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Articles

Generation and Trapping of a 1,1′-Diphosphazirconocene

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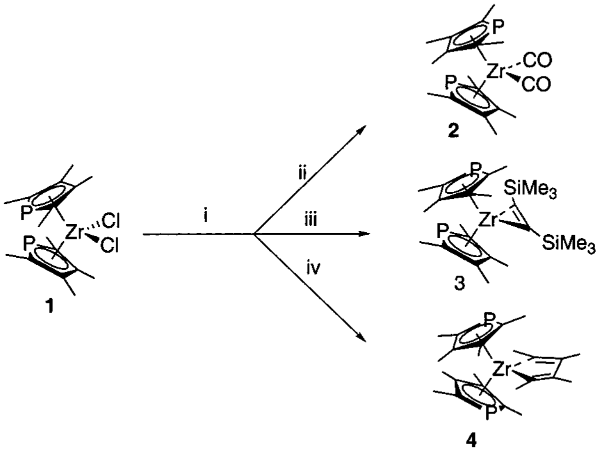
The reduction of $[(\eta^5\text{-}C_4Me_4P)_2ZrCl_2]$ (**1**) by magnesium in THF affords a transient octamethyl-1,1′-diphosphazirconocene which can be trapped by CO, bis(trimethylsilyl)-acetylene, and 2-butyne to give the corresponding dicarbonyl **2**, zirconacyclopropene **3**, and zirconacyclopentadiene **4**; all of these products have been characterized by X-ray analyses. An assessment of the π-basicity of the η^5-C_4Me_4P ligand has been made by several methods: (a) a comparison of the IR carbonyl stretching frequencies of **2** and of other dicarbonylzirconocene complexes, (b) a correlation of the ^{13}C NMR and IR data in **3** and in similar zirconacyclopropenes, and (c) an electrochemical study on **1**. All these experiments confirm that the η^5-C_4Me_4P ligand is a poorer π-base than the Cp ligand.

Introduction

The transient 14-electron zirconocenes are now well-established as major intermediates in various zirconium-based synthetic processes.[1] For instance, they have been successfully used as powerful tools in main-group chemistry for the synthesis of conventional or metalated heterocycles.[2] We have developed in our laboratory the synthesis of π-phospholyl (phosphacyclopentadienyl) transition-metal complexes as analogues of the conventional π-cyclopentadienyl complexes,[3] and, in group 4 metal chemistry, we have been able to synthesize mono- and diphospholyl titanium[4] and zirconium complexes.[5] Recently, several 1,1′-diphospholylzirconium dichlorides (1,1′-diphosphazirconocene dichlorides) have attracted some attention as possible substitutes of their all-carbon analogues in olefin polymerization catalysis and other related applications.[6] In such a context, additional knowledge on their little investigated reactivity[7] appeared desirable. In particular, we wished to clarify the differences between the π-phospholyl and the π-cyclopentadienyl ligands by the study of several new 1,1′-diphosphazirconocene derivatives. We also wanted to investigate the chemistry of the still unknown 14-electron 1,1′-diphosphazirconocene intermediates, available in principle by 2-electron reduction of the corresponding 1,1′-diphosphazirconocene dichlorides. We now report on the generation of a transient 14-electron 1,1′-diphosphazirconocene and of its trapping into three new 1,1′-diphosphazirconocene derivatives, fully characterized by their spectroscopic data and their X-ray crystal structures.

Scheme 1[a]



[a] Reagents and conditions: (i) Mg, THF; (ii) 1 atm of CO; (iii) $Me_3SiC{\equiv}CSiMe_3$; (iv) 2-butyne.

Results and Discussion

The synthetic results are outlined in Scheme 1. Following earlier work in the all-carbon series,[8−10] the readily available 1,1′,2,2′,3,3′,4,4′-octamethyl-1,1′-diphos-

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phazirconocene dichloride (**1**)[5] was used as starting material for the reduction experiments. In all cases, we used commercial magnesium powder as the reducing agent and the resulting 1,1′-diphosphazirconocene (which was not isolated) was reacted in situ with three different trapping agents: carbon monoxide,[8] bis(trimethylsilyl)-acetylene,[9] and 2-butyne;[10] we found that the use of an activator such as mercuric chloride was not necessary. Reduction of **1** usually started after a short induction period, as indicated by darkening of the solution; gentle warming (40 °C) was sometimes used in order to initiate the reaction. Good yields of dicarbonyl **2**, zirconacyclopropene **3**, and zirconacyclopentadiene **4** were respectively obtained.

All physical and analytical data obtained on compounds **2**−**4** are fully compatible with the proposed structures; ultimately, X-ray crystal diffraction data have been obtained for all three complexes and confirm these structures. Since several all-carbon analogues of these compounds have been described in the literature, we can try to compare the different ligating properties of the cyclopentadienyl and phospholyl groups.

There is already evidence, by electrochemical measurements on comparable phospholyl and cyclopentadienyl complexes of chromium,[11] iron,[12] cobalt,[13] and uranium,[14] that phospholyl ligands are significantly less electron-donating than cyclopentadienyl ligands; therefore, the zirconium should be more electrophilic in complexes **2**−**4** than in their all-carbon analogues. We now have the opportunity to study the influence of this factor on the structural and spectral properties of the ligand bonded to the diphosphazirconocene moiety.

Spectroscopic Data. Several interesting features are present in the NMR data of complex **2**. Its ^{31}P resonance (21 ppm) and also the phospholyl ring ^{13}C signals (122 and 125 ppm) are located at much higher field than those of **3**, **4**, or **1** (in the 75−95 ppm range for ^{31}P and 135−145 ppm for ^{13}C). The high-field shift of the ^{13}C resonances of $(C_5Me_4H)_2Zr(CO)_2$ with respect to those for $(C_5Me_4H)_2ZrCl_2$ has already been reported.[15] The upfield shifts observed in **2** are likely due to the fact that this 18-electron diphosphazirconocene dicarbonyl is more electron-rich than **3**, **4**, or **1**, which are 16-electron complexes.

The ^{13}C resonance and the IR stretching frequencies of the carbonyl groups in **2** are indicative of the reduced electron donating properties of the C_4Me_4P ligand. The ^{13}C chemical shift of **2**, δ 249.3 (C_6D_6), can be compared to those of $(C_5Me_4H)_2Zr(CO)_2$ (δ 274.15 (C_6D_6))[13] and of $PhP(C_5Me_4)_2Zr(CO)_2$ (δ 271.8 and 272.0 (C_6D_6)).[16] The carbonyl stretching frequencies of several zirconocene dicarbonyl complexes are presented in Table 1.

Table 1. IR Stretching Frequencies of $L_2Zr(CO)_2$ Complexes

compd	ν(C≡O) (cm^{-1})	ref
$(indenyl)_2Zr(CO)_2$	1985, 1899 (pentane)	17
$Cp_2Zr(CO)_2$	1975, 1885 (hexane)	8
$[PhP(C_5Me_4)_2]Zr(CO)_2$	1959, 1874 (pentane)	16
$[Me_2Si(C_5Me_4)_2]Zr(CO)_2$	1956, 1869 (hexane)	16
$(C_5Me_4H)_2Zr(CO)_2$	1948, 1854 (hexane)	15
$(C_5Me_5)_2Zr(CO)_2$	1946, 1853 (hexane)	8
2	1968, 1899 (hexane)	this work

Table 2. IR Stretching Frequencies and ^{13}C NMR Data of $L_2Zr(Me_3SiC_2SiMe_3)$ Complexes

compd	ν(C≡C) (KBr; cm^{-1})	δ(^{13}C; C≡C) (C_6D_6)	ref
$(C_5H_3Me_2)_2Zr(Me_3SiC_2SiMe_3)$	1566	258.2	9b
$(C_5H_2Me_3)_2Zr(Me_3SiC_2SiMe_3)$	1535	260.0	9b
$(C_5HMe_4)_2Zr(Me_3SiC_2SiMe_3)$	1516	260.2	9b
$(C_5Me_5)_2Zr(Me_3SiC_2SiMe_3)$	1516	260.5	9b
3	1617	253.0	this work

The average between the two stretching modes is slightly higher for **2** than for $[Cp_2Zr(CO)_2]$ but lower than for $[(indenyl)_2Zr(CO)_2]$; the π-basicity of the phospholyl ligand in **2** probably follows the same trend, being lower that of the Cp ligand in $[Cp_2Zr(CO)_2]$ but higher than that of the indenyl ligand in $[(indenyl)_2Zr(CO)_2]$.

^{13}C NMR data and IR stretching frequencies have also been reported for a series of zirconocene alkyne complexes with increasing methyl substitution on the cyclopentadienyl ring. It also appeared interesting to compare these values with that of **3** (Table 2).

This table shows that, in **3**, the bis(trimethylsilyl)-acetylene ligand, although less strongly bonded to zirconium than in the $(C_5Me_nH_{5-n})_2Zr(Me_3SiC_2SiMe_3)$ analogues, still behaves as a four-electron ligand.

Finally, an interesting aspect of the NMR data of compounds **2**−**4** is that, even though the compounds are symmetrical and that the phosphorus atoms on the two phospholyl rings are chemically equivalent, they are not magnetically equivalent when there exists a nonzero $J_{PP'}$ coupling constant, and this may give rise to second-order effects in the NMR spectra; this constant can be estimated by matching experimental and simulated spectra. In the ^{13}C spectra second-order effects are complicated by an additional isotope effect: the presence of one ^{13}C at a given position on one ring induces a small chemical inequivalence (a few hertz) between the two phosphorus atoms, which thus remain strongly coupled in the usual sense even when the $J_{PP'}$ coupling constant is small. This isotope effect is present on the carbon α to phosphorus in **3** and **4**, as had been noted before in **1**,[5] but we also found that, surprisingly, a smaller effect was also present on the carbon β to phosphorus in the phospholyl ring: the experimental signals of C_β in **3** and **4** could be satisfactorily reproduced in line positions and intensities only by setting a chemical shift difference of ca. 2.5 Hz (0.03 ppm) between the two phosphorus atoms. In particular, inclusion of this effect satisfactorily reproduced the pseudo-doublet structure of the C_β in **3**; otherwise, simulation showed a broad singlet (see the

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Table 3. Structural Parameters of $L_2Zr(CO)_2$ Complexes

compd	C−O bond (Å)	Zr−C(σ) bond (Å)	ref
$(indenyl)_2Zr(CO)_2$	1.127(7)	2.221(7)	17
	1.133(8)	2.186(7)	
$Cp_2Zr(CO)_2$	1.138	2.187(4)	18
$[PhP(C_5Me_4)_2]Zr(CO)_2$	1.109(2)	2.221(2)	16
	1.115(2)	2.222(2)	
$(C_5Me_5)_2Zr(CO)_2$	1.16(1)	2.145(9)	8
2	1.143(2)	2.189(2)	this work

Table 4. X-ray Diffraction Summary

	2	**3**	**4**
mol formula	$C_{18}H_{24}O_2P_2Zr$	$C_{24}H_{42}P_2Si_2Zr$	$C_{24}H_{36}P_2Zr$
mol wt	425.54	539.92	477.69
cryst habit	brownish red cube	emerald green plate	brownish yellow cube
cryst dimens (mm)	0.16 × 0.16 × 0.16	0.20 × 0.16 × 0.14	0.22 × 0.22 × 0.22
cryst syst	orthorhombic	triclinic	monoclinic
space group (No.)	*Pnma* (62)	$P\bar{1}$ (2)	*C*2/*c* (15)
a (Å)	7.309(5)	10.792(5)	14.079(5)
b (Å)	15.823(5)	15.871(5)	11.257(5)
c (Å)	16.420(5)	16.520(5)	14.375(5)
α (deg)	90	86.040(5)	90.010(5)
β (deg)	90	81.310(5)	90.200(5)
γ (deg)	90	89.270(5)	89.980(5)
V (Å^3)	1899.0(15)	2790.4(18)	2278.2(15)
Z	4	4	4
d (g cm^{-3})	1.488	1.285	1.393
F(000)	872	1136	1000
μ (cm^{-1})	0.753	0.604	0.630
max θ	30.02	27.48	30.02
h range	−10 to +10	−14 to +13	−19 to +19
k range	−22 to +22	−20 to +20	−14 to +15
l range	−22 to +23	−21 to +17	−19 to +20
no. of rflns measd	5182	18 950	7418
no. of indep rflns	2866	12 741	3312
no. of rflns used ($I > 2\sigma(I)$)	2535	11 379	3080
wR2 (all data)	0.0715	0.0737	0.0642
R1	0.0259	0.0256	0.0231
GOF	1.041	0.998	1.018

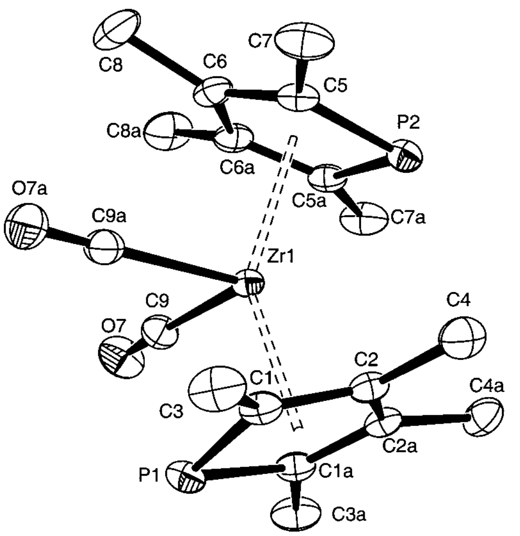

Figure 1. Molecular structure of **2** in the crystal form. Significant bond distances (Å) and angles (deg): Zr(1)−C(9) = 2.189(2), Zr(1)−CE(1) = 2.1877, Zr(1)−CE(2) = 2.2143, P(1)−C(1) = 1.788(2), P(2)−C(5) = 1.781(2), C(1)−C(2) = 1.407(2), C(2)−C(2)a = 1.430(3), C(5)−C(6) = 1.410(2), C(6)−C(6)a = 1.422(3), C(9)−O(7) = 1.143(2); CE(1)−Zr(1)−CE(2) = 143.09, C(9)−Zr(1)−C(9)a = 91.3(1), C(1)−P(1)−C(1)a = 89.9(1), C(5)−P(2)−C(5)a = 90.0(1).

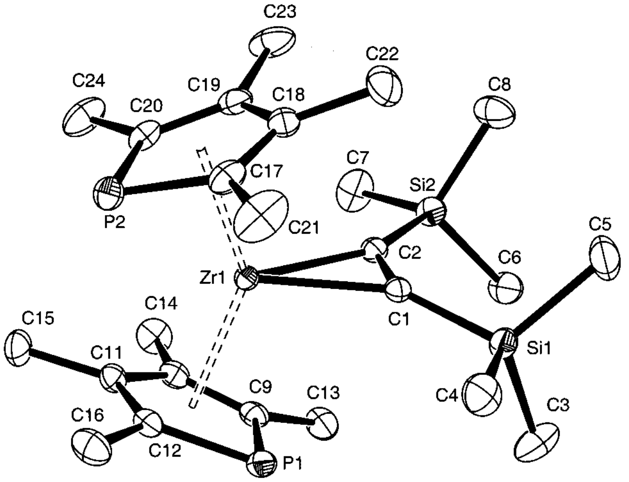

Figure 2. Molecular structure of **3** in the crystal form. Significant bond distances (Å) and angles (deg): Zr(1)−C(1) = 2.226(2), Zr(1)−C(2) = 2.228(2), C(1)−C(2) = 1.315(2), Zr(1)−CE(1) = 2.2539, Zr(1)−CE(2) = 2.2809, P(1)−C(9) = 1.773(2), P(1)−C(12) = 1.776(2), P(2)−C(17) = 1.767(2), P(2)−C(20) = 1.765(2), C(9)−C(10) = 1.406(2), C(10)−C(11) = 1.428(2); C(1)−Zr(1)−C(2) = 34.36(2), CE(1)−Zr(1)−CE(2) = 139.20, C(9)−P(1)−C(12) = 89.88(8), C(17)−P(2)−C(20) = 90.17(8).

figures in the Supporting Information). The $J_{PP'}$ values for **3** and **4** were found to be 3.2 and 8.9 Hz, respectively; from the absence of second-order effects in the spectra of **2**, it was concluded that the $J_{PP'}$ coupling constant in this case was close to zero.

X-ray Data. A summary of the X-ray data collection and solution parameters is presented in Table 4. The X-ray crystal structure analysis of **2** (Figure 1) showed the expected bent-metallocene structure with the two phospholyls in a head-to-tail disposition, probably in order to minimize the steric repulsion between the rings. At 143.1°, the centroid−Zr−centroid angle appears to be smaller than in the analogous decamethylzirconocene dicarbonyl (147.5°),[8] which is probably the result of a smaller steric repulsion between the phospholyl rings. In contrast, the Zr−centroid distances are similar in both cases at 2.19−2.21 vs 2.20 Å; the OC−Zr−CO angle is rather large in **2** at 91.3(1) vs 86.3(5)° in the decamethylzirconocene analogue.[8]

Since the structures of several other substituted zirconocene dicarbonyls have appeared in the literature, it appeared interesting to compare the structural parameters of the carbonyl groups in these compounds to that of **2** (Table 3). In this series, there is no clear correlation between the electrophilicity at zirconium and the lengths of the Zr−C(σ) and C−O bonds, except for $(C_5Me_5)_2Zr(CO)_2$, which displays the shortest Zr−C(σ) bond and the longest C−O bond,[8] consistent with the largest π-back-bonding of Zr to CO. Thus, it appears that the values of the CO stretching frequencies are more indicative of the electronic properties of the molecule than the structural data.

The X-ray analysis of **3** (Figure 2) shows the expected structure with, in that case, a lower bending than the analogous (C_5Me_4H) derivative: the centroid−Zr−centroid is 138.9−139.2 for **3** vs 134.5° for $[(C_5Me_4H)_2Zr(Me_3SiCCSiMe_3)]$.[9b] Again, there is no trend in the structural parameters of the zirconacyclopropene ring

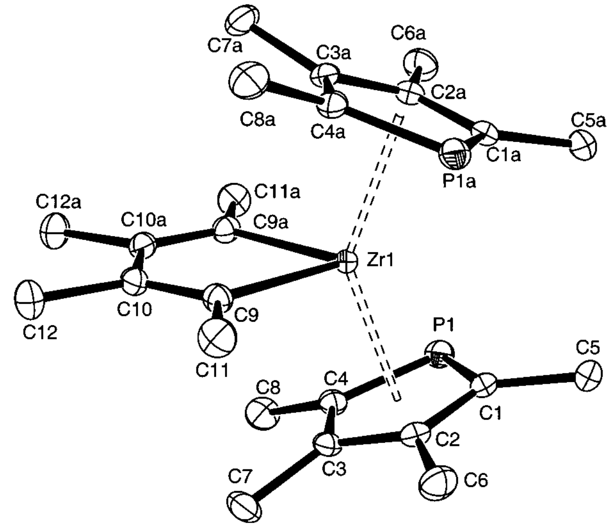

Figure 3. Molecular structure of **4** in the crystal form. Significant bond distances (Å) and angles (deg): Zr(1)−C(9) = 2.240(1), Zr(1)−CE(1) = 2.2960, C(9)−C(10) = 1.357(2), C(10)−C(10)a = 1.501(3), P(1)−C(1) = 1.777(2), P(1)−C(4) = 1.773(2), C(1)−C(2) = 1.401(2), C(2)−C(3) = 1.431(2), C(3)−C(4) = 1.409(2); C(9)−Zr(1)−C(9)a = 78.67(7), CE(1)−Zr(1)−CE(2) = 141.35, C(1)−P(1)−C(4) = 90.28(6).

that can be clearly related to the difference in electrophilicity at the zirconium atom in [$(C_5Me_4H)_2Zr(Me_3SiCCSiMe_3)$], [$(C_5Me_5)_2Zr(Me_3SiCCSiMe_3)$], and **3**. The variations in the Zr−C(alkyne) bond distances in these molecules (2.202(2), 2.216−2.221(2), and 2.226−2.228(2) Å, respectively) are likely due to both electronic and steric factors, while the variations in the C−C(alkyne) distance (1.316(3), 1.320(3), and 1.315−1.323(2) Å, respectively) are not very significant.

The X-ray crystal structure analysis of **4** (Figure 3) has also been obtained; however, since no bis(cyclopentadienyl)tetramethylzirconacyclopentadiene has been structurally characterized, the structure of **4** cannot be directly compared to that of an all-carbon analogue. However, the structure of the zirconacyclopentadiene ring in **4** is closely similar to that of other zirconacyclopentadienes, as reported in the literature.[19]

Finally, it is interesting to note that the solid-state conformation of the two phospholyl rings is different in **2**−**4** and also in the previously described **1**. In **2**, both phosphorus atoms are lying in a plane of symmetry mediating the OC−Zr−CO angle and are in an anti conformation. In **3** two different molecules are present in the unit cell, in which the two phosphorus atoms are in a gauche conformation; in one molecule, these atoms are in located on two opposite sides of a plane mediating the C(alkyne)−Zr−C(alkyne) angle, whereas in the other molecule they are on the same side of this plane. In **4**, there is an axis of symmetry and the phosphorus atoms, also in a gauche conformation, are equidistant from a plane mediating the zirconacyclopentadiene ring. If one now tries to correlate the $J_{PP'}$ coupling constant with the solid-state conformation of the two phosphorus atoms, one can notice that the value of this constant is zero when these atoms are farthest apart in **2**, intermediate (3−8 Hz) when they are in a gauche configuration in **3** and **4**, and large (50 Hz) in **1**, where the two phosphorus atoms are close to each other in a syn conformation.[5] The conformation of the phospholyl rings is unlikely to be fixed in solution in any of the complexes, but there is probably a preference for the solid-state conformation. The presence of a $J_{PP'}$ coupling constant may be due either to a through-space interaction of the phosphorus lone pairs or to a through-metal ^2J interaction, but in any case the presence of a correlation of $J_{PP'}$ vs conformation is worthy of note.

Electrochemical Measurements. Finally, to further assess the reduced π-basicity of the phospholyl ring, it seemed appropriate to study the electrochemical reduction of **1**. In THF, with a scan rate of 250 mV s^{-1}, a first, fully reversible monoelectronic reduction wave is observed at −1.50 V (SCE) and a second, irreversible one at −2.34 V (SCE). Only one reduction wave is observed with other dichlorozirconocenes: for instance, in similar conditions with $(C_5Me_4H)_2ZrCl_2$, irreversible reduction occurs at −2.02 V (SCE) and with Cp_2ZrCl_2, only one quasi-reversible wave is observed at −1.70 V (SCE).[20] Thus, with a similar substitution scheme, the replacement of a cyclopentadienyl by a phospholyl facilitates the reduction by ca. 0.25 V, the C_4Me_4P ligand being even a poorer π-donor than the Cp ligand. These results are fully consistent with those of the literature.[9−12] In addition, the reversibility of the first wave is in agreement with the stabilization of the electrogenerated low-valent Zr(III) species by the electron-poor phospholyl ligand.

Experimental Section

General Considerations.[21] All reactions were performed under an inert atmosphere with dry, deoxygenated solvents by using vacuum line and drybox techniques. $(C_4Me_4P)_2ZrCl_2$ was prepared according to a known procedure.[5] All other reagents were commercial and used as received. NMR spectra were measured with Bruker instruments operating at 4.68 or 7.02 T. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. Mass spectra were measured at 70 eV on a Hewlett-Packard spectrometer. Electrochemical measurements were made in THF solutions with a Radiometer (Copenhagen) DEA 332 potentiostat, using tetrabutylammonium tetrafluoroborate as carrier electrolyte and saturated calomel electrode (SCE) as internal potential standard.

1,1-Bis(tetramethylphospholyl)dicarbonylzirconium (2). CO gas was bubbled for 15 min into a solution of **1** (140 mg, 0.314 mmol) and magnesium metal (8 mg, 0.33 mmol) in THF (2 mL). The Schlenk vessel was then stoppered and the orange solution stirred at 40 °C. After an induction period, the reaction started, as indicated by a darkening of the solution. After 3 h, the dark red solution was evaporated to dryness, the residue was taken up in hexane, and this solution was filtered. The resulting red product (110 mg, 82%) was crystallized in cold hexane.

NMR (C_6D_6): ^1H, δ 1.78 (s, CH_3CCP), 1.81 (d, J_{PH} 11.0, CH_3CP); $^{31}P\{^1H\}$, δ 20.8; $^{13}C\{^1H\}$, δ 14.9 (s, CH_3CCP), 16.4 (d, J_{PC} 24.8, CH_3CP), 121.5 (d, J_{PC} 54.9, CH_3CP), 124.9 (d, J_{PC} 4.4, CH_3CCP). MS: *m/z* 367 ($M^+ - 2CO$, 25%), 140 ($C_4Me_4PH^+$, 100%).

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(21) Correct elemental analyses could not be obtained for compounds **2**−**4**. Original proton spectra for these compounds have been included in the Supporting Information, as evidence of purity.

1,1-Bis(tetramethylphospholyl)-2,3-bis(trimethylsilyl)-zirconacycloprop-2-ene (3). A solution of **1** (0.33 g, 0.75 mmol) and bis(trimethylsilyl)acetylene (0.17 mL, 0.75 mmol) in THF (10 mL) was stirred under argon in the presence of magnesium (17 mg, 0.76 mmol). The reaction mixture turned progressively dark brown. The reaction mixture was evaporated to dryness, the residue was taken up into hexane, and this solution was filtered. **3** was obtained as green microcrystals after evaporation of the solvent (0.35 g, 0.65 mmol, 86%).

NMR (C_6D_6): ^{1}H, δ 0.11 (s, Si(CH_3)$_3$), 1.84 (s, CH_3CCP), 1.93 (d, J_{PH} 11.0, CH_3CP); ^{31}P{^{1}H}, δ 90.6; ^{13}C{^{1}H}, δ 4.38 (s, Si(CH$_3$)$_3$), 17.57 (s, CH$_3$CCP), 17.87 (m, AXX′, J_{PC} 24.4, $J_{P'C}$ 4.9, $J_{PP'}$ 3.2, CH$_3$CP), 136.95 (ps d, AXY, J_{PC} 4.5, $J_{PP'}$ 3.2, $\Delta\nu_{PP'}$ 2.3, CH$_3$$C$CP), 143.82 (ps d, AXY, J_{PC} 51, $J_{PP'}$ 3.2, $\Delta\nu_{PP'}$ 7.0, CH$_3$$C$P), 253.02 (s, Si($CH_3$)$_3$)). MS: *m*/*z* 538 (M$^{•+}$, 1%) 140 (HPC$_4Me_4$$^{•+}$, 100%).

1,1-Bis(tetramethylphospholyl)-2,3,4,5-tetramethylzirconacyclopenta-2,4-diene (4). A solution of **1** (0.44 g, 1 mmol) and 2-butyne (0.15 mL, 2 mmol) in THF (10 mL) was stirred under argon in the presence of magnesium (25 mg, 1.04 mmol). The reaction mixture turned progressively dark red. After 16 h, the reaction mixture was evaporated to dryness, the residue was taken up into hexane, and this solution was filtered. **4** was obtained as a red powder (0.380 g, 80%) that was crystallized in dichloromethane.

NMR (CDCl$_3$): ^{1}H, δ 1.49 (s, CH_3CCZr), 1.60 (s, CH_3CZr), 1.97 (d, J_{PH} 11.0, CH_3CCP), 2.13 (m, A$_6$XX′A′$_6$, $J_{HP} = 9.9$, $J_{HP'} = 0.3$, $J_{PP'} = 8.9$, CH_3CP); ^{31}P{^{1}H}, δ 77.3; ^{13}C{^{1}H}, δ 15.66 (s, CH$_3$CC), 16.66 (s, CH$_3$CC), 17.83 (m, AXX′, J_{PC} 24.0, $J_{P'C}$ 4.7, $^2J_{PP'}$ 8.9, CH$_3$CP), 136.75 (s, CH$_3$$C$CZr), 138.57 (ps.t, AXY, J_{PC} 4.5, $J_{PP'}$ 8.9, $\Delta\nu_{PP'}$ 2.4, CH$_3$$C$CP), 143.82 (m, AXY, J_{PC} 49.3, $J_{PP'}$ 8.9, $\Delta\nu_{PP'}$ 7.3, CH$_3$$C$P), 192.90 (s, CH$_3$$C$Zr). MS: *m*/*z* 477 (M$^{•+}$, 3%), 141 (Me$_4C_4PH_2$$^+$, 100%).

X-ray Structure Determination. X-ray intensities were measured with a Nonius KappaCCD diffractometer at 150(1) K using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. A summary of the crystal structure determinations is presented in Table 4. All structures were solved by direct methods using SIR97 and refined using SHELXL97. All atoms except hydrogens were refined anisotropically on F^2 using all data, A mixed model was used for the refinement of the hydrogen atoms. No absorption corrections were necessary.

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Supporting Information Available: Figures giving proton spectra of compounds **2**−**4**, experimental and simulated NMR spectra for compounds **3** and **4**, and the cyclic voltammogram of **1** and tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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