Coupling of Benzynezirconocene with 1,4-Diphenyl-1,3-butadiyne

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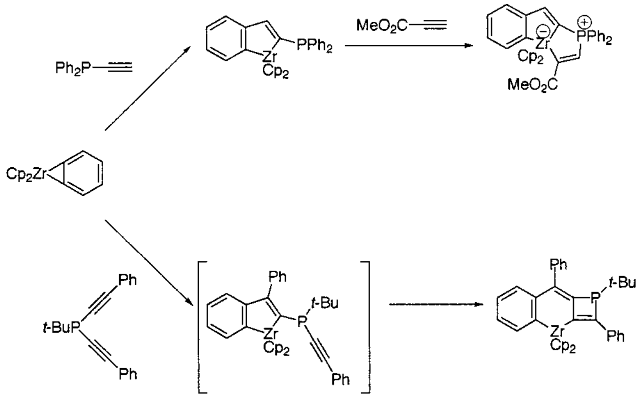
The thermolysis of diphenylzirconocene in the presence of 1,4-diphenyl-1,3-butadiyne to yield the seven-membered zirconacyclocumulene **1** via the intermediacy of benzynezirconocene is described. This complex has been characterized by an X-ray diffraction study. Additionally, better knowledge of the bonding of the cumulene moiety was achieved by DFT calculations. Cleavage of the Zr−C bonds of **1** with methanol provided the corresponding butatriene **2**.

For some time now, our investigations have been concerned with the study of interactions of in situ generated benzynezirconocene with main-group-element-containing unsaturated substrates[1] and have been focused on the reactivity of alkyne derivatives. Starting from alkynylphosphanes, we developed the regiospecific preparation of 2-phosphino-1-zirconaindenes,[2] which on further treatment with various unsaturated species led to stable zwitterionic five-coordinated anionic zirconium complexes (Scheme 1).[3] We also reported the intramolecular coupling reaction of a dialkynylphosphane and transient zirconabenzyne, which provided a 1,2-dihydrophosphete−zirconium complex (Scheme 1).[4]

These original results prompted us to investigate the chemistry of 1,3-diynes with benzynezirconocene. An analogous reaction was only described for the related tantalum carborane complex $(Et_2C_2B_4H_4)CpTa(\eta^2-C_6H_4)$, affording a monoinserted metallaindene complex with an alkynyl substituent in the β-position as a major product.[5] Here we detail the formation of a seven-membered zirconacyclocumulene by double insertion of triple carbon−carbon bonds of a 1,3-diyne into the zirconium−carbon bond of benzynezirconocene.

Scheme 1



Results and Discussion

A clean coupling reaction of PhC≡CC≡CPh with the transient $Cp_2Zr(\eta^2-C_6H_4)$ occurs when 1,4-diphenyl-1,3-butadiyne is heated with diphenylzirconocene at 80 °C for 6 h (Scheme 2).

Only one bis(cyclopentadienyl)zirconium complex is formed quantitatively ($\delta_{^1H}$(Cp) 5.68 ppm). The mass spectrum (EI 70 eV) shows a molecular ion peak (M^+) at *m*/*z* 498, indicative of a mononuclear complex. In the IR spectrum (KBr), no absorption is observed in the region characteristic of the stretching vibrations for coordinated (1700−1800 cm^{-1}) or free carbon−carbon triple bonds (2050−2200 cm^{-1}).[6] Identification of **1** as a seven-membered zirconacyclocumulene follows from its X-ray crystal structure analysis; the ORTEP diagram of **1** is illustrated in Figure 1, and crystallographic data and selected bond distances and angles are given in Table 1 and Figure 2, respectively. Structural features for similar highly strained cyclic zirconacumulenes described in the literature closely resemble those in **1** (Table 2). Obviously, the remarkable stability of **1**, as

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‡ Laboratoire de Chimie de Coordination (LCC-UPR8241).

[1] Majoral, J.-P.; Meunier, P.; Igau, A.; Pirio, N.; Zablocka, M.; Skowronska, A.; Bredeau, S. *Coord. Chem. Rev.* **1998**, *178−180*, 145.

[2] Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P.; Dupuis, L.; Pirio, N.; Meunier, P. *Chem. Commun.* **1997**, 279.

[3] (a) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P.; Pirio, N.; Meunier, P. *J. Am. Chem. Soc.* **1998**, *120*, 3504. (b) Cadierno, V.; Igau, A.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *Organometallics* **1999**, *18*, 1580. (c) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J.-P. *Organometallics* **1999**, *18*, 1882. (d) Miquel, Y.; Cadierno, V.; Donnadieu, B.; Igau, A.; Majoral, J.-P. *Organometallics* **2000**, *19*, 54. (e) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J.-P.; Skowronska, A. *Chem. Eur. J.* **2000**, *6*, 345.

[4] Dupuis, L.; Pirio, N.; Meunier, P.; Igau, A.; Donnadieu, B.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 987.

[5] Boring, E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1998**, *17*, 3865.

[6] A medium-large absorption band at 1877 cm^{-1} is consistent with a zirconacyclocumulene fragment (see ref 7: 1875 cm^{-1} for the seven-membered zirconacyclic cumulene **A**).

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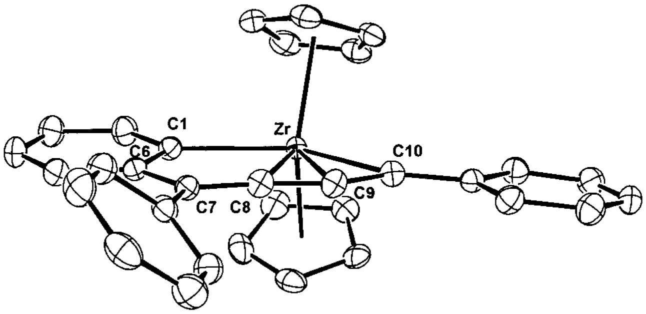
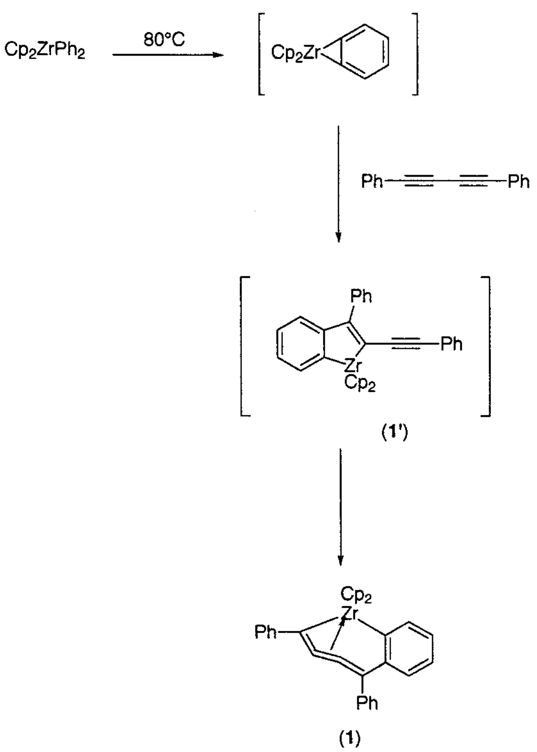


Figure 1. ORTEP view of the structure of **1**.

Scheme 2



well as of **A**,[7] **B**,[8] **C**,[9] **D**,[10] **E**,[11] **F**,[11] and **G**[12](Chart 1), arises from the coordination of the central carbon–carbon double bond of the tetraene moiety.

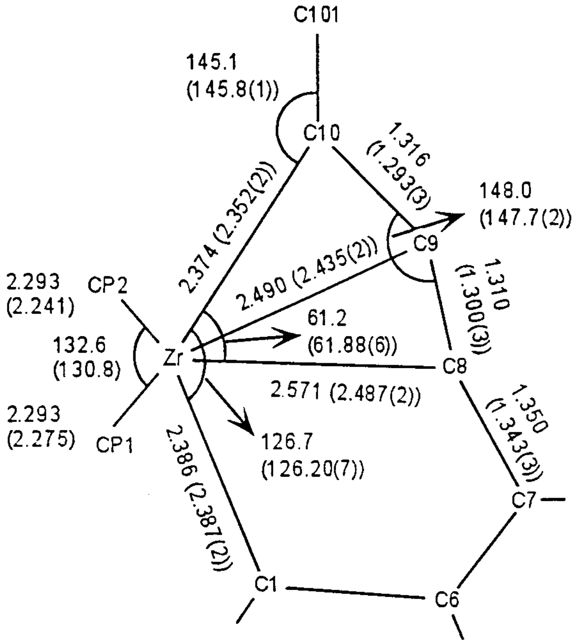


Figure 2. Geometry of the zirconium coordination scheme. Bond lengths are in angstroms and bond angles in degrees. The numbers are those obtained by geometry optimization (numbers in parentheses are the parameters obtained from the X-ray structure). CP denotes the geometry centers of the cyclopentadienyl rings.

Table 1. Crystallographic Data for 1

chem formula	$C_{32}H_{24}Zr$
fw	499.76
cryst syst	monoclinic
space group	$P2_1/c$
Z	4
a, Å	11.729(2)
b, Å	11.639(2)
c, Å	17.122(3)
β, deg	101.33(2)
V, Å^3	2291.9(5)
$F(000)$	1024
D_{calcd}, g cm^{-3}	1.45
μ(Mo Kα), mm^{-1}	0.49
2θ range, deg	2.9–48.4
no. of data collected	15 625
no. of unique data	3612
R_{int}	0.032
no. of params varied	298
S	1.04
$R(F)$, $R_w(F^2)$ (all data)	0.029, 0.062
$R(F)$, $R_w(F^2)$ ($I > 2\sigma(I)$)	0.024, 0.059
max, min Δ/ρ, e Å^{-3}	0.373, −0.228

To understand the interactions between zirconium and the cumulene fragment, calculations using density functional methods were performed. The cumulene is a versatile ligand which can lead to different bonding schemes with one or two metallic centers.[7–9,13] A reason for this behavior is the existence of two orthogonal π systems, both able to be involved in a bonding interaction. From simple considerations, the out-of-plane π system is delocalized over the four carbon atoms, generating two occupied π MO's, while only one occupied in-plane π MO is located between the two central carbon atoms. To get an insight into the bonding interaction between the metal center and the cumulene moiety, a molecular orbital calculation was carried out. Extended theoretical studies, including ab initio MO and density functional methods, have already been carried out for five-membered metallacyclic cumulenes.[14] However, the coordination geometries studied are different from our system, and these results are not directly applicable for **1**. The first step was to reproduce the geometry of the complex. The chosen model was very close to the real one: for the calculation the phenyl group noncoplanar with the cumulene moiety was replaced by a methyl group, and all other structural features were left un-

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(7) Hsu, D. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 10394.

(8) Kempe, R.; Ohff, A.; Rosenthal, U. *Z. Kristallogr.* **1995**, *210*, 707.

(9) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605.

(10) Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1999**, *18*, 4234.

(11) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 8313.

(12) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967.

(13) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112.

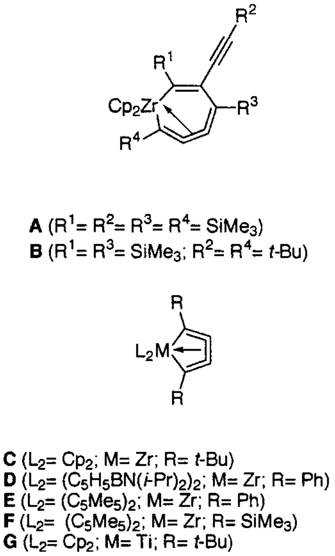
(14) Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952.

Table 2. Distances and Angles of Comparable Structural Elements in Seven-Membered (A, B, 1) and Five-Membered (C−G) Metallacyclic Cumulenes

	A	B	1		A	B	1
Distances (Å)							
C(7)−C(8)	1.337(6)	1.323	1.343(3)	M−C(10)	2.442(5)	2.392	2.3515(19)
C(8)−C(9)	1.298(6)	1.325	1.300(3)	M−C(9)	2.423(5)	2.445	2.4346(19)
C(9)−C(10)	1.279(6)	1.281	1.293(3)	M−C(8)	2.396(5)	2.467	2.487(2)
Angles (deg)							
C(7)−C(8)−C(9)	160.1(5)	112.8	163.6(2)	C(8)−C(9)−C(10)	148.8(5)	147.6	147.7(2)

	C	D	E	F	G	1
Distances (Å)						
C(7)−C(8)	1.29(1)	1.289(8)	1.305(5)	1.291(6)	1.243(13)	1.343(3)
C(8)−C(9)	1.31(1)	1.325(8)	1.327(4)	1.337(6)	1.339(13)	1.300(3)
C(9)−C(10)	1.28(1)	1.300(8)	1.296(5)	1.293(6)	1.276(11)	1.293(3)
M−C(10)		2.313(6)	2.345(4)	2.422(4)	2.298(10)	2.3515(19)
		2.308(6)	2.357(4)	2.426(5)	2.252(9)	
M−C(9)		2.304(7)	2.328(4)	2.305(4)	2.209(9)	2.4346(19)
M−C(8)		2.273(7)	2.330(4)	2.307(4)	2.213(9)	2.487(2)
Angles (deg)						
C(7)−C(8)−C(9)	147.2(5)	145.8(7)	148.0(4)	152.5(4)	150.0(10)	163.6(2)
C(8)−C(9)−C(10)	150.0(5)	149(7)	148.5(4)	152.3(4)	147.8(10)	147.7(2)

Chart 1



A ($R^1 = R^2 = R^3 = R^4 = SiMe_3$)
B ($R^1 = R^3 = SiMe_3$; $R^2 = R^4 = t$-Bu)

C ($L_2 = Cp_2$; M= Zr; R= *t*-Bu)
D ($L_2 = (C_5H_5BN(i\text{-}Pr)_2)_2$; M= Zr; R= Ph)
E ($L_2 = (C_5Me_5)_2$; M= Zr; R= Ph)
F ($L_2 = (C_5Me_5)_2$; M= Zr; R= $SiMe_3$)
G ($L_2 = Cp_2$; M= Ti; R= *t*-Bu)

changed. The geometry was optimized[15] with a standard LanL2DZ basis set[16−19] with a DFT method.[20] The single-point calculation was performed with the same basis set and method. Figure 2 shows the excellent agreement between the X-ray structural parameters and the calculated ones.

Figure 3 displays the electron density[21] in the metal−cumulene bond region. Bonding electron density is located between the zirconium atom and the C(10) and C(8) carbon atoms of the cumulene. Careful inspection of the molecular orbitals shows that the interaction between these latter atoms is achieved by an overlap of a d metal atomic orbital with one severely distorted terminal σ orbital (C(10) centered) and the central in-plane π orbital (C(9)−C(8)) of the cumulene.

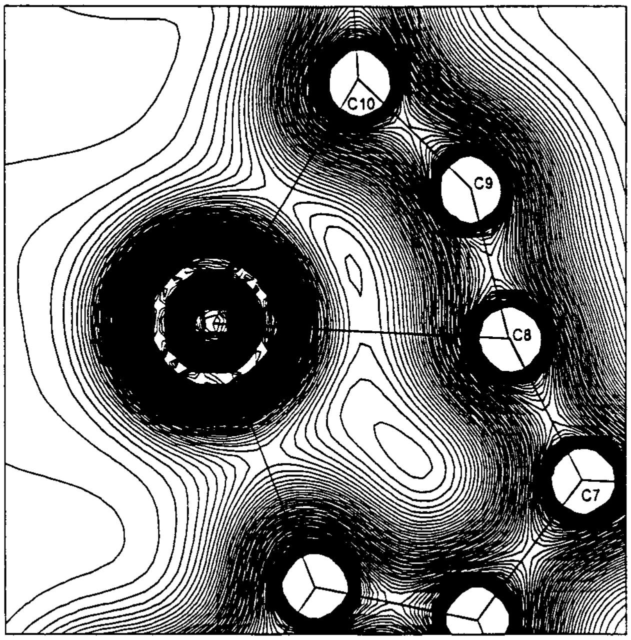


Figure 3. Plot of the electron density in the metal−cumulene bond region.

Figure 4 shows the main orbital contributing (HOMO-2) to this overlap. It is noteworthy that no significant overlap population was found between the zirconium atom and the out-of-plane cumulene π system.

The formation of **1** probably involved a consecutive insertion of the two carbon−carbon triple bonds of PhC≡CC≡CPh into the zirconium−carbon bond of the transient zirconabenzyne, but the 2-alkynylzirconaindene intermediate **1′** was never observed in the reaction mixture (Scheme 2).[22]

For the present, the reaction chemistry of **1** was not examined in detail but successful cleavage of the two zirconium−carbon bonds was achieved with methanol

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[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen. W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94 (Revision E.1); Gaussian, Inc., Pittsburgh, PA, 1995.

[16] Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976; p 1.

[17] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

[18] Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

[19] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[20] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[21] Schaftenaar, G. MOLDEN3.5; University of Nijmegen, Nijmegen, The Netherlands.

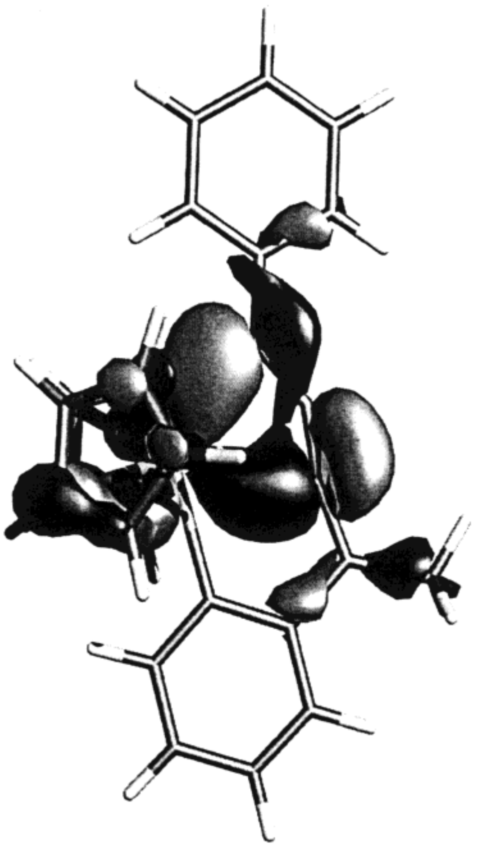
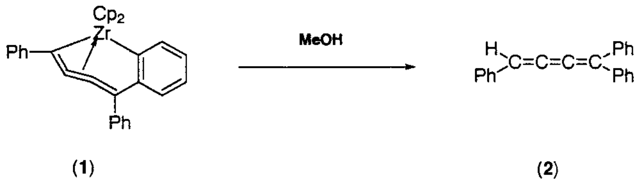


Figure 4. HOMO-2 obtained at the B3LYP level using MOLDEN[21] and the POV-ray program.

Scheme 3



(Scheme 3). 1,1′,4-Triphenylbuta-1,2,3-triene (**2**) and also 1,1′,4-triphenylbut-3-ene-1-yne were the two conceivable molecular structures. Spectroscopic data (in particular IR and inverse gradient $\delta(^1H)-\delta(^{13}C)$ HMBC experiments) are by means of the first one, and ^1H NMR data are in accord with those reported for ArCHC=C=CPh$_2$.[23]

In summary, diphenylzirconocene reacts with 1,4-diphenyl-1,3-butadiyne to give the strained zirconacyclocumulene **1**, which on methanolysis provides the corresponding butatriene **2**. The remarkable stability of **1** results from an interaction between the d_{xy} metal atomic orbital with one terminal σ orbital and with the in-plane π orbital of the cumulene. Extension of this reaction to other 1,3-diynes and studies of the chemical properties and reactivities of these complexes are currently under active investigation.

Experimental Section

General Remarks. All manipulations were carried out under an argon atmosphere. Mass spectra were determined by using a Kratos concept IS spectrometer (EI, 70 eV), while NMR spectra were obtained by using a Bruker DRX500 spectrometer. NMR chemical shifts are expressed in ppm upfield from Me$_4$Si. IR spectra were recorded on a Bruker IFS66V spectrometer. Only significant IR bands are reported. Combustion analyses were performed by the analytical service of LSEO of the Université de Bourgogne.

Typical Procedure for the Preparation of 1. A solution of Cp$_2$ZrPh$_2$ (0.28 g, 0.75 mmol) and PhC≡CC≡CPh (0.15 g, 0.75 mmol) in 30 mL of toluene was heated to 80 °C for 6 h. After removal of the solvent in vacuo, the solid obtained was washed with pentane to afford a yellow powder (0.26 g, 0.52 mmol, 70%), which was recrystallized from toluene/pentane to yield 0.12 g (0.24 mmol, 32%) of zirconacyclocumulene **1** as yellow crystals.

$^{13}C\{^1H\}$ NMR (CDCl$_3$, 125 MHz): δ 184.3 (C_{quat}), 171.0 (C_{quat}), 164.3 (C_{quat}), 160.7 (C_{quat}), 144.7, 142.1 (C_{quat}), 140.0 (C_{quat}), 135.4 (C_{quat}), 133.0, 129.4, 129.3, 128.8, 128.2, 125.3, 124.0, 123.5, 112.0, 106.6 (CH_{Cp}), 88.0 (C_{quat}). Anal. Calcd for $C_{32}H_{24}Zr$: C, 76.90; H, 4.84. Found: C, 76.69; H, 4.89.

Typical Procedure for the Preparation of 2. To a solution of **1** (0.35 g, 0.70 mmol) in 20 mL of toluene cooled to −30 °C was added 2.2 equiv (1.54 mmol, 40 μL) of methanol. The reaction mixture was warmed to room temperature and then stirred for 3 h. After removal of the solvent in vacuo, the residue was purified by column chromatography (SiO$_2$, ether) to afford butatriene **2** as a yellow powder (0.15 g, 0.54 mmol, 76%).

^1H NMR (CDCl$_3$, 500 MHz): δ 7.6−7.3 (m, 15H, CH_{arom}), 6.28 (s, 1H, =CH). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 125 MHz): δ 153.1 (C_{quat}), 141.8 (C_{quat}), 139.6 (C_{quat}), 131.8, 130.6, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 124.1(C_{quat}), 107.5 (=CH), 94.1 (C_{quat}), 88.0 (C_{quat}). IR (KBr): 2192 (w), 1964(w), 1949 (m) cm^{-1}. MS: m/z 280 [M$^+$, 100]. Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.22; H, 5.82.

X-ray Analysis of 1. Data were collected at low temperature on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); the final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. Any fluctuations of the intensity were observed over the course of the data collection. Numerical absorption corrections[24] were applied to the data. The structure was solved by direct methods using SIR92[25] and refined by least-squares procedures on F^2 with the aid of SHELXL97,[26] by minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors. The atomic scattering factors were taken from ref 27. All hydrogen atoms were located on a difference Fourier map and isotropically refined with a riding model, and all non-hydrogen atoms were anisotropically refined. In the last cycles of refinement a weighting scheme was used where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecule was performed with the program ORTEP,[28] with 50% probability displacement ellipsoids for non-hydrogen atoms.

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(22) This two-step mechanism was already evidenced in the formation of a 1,2-dihydrophosphete−zirconium complex resulting from reaction of a dialkynylphosphane and diphenylzirconocene and was discussed similarly in ref 11 (see ref 4).

(23) Ratts, K. W.; Partos, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 6112.

(24) X-SHAPE (revision 1.01): A Crystal Optimisation for Numerical Correction; STOE and Cie, July 1996 (X-SHAPE is based on the program HABITUS by Dr. Wolfgang Herrendorf, Institut für Anorganische Chemie, Universität Giessen).

(25) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagiardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92 Program for Automatic Solution of Crystal Structures by Direct Methods. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(26) Sheldrick, G. M. SHELXL97: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(27) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1994; Vol. IV.

Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, GB−Cambridge, U.K., on quoting the full journal citation.

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Supporting Information Available: Tables giving crystal data and data collection and structure refinement details (S1), atomic coordinates and equivalent isotropic displacements (S2), all bond lengths and angles (S3), anisotropic displacement parameters (S4), and hydrogen coordinates and displacement parameters (S5) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Burnett, M. N.; Johnson, C. K. ORTEP−III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations; Oak Ridge National Laboratory Report ORNL-6895; Oak Ridge National Laboratory, Oak Ridge, TN, 1996. Windows implementation: Farrugia, L. J. *J. Appl. Crystallogr*. **1997**, *30*, 565.