species, in principle having an empty orbital available for coordination of a third molecule of alkyne. However, the high steric congestion of these complexes probably allows the preliminary precoordination only upon dissociation (or partial dissociation) of the chelating phosphine. In this case a significant decrease of the steric hindrance is expected and no significant preference for one coordination geometry rather than another results. The random product distri-

bution is probably a consequence of that.

Discussion

A puzzling question arises about which factors are responsible for the high stereoselectivity. It seems reasonable to assume that the preliminary cis precoordination of the two molecules of alkyne is the prerequisite for the formation of metallacyclopentadiene rings. As mentioned before, there are two possible geometries that can be adopted by the two coordinated alkynes: coplanar[11] and upright,[12] both in respect to the equatorial plane of the molecule (Chart I). The strong steric interaction between the Cp ring and the ligands in the equatorial plane [in all the complexes 1–6, the pseudooctahedral coordination geometry is severely distorted and the zirconium atom is remarkably above the equatorial plane], together with the *quantitative* formation of the head-to-tail dimerization products, makes the upright arrangements (Chart I) quite unrealistic. With the assumption of the presence of a coplanar arrangement of the two alkyne molecules in the intermediate, four different geometries are possible in principle. Due to the formation of 5 exclusively, we conclude that the most favored arrangement is that reported for intermediate A in eq 5. It should be noted that this

(5)

A
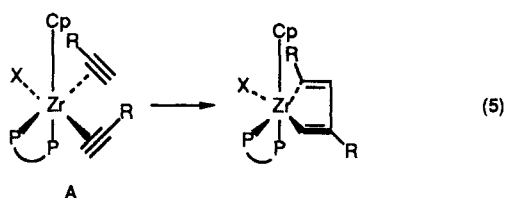
is the opposite of the bis(cyclopentadienyl) systems, where the alkyl substituents of the coordinated alkynes point away from each other (Chart I) with an angle subtended at Zr by the two acetylene molecules up to 109°. Conversely, in the pseudooctahedral complexes 3–6 the widest possible angle subtended at Zr by the ligands is only 75°. This requires a very close proximity between the two coplanar acetylenes with a resulting prohibitive interaction between the ligands in the equatorial plane of the molecule. Probably, intermediate A better satisfies the steric requirements, and we believe that its selective formation is responsible for the high regioselectivity of the reaction. In accordance with this hypothesis no reaction was observed

in the case of the bulky $(Me_3Si)C{\equiv}C(SiMe_3)$. The steric crowding in these complexes might also be the driving force for the hydrogen-transfer reactions observed with $HC{\equiv}C(t\text{-Bu})$ (eq 6). Even in this case the reaction is quan-

(6)
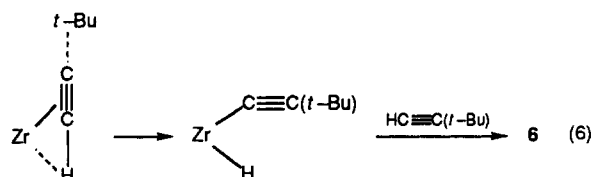
titative and no other products are formed. Furthermore there are no special stability factors that could prevent the formation of the usual metallacyclopentadiene ring in this case. α,α'-Bis(trimethylsilyl)zirconacyclopentadienyl derivatives, for example, have been obtained and fully characterized for the bis(cyclopentadienyl) systems.[16b] The remarkably high asymmetry of the $HCC(t\text{-Bu})$ probably enforces a unique coordination mode with the crowded metal center. If the bulky organic moiety deflects the core of the molecule, a strong Zr⋯H interaction is enforced, which is probably the preliminary step for a further oxidative addition into the C–H bond (eq 7). The resulting hydride–acetylide complex can form the final product via simple insertion reaction of a second molecule of alkyne into the Zr–H bond. It is remarkable that no such reaction has been observed in the case of propyne where the reaction leads to the quantitative formation of the metallacycle derivative 5. This further supports the idea that even the formation of 6 can be ascribed to steric factors. However, this fascinating mechanistic possibility [already observed in the chemistry of bis(cyclopentadienyl)titanium systems][8b] so far remains only a suggestion. Other mechanisms including the through-space direct H transfer between the two molecules of coordinated alkyne cannot at present be excluded.

Supplementary Material Available: Tables of atomic coordinates, hydrogen atoms coordinates, thermal parameters, bond distances and angles, and torsion angles for 3–6 (38 pages); listings of structure factors for 3–6 (84 pages). Ordering information is given on any current masthead page.