Reaction of Rosenthal's Zirconacyclocumulenes with Chlorophosphines

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The zirconacyclocumulenes **1a** (R = CH_3) and **1b** (R = Ph) were prepared by isomerization of bis(propynyl)$ZrCp_2$ or bis(phenylethynyl)$ZrCp_2$, respectively, catalyzed by $B(C_6F_5)_3$ (6 mol %). The compounds **1** added PCl_3, $PhPCl_2$, or Ph_2PCl with cleavage of only one zirconium−carbon single bond. Chloride was added to zirconium and the remaining $-PCl_2$, −P(Ph)Cl, or $-PPh_2$ moiety attached at the distal β-carbon atom of the strained ZrC_4R_2 metallacycle to yield the respective ring-opened Zr/P-substituted enyne systems (**5**−**7**). The complexes **7a** and **7b** (both with $-PPh_2$) and **6b** (with −P(Ph)Cl) were characterized by X-ray diffraction.

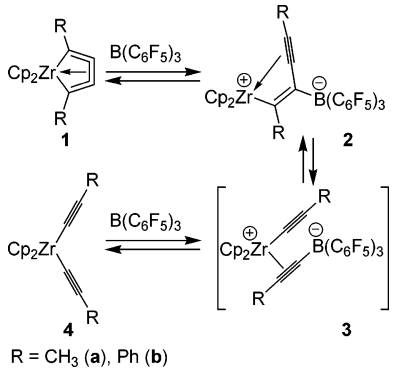
Introduction

The reaction of titanocene or zirconocene derivatives "RCp_2M" derived from a variety of sources with substituted butadiynes leads to the formation of the unique five-membered group 4 metallacyclocumulenes **1**.[1] Rosenthal et al. have characterized several examples of this type of complexes by X-ray diffraction and have largely developed the chemistry of such compounds.[1,2]

We had subsequently shown that such compounds can be prepared by catalytic isomerization of bis(alkynyl)-zirconocenes (**4**) under the influence of $B(C_6F_5)_3$. We had demonstrated that the zwitterion **2** is an intermediate in this catalytic conversion that can be obtained by treatment of either **1** or **4** with $B(C_6F_5)_3$ (see Scheme 1).[3]

Formally, complex **1** has a hetaryne-type composition, but it is enormously stabilized by internal σ-interaction of the central C═C multiple bond with the electron-deficient group 4 metallocene.[4] The metallacyclocumulenes exhibit a remarkable stability. Surprisingly few specific reactions of these uniquely structured metallacycles have been observed so far.[1] We will here describe a series of reactions of two derivatives of **1**, namely, the zirconacyclocumulenes **1a** (R = CH_3) and **1b** (R = Ph), with the reagents PCl_3, $PhPCl_2$, or Ph_2PCl. These reactions gave a surprising result.

Scheme 1



Results and Discussion

The zirconacyclocumulenes (**1a**, **1b**) used in this study were both synthesized by isomerization of the respective bis(alkynyl)zirconocenes (**4a**, **4b**) catalyzed by $B(C_6F_5)_3$ (6 mol %) at room temperature in toluene. Complex **1a** reacted readily with 1 molar equiv of PCl_3 in THF to yield **5a**. The product features a single ^1H NMR Cp resonance (in d_6-benzene) at δ 5.87 (10H) and two CH_3 signals at δ 2.33 (3H) and 1.63 (3H), quite different from the starting material **1a** [δ 5.08 (s, 10H), 2.83 (s, 6H)]. Complex **5a** features typical ^{13}C NMR Zr-alkenyl signals for **5** at δ 223.6 ($^2J_{PC}$ = 23 Hz, C2) and 133.2 ($^1J_{PC}$ = 70.0 Hz, C3), alkynyl resonances at δ 79.0 (C4) and 90.1 (C5), and a ^{31}P NMR feature at δ 154.3. The reaction of **1b** with PCl_3 proceeds analogously to give the addition product **5b** (isolated in a yield of 66%; see Scheme 2 and Table 1). In this case the attachment of a $-PCl_2$ group at C3 of the σ-ligand framework is illustrated by the observation of three separated signals of the respective isotopomers in close to statistical experimental intensity

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† X-ray crystal structure analyses.

‡ Quantum chemical calculations.

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Scheme 2

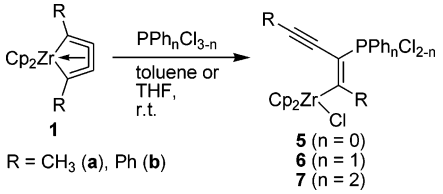


Table 1. Selected NMR Data of the Complexes 5−7[a]

compd	R	*n*	^{1}H (Cp)	^{31}P	[Zr]−*C*= ($^2J_{PC}$)[b]	=*C*−[P] ($^1J_{PC}$)[b]	*C*≡*C*R
5a[c,d]	Me	0	5.87	154.3	223.6 (23)	133.2 (70)	79.0
							90.1
5b[c]	Ph	0	6.04	151.4	223.9 (27)	129.1 (59)	87.8
							85.8
6a[d,e]	Me	1	6.50	68.1	222.0 (20)	130.7 (47)	81.3
			6.30				89.8
6b	Ph	1	6.47	70.4	224.5 (23)	132.6 (50)	91.0
			6.35				95.4
7a	Me	2	6.37	-12.3	217.3 (15)	127.4 (39)	84.7
							89.1
7b	Ph	2	6.43	-7.8	223.1 (19)	129.1 (28)	94.4
							94.4

[a] ^{1}H NMR (599.8 MHz), ^{31}P (81.0 MHz), ^{13}C (150.8 MHz) in d_8-THF, 300 K, if not noted otherwise. [b] J_{PC} coupling constants in Hz. [c] In d_6-benzene. [d] ^{13}C NMR at 125.7 MHz. [e] ^{1}H NMR at 499.8 MHz.

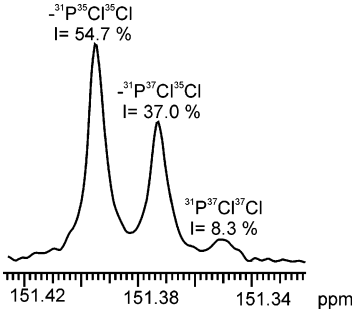


Figure 1. ^{31}P NMR spectrum (in d_6-benzene, 242.8 MHz, 300 K) of complex **5b**, showing the features of the three isotopomers in a close to statistical intensity ratio.

ratio of (^{31}P^{35}Cl^{35}Cl:^{31}P^{37}Cl^{35}Cl:^{31}P^{37}Cl^{37}Cl of 55:37:8; calcd 58:36:6; see Figure 1).

The addition of $PhPCl_2$ to **1a** and **1b** gave the products **6a** and **6b**, respectively. The replacement of a chloride at phosphorus by C3 of the σ-ligand chain has made the P center of the −P(Ph)Cl substituent chiral, and consequently the cyclopentadienyl ligands in **6a** and **6b** have become diastereotopic (see Table 1). The reaction of **1a** and **1b** with Ph_2PCl gave the products **7a** and **7b**, respectively. Both were characterized by X-ray diffraction (see Figures 2 and 3).

The structure of **7a**, which is depicted in Figure 2, shows that the five-membered metallacycle of the starting material (**1a**) was opened by the addition of a chloride ligand to zirconium. The remaining Ph_2P− moiety was attached at C3 of the σ-ligand chain to form an *E*-configured substituted σ-enyne ligand, which has remained attached to the metal via the Zr−C2 σ-bond (2.299(2) Å). The organic σ-ligand is planar and oriented in the metallocene σ-ligand plane (angle Cl−Zr−C2 102.76(6)°). The large enyne σ-ligand is oriented toward a lateral sector of the bent metallocene wedge (dihedral angles Cl−Zr−C2−C3 −179.9(2)°, Zr−C2−C3−P −177.6-

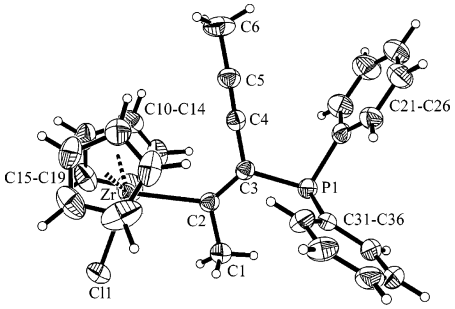


Figure 2. Molecular structure of complex **7a**. Selected structural parameters: C1−C2 1.504(3) Å, C2−C3 1.347-(3) Å, C3−C4 1.432(3) Å, C4−C5 1.188(3) Å, C5−C6 1.460-(3) Å, C3−P 1.844(2) Å, Zr−C2−C3 130.6(2)°.

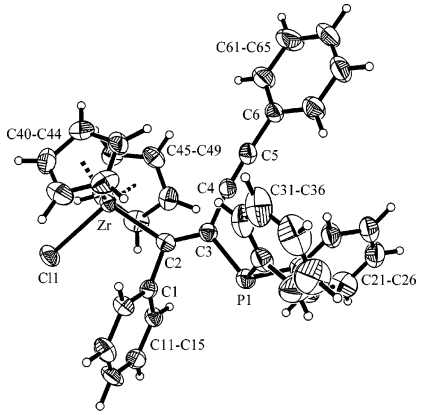


Figure 3. Molecular structure of complex **7b**. Selected structural parameters: C1−C2 1.482(4) Å, C2−C3 1.352-(5) Å, C3−C4 1.426(6) Å, C4−C5 1.192(6) Å, C5−C6 1.444-(6) Å, C3−P 1.849(4) Å, Zr−C2−C3 135.9(3)°, C3−C4−C5 173.1(4)°, Cl−Zr−C2−C3 178.1(4)°, Cl−Zr−C2−C1 −2.9-(3)°, Zr−C2−C3−C4 −1.6(7)°, Zr−C2−C3−P 179.1(2)°.

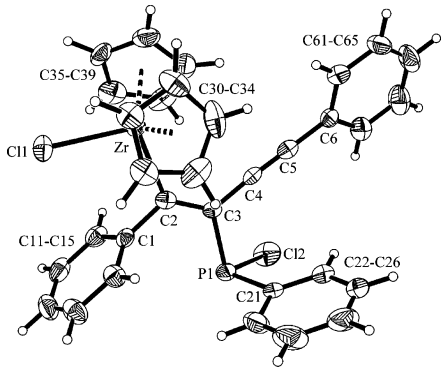


Figure 4. View of the molecular structure of complex *rac*-**6b** (only one enatiomer is depicted). Selected bond lengths and angles: Zr−C2 2.320(3) Å C1−C2 1.493(4) Å, C2−C3 1.353(4) Å, C3−P1 1.851(3) Å, C3−C4 1.426(4) Å, C4−C5 1.200(4) Å, C5−C6 1.444(5) Å, Zr−C2−C1 111.1(2)°, Zr−C2−C3 128.2(2)°, C1−C2−C3 120.5(3)°, C2−C3−P1 118.7(2)°, C4−C3−P1 116.7(2)°, C2−C3−C4 124.3(3)°, C3−C4−C5 175.1(3)°, C4−C5−C6 177.8(4)°.

(1)°). Complex **7b** features a similar molecular structure in the crystal (Figure 3). In this case the presence of the bulky phenyl substituents has resulted in a few minor distortions. Complex **6b** was also characterized by X-ray diffraction (see Figure 4). In this case the product contains a stereogenic phosphorus center, featuring three different substituents. Single crystals were

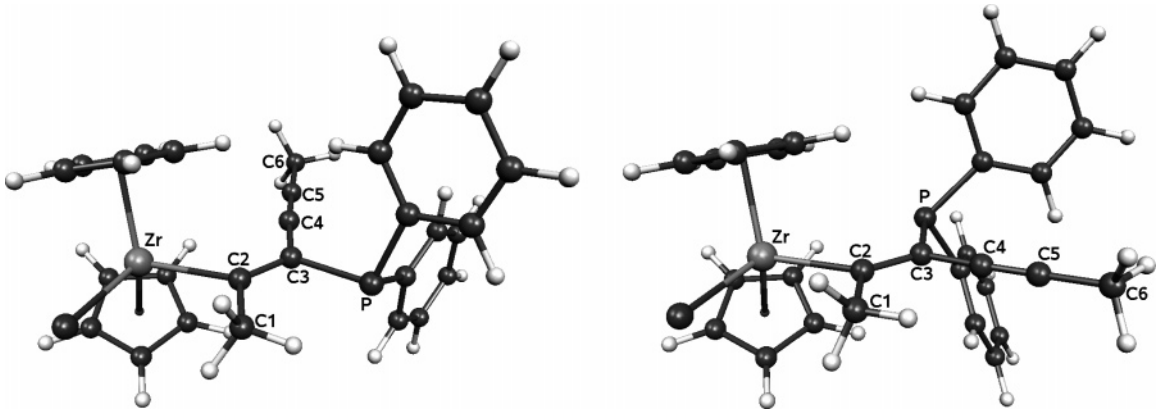
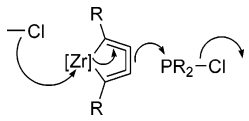


Figure 5. View of the DFT-calculated (B-LYP/TZVP, Zr: def-TZVPP) structures of ***E*-7a** (left, calcd Zr−C2 2.350 Å, C1−C2 1.524 Å, C2−C3 1.369 Å, C3−P 1.922 Å, C3−C4 1.423 Å, C4−C5 1.221 Å, C5−C6 1.462 Å, Cl−Zr−C2 101.8°, Zr−C2−C3 129.8°) and ***Z*-7a** (right, calcd Zr−C2 2.357 Å, C1−C2 1.532 Å, C2−C3 1.372 Å, C3−C4 1.427 Å, C3−P 1.891 Å, C4−C5 1.220 Å, C5C6 1.461 Å, Cl−Zr−C2 101.3°, Zr−C2−C3 134.9°).

Scheme 3



obtained from the racemate. Figure 4 shows one of the enantiomeric forms.

So far we have identified only the *E*-configured products that were formed from the reaction of the zirconacyclocumulenes **1** with these P−Cl-containing reagents. The structures (see Figure 5) and relative energies of both the ***E*-7a** and ***Z*-7a** isomers were calculated by DFT. The ***E*-7a** isomer was found to be favored by only 0.8 kcal mol^{-1} over the ***Z*-7a** isomer. This indicated that the observed reaction of **1** with the R_2P-Cl reagents was kinetically controlled *E*-selective. The direct addition of X−Y molecules either to the starting materials **1** or to their η^2-butadiyne metallocene isomers would be expected to be cis-additions, as was shown for many examples by Rosenthal and others.[7] The fact that we have here observed a trans-selective addition/ring-opening reaction points to an intermolecular addition pathway, e.g., as schematically depicted in Scheme 3, although any detailed mechanistic interpretation at this time must await further specific experimental evidence.

Conventional zirconacyclopentadienes often react with $RPCl_2$ reagents to yield the corresponding phospholes.[8] This reaction pathway is apparently not favored for the systems **1** due to the high endothermicity that would be associated with the formation of a hypothetical five-ring "phosphacyclocumulene" product.[9] Ring opening with formation of a phosphorus-substituted conjugated enyne system,[10] remotely related to the pathway involved in the catalytic formation of **1** from **4** (see Scheme 1), seems to provide a favored alternative. This study, thus, provides evidence for the special chemical features that are derived from the unusual electronic structure of the zirconacyclocumulenes **1**.

Experimental Section

General Procedures. Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information see, for example, ref 3. The bis(alkynyl)zirconocenes (**1**) were prepared analogously as described in the literature.[3,5]

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000).

Quantum Chemical Calculations. Quantum chemical calculations have been performed with the TURBOMOLE 5.6 suite of programs (Universität Karlsruhe, 2003). The structures have been fully optimized at the density functional (DFT) level employing the B-LYP functional (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098−3100. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789). A Gaussian AO basis of valence-triple-ζ quality including polarization functions (TZVP) (A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829−5835) was used for all heavy atoms. One additional f-polarization function (α = 0.988993) and a relativistic pseudopotential (small core) were employed for Zr (D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123−141). The RI approximation was used for the two-electron integrals (K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283−290).

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(8) Fagan, P.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312. Fagan, P.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889. Takahashi, T.; Hara, R.; Nishihara, Y., Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154−5155. Ura, Y.; Li, Y.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* **1998**, *39*, 2787−2790.

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(10) See for comparison: Kawatkar, S., P.; Schreiner, P. R. *Org. Lett.* **2002**, *4*, 3643−3646.

General Procedure for the Preparation of 5a, 6a, and 7a. Zirconacyclocumulene **1a** was dissolved in 50 mL of THF. The respective chlorophosphine was added, and the reaction mixture was stirred for 3 h at ambient temperature. The solvent was removed in vacuo, and the residue was washed with pentane (3 × 10 mL) and dried in vacuo. For **5b** and **6b**, the same procedure was used as for the preparation of **5a**−**7a** except that the solvent was changed to toluene.

Preparation of Complex 5a. A sample of 1.58 g (5.3 mmol) of **1a** was treated with 0.50 mL (0.76 g, 5.5 mmol) of phosphorus trichloride to yield 0.80 g (35%) of **5a**, mp 120 °C (DSC, dec). Anal. Calcd for $C_{16}H_{16}Cl_3PZr$ (436.9): C, 43.99; H, 3.69. Found: C, 44.63; H, 3.60. ^{1}H NMR (d_6-benzene, 599.8 MHz, 300 K): δ 5.87 (s, 10H, Cp), 2.33 (s, 3H, *Me*-C═), 1.63 (s, 3H, *Me*-C≡). ^{13}C{^{1}H} NMR (d_6-benzene, 150.7 MHz, 300 K): δ 223.6 (d, $^2J_{PC}$ = 23 Hz, C1), 133.2 (d, $^1J_{PC}$ = 70 Hz, C2), 113.5 (Cp), 90.1 (d, $^3J_{PC}$ = 2.9 Hz, C4), 79.0 (d, $^2J_{PC}$ = 2.9 Hz C3), 25.5 (d, $^3J_{PC}$ = 62 Hz, *Me*-C═), 4.2 (*Me*-C≡). ^{31}P NMR (d_6-benzene, 202.4 MHz, 300 K): δ 154.3 ($\nu_{1/2}$ = 5 Hz).

Preparation of Complex 6a. A sample of 1.14 g (3.8 mmol) of **1a** was treated with 0.53 mL (0.68 g, 3.8 mmol) of dichlorophenylphosphine to yield 0.83 g (46%) of **6a**, mp 120 °C (DSC, dec). Anal. Calcd for $C_{22}H_{21}Cl_2PZr$ (478.5): C, 55.22; H, 4.42. Found: C, 53.80; H, 4.08. ^{1}H NMR (d_8-THF, 499.8 MHz, 300 K): δ 7.64 (m, 2H, o-*Ph*), 7.41 (m, 2H, m-*Ph*), 7.35 (m, 1H, p-*Ph*), 6.50, 6.30 (each s, each 5H, Cp), 2.39 (s, 3H, *Me*-C═), 1.89 (s, 3H, *Me*-C≡). ^{13}C{^{1}H} NMR (d_8-THF, 125.7 MHz, 300 K): δ 222.0 (d, $^2J_{PC}$ = 19.6 Hz, C1), 140.6 (d, $^1J_{PC}$ = 34.0 Hz, i-*Ph*), 131.2 (d, $^2J_{PC}$ = 23.7 Hz, o-*Ph*), 130.7 (d, $^1J_{PC}$ = 65.0 Hz, C2), 129.7 (p-*Ph*), 128.6 (d, $^3J_{PC}$ = 6.2 Hz, m-*Ph*), 114.3, 114.2 (Cp), 89.8 (C4), 81.3 (C3), 26.5 (*Me*-C═), 3.9 (*Me*-C≡). ^{31}P NMR (d_6-benzene, 81.0 MHz, 300 K): δ 68.1 ($\nu_{1/2}$ = 3 Hz).

Preparation of Complex 7a. A sample of 1.14 g (3.8 mmol) of **1a** was treated with 0.44 mL (0.885 g, 3.8 mmol) of chlorodiphenylphosphine to yield 1.07 g (54%) of **7a**, mp 171 °C (DSC, dec). Anal. Calcd for $C_{28}H_{26}ClPZr$ (520.2): C, 64.65; H, 5.04. Found: C, 64.66; H, 5.22. ^{1}H NMR (d_8-THF, 599.8 MHz, 300 K): δ 7.43 (m, 2H, o-*Ph*), 7.31 (m, 2H, m-*Ph*), 7.27 (m, 1H, p-*Ph*), 6.37 (s, 10H, Cp), 2.20 (s, 3H, *Me*-C═), 1.66 (s, 3H, *Me*-C≡). ^{13}C{^{1}H} NMR (d_8-THF, 150.8 MHz, 300 K): δ 217.3 (d, $^2J_{PC}$ = 14.9 Hz, C1), 140.3 (d, $^1J_{PC}$ = 14.3 Hz, i-*Ph*), 134.3 (d, $^2J_{PC}$ = 19.5 Hz, o-*Ph*), 128.5 (d, $^3J_{PC}$ = 6.5 Hz, m-*Ph*), 128.5 (p-*Ph*), 127.4 (d, $^1J_{PC}$ = 39.0 Hz, C2), 117.1 (Cp), 89.1 (C4), 84.7 (C3), 26.3 (d, $^3J_{PC}$ = 45.4 Hz, *Me*-C═), 4.0 (*Me*-C≡). ^{31}P NMR (d_6-benzene, 81.0 MHz, 300 K): δ −12.3 ($\nu_{1/2}$ = 10 Hz).

X-ray Crystal Structure Analysis of 7a: formula $C_{28}H_{26}ClPZr$, M = 520.13, yellow crystal 0.35 × 0.20 × 0.10 mm, a = 7.732(1) Å, b = 18.380(1) Å, c = 33.917(1) Å, V = 4820.1(7) Å^3, ρ_{calc} = 1.433 g cm^{-3}, μ = 6.47 cm^{-1}, empirical absorption correction (0.805 ≤ T ≤ 0.938), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.71073 Å, T = 198 K, ω and φ scans, 36 846 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 5745 independent (R_{int} = 0.058) and 4315 observed reflections [$I \geq 2\sigma(I)$], 282 refined parameters, R = 0.035, wR_2 = 0.083, max. residual electron density 0.40 (−0.40) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 5b. A sample of 1.15 g (2.7 mmol) of **1b** was treated with 0.25 mL (0.37 g, 2.7 mmol) of phosphorus trichloride to yield 1.00 g (66%) of **5b**, mp 181.0 °C (DSC, dec). Anal. Calcd for $C_{26}H_{20}Cl_3PZr$ (561.0): C, 55.67; H, 3.59. Found: C, 56.47; H, 3.69. ^{1}H NMR (d_6-benzene, 599.8 MHz, 300 K): δ 7.56 (m, 2H, o-*Ph*C≡), 7.07 (m, 2H, m-*Ph*C═), 7.05 (m, 2H, m-*Ph*C≡), 7.02 (m, 1H, p-*Ph*C≡), 7.01 (m, 1H, p-*Ph*C═), 6.87 (m, 2H, o-*Ph*C═), 6.04 (s, 10H, Cp). ^{13}C{^{1}H} NMR (d_6-benzene, 150.8 MHz, 300 K): δ 223.9 (d, $^2J_{CP}$ = 26.9 Hz, C1), 142.0 (d, $^2J_{CP}$ = 26.7, i-*Ph*C═), 131.5 (o-*Ph*C≡), 129.1 (d, $^1J_{PC}$ = 59.0 Hz, C2), 128.6 (m-*Ph*C≡), 128.5 (p-*Ph*C≡), 128.4 (m-*Ph*C═), 127.1 (p-*Ph*C═), 126.7 (d, $^4J_{CP}$ = 4.2 Hz, o-*Ph*C═), 123.4 (i-*Ph*C≡), 112.9 (Cp), 95.8 (C4), 87.8 (C3). ^{31}P NMR (d_6-benzene, 242.8 MHz, 300 K): δ 151.37, 151.35, 151.32 (Cl isotopomeres: 57%:35%:8% ≡ ^{31}P(^{35}Cl, ^{35}Cl):^{31}P(^{35}Cl, ^{37}Cl):^{31}P(^{37}Cl, ^{37}Cl).

Preparation of Complex 6b. A sample of 1.20 g (2.8 mmol) of **1b** was treated with 0.39 mL (0.51 g, 2.8 mmol) of dichlorophenylphosphine to yield 0.50 g (29%) of **6b**, mp 154.0 °C (DSC, dec). Anal. Calcd for $C_{32}H_{25}Cl_2PZr$ (602.64): C, 63.78; H, 4.18. Found: C, 63.51; H, 3.83. ^{1}H NMR (d_8-THF, 599.8 MHz, 300 K): δ 7.72 (m, 2H, o-PhP), 7.43 (m, 2H, m-PhP), 7.40 (m, 1H, p-PhC≡), 7.38 (m, 1H, p-PhP), 7.34 (m, 2H, o-PhC≡), 7.33 (m, 2H, m-PhC≡), 7.23, 7.16 (each m, each 1H, m-PhC═), 7.14 (m, 1H, p-PhC═), 7.12, 6.92 (each m, each 1H, o-PhC═), 6.47, 6.35 (each s, each 5H, Cp). ^{13}C{^{1}H} NMR (d_8-THF, 150.8 MHz, 300 K): δ 224.5 (d, $^2J_{PC}$ = 22.6 Hz, C1), 144.0 (d, $^3J_{PC}$ = 22.0 Hz, i-*Ph*C═), 140.9 (d, $^1J_{PC}$ = 38.5 Hz, i-*Ph*P), 132.6 (d, $^1J_{PC}$ = 49.9 Hz, C2), 132.1 (p-*Ph*C≡), 131.5 (d, $^1J_{PC}$ = 24.8 Hz, o-*Ph*P), 130.1 (p-*Ph*P), 129.4 (o-*Ph*C═), 129.0, 129.0 (m-*Ph*P), 128.9 (m-*Ph*C≡), 128.8 (d, $^4J_{PC}$ = 2.3 Hz, o′-*Ph*C═), 128.6 (m-*Ph*C═), 127.8 (d, $^6J_{PC}$ = 3.1 Hz p-*Ph*C═), 127.1 (p-*Ph*C≡), 124.7 (i-*Ph*C≡), 114.0, 113.8 (Cp), 95.4 (C4), 91.0 (C3). ^{31}P NMR (d_6-benzene, 242.8 MHz, 300 K): δ 70.4 ($\nu_{1/2}$ = 8 Hz).

X-ray crystal structure analysis of 6b: formula $C_{32}H_{25}Cl_2PZr$, M = 602.61, yellow crystal 0.25 × 0.06 × 0.03 mm, a = 9.259(1) Å, b = 20.346(1) Å, c = 14.921(1) Å, β = 99.86(1)°, V = 2769.4(4) Å^3, ρ_{calc} = 1.445 g cm^{-3}, μ = 6.67 cm^{-1}, empirical absorption correction (0.851 ≤ T ≤ 0.980), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 18 363 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 6554 independent (R_{int} = 0.075) and 4471 observed reflections [$I \geq 2\sigma(I)$], 325 refined parameters, R = 0.060, wR_2 = 0.089, max. residual electron density 0.53 (−0.48) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7b. The zirconacyclocumulene **1b** (1.60 g, 3.8 mmol) was dissolved in 50 mL of toluene. Chlorodiphenylphosphine (0.43 mL, 0.84 g, 3.8 mmol) was added and the reaction mixture stirred for 3 h at ambient temperature. The product precipitated as a white solid. It was collected by filtration, washed with pentane (3 × 10 mL), and dried in vacuo to yield 1.52 g (62%) of **7b**, mp 250.4 °C (DSC, dec). Anal. Calcd for $C_{38}H_{30}ClPZr$ (602.6): C, 70.84; H, 4.69. Found: C, 70.28; H, 4.47. ^{1}H NMR (d_8-THF, 499.8 MHz, 300 K): δ 7.46 (m, 4H, o-*Ph*P), 7.33 (m, 4H, m-*Ph*P), 7.30 (m, 2H, p-*Ph*P), 7.23 (m, 2H, m-*Ph*C≡), 7.22 (m, 2H, o-*Ph*C≡), 7.09 (m, 2H, m-*Ph*C═), 7.08 (m, 1H, p-*Ph*C≡), 7.07 (m, 1H, p-*Ph*C═), 6.87 (m, 2H, o-*Ph*C═), 6.43 (s, 10H, Cp). ^{13}C{^{1}H} NMR (d_8-THF, 125.7 MHz, 300 K): δ 223.1 (d, $^2J_{PC}$ = 18.9 Hz, C1), 143.9 (d, $^3J_{PC}$ = 18 Hz, i-*Ph*C═), 140.8 (d, $^1J_{PC}$ = 17.7 Hz, i-*Ph*P), 134.1 (d, $^2J_{PC}$ = 19.9 Hz, o-*Ph*P), 131.8 (p-*Ph*C≡), 129.1 (m-*Ph*C≡), 129.1 (d, $^1J_{PC}$ = 28.3 Hz, C2), 128.8 (d, $^2J_{PC}$ = 5.8 Hz, m-*Ph*P), 128.8 (o-*Ph*P═), 128.7 (d, $^3J_{PC}$ = 2.0 Hz, p-*Ph*P), 128.6 (d, $^5J_{PC}$ = 1.8 Hz, m-*Ph*C═), 128.5 (o-*Ph*C≡), 126.7 (p-*Ph*C═), 125.0 (i-*Ph*C≡), 113.6 (Cp), 94.4 (C4), 94.4 (C3). ^{31}P NMR (d_6-benzene, 81.0 MHz, 300 K): δ −7.8 ($\nu_{1/2}$ = 6 Hz).

X-ray crystal structure analysis of 7b: formula $C_{38}H_{30}ClPZr \cdot 1/2C_4H_8O$), M = 680.31, light yellow crystal 0.15 × 0.10 × 0.03 mm, a = 8.557(1) Å, b = 8.631(1) Å, c = 2.404-(1) Å, α = 84.47(1)°, β = 89.37(1)°, γ = 64.53(1)°, V = 1618.7-(3) Å^3, ρ_{calc} = 1.396 g cm^{-3}, μ = 5.01 cm^{-1}, empirical absorption correction (0.929 ≤ T ≤ 0.985), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 18 330 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 5690 independent (R_{int} = 0.070) and 4395 observed reflections [$I \geq 2\sigma(I)$], 410 refined parameters, R = 0.064, wR_2 = 0.101, max. residual electron density 0.42 (−0.48) e Å^{-3}, due to crystal size and disordered solvent molecule (refined as half a molecule of THF, split over two positions, geometrically fixed by constraints, isotropic thermal displacement parameters are

used) only limited accurancy, hydrogen atoms calculated and refined as riding atoms.

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Supporting Information Available: Details of the X-ray crystal structure analyses and the DFT calculations and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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