Five-Coordinate Organo-Zirconocene-ate Complexes: Synthesis and Reactivity

Yannick Miquel, Victorio Cadierno, Bruno Donnadieu, Alain Igau,* and Jean-Pierre Majoral*,†

Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 04, France

Received June 7, 1999

A variety of stable five-coordinate organo-zirconocene-ate complexes, **2-4**, **9**, **12a**,**b**, **16**, and **18**, have been prepared and structurally characterized. The reaction process is based on both (i) the nucleophilic attack of tertiary phosphines on acetylenic reagents and (ii) the ability for 16-electron d^0-zirconocene(IV) complexes to coordinate two electron donor ligands. We have shown that the nature of the heteroelement directly bonded to the triple bond of the terminal acetylenic system directs the nucleophilic attack of the phosphine; in all cases only one regioisomer is observed. Surprisingly, the nucleophilic attack of the phosphine in **1a** occurs on propargyl derivatives **19**−**21** to give the corresponding zwitterionic zirconate complexes **22**−**24**. The reactivity of **12a** with HCl and MeI has been tested.

Introduction

Group 4 Cp_2M^{IV} complexes typically exist as four-coordinate, 16-electron, unsaturated species in the ground state.[1,2] However, it is generally accepted that the transition state for many reactions using group 4 d^0 complexes involves a five-coordinate geometry. For example, an α-agostic interaction in chain propagation mechanism studies has been proposed to rationalize the stereospecific polymerization of α-olefins.[3] Moreover group 4 neutral five-coordinate, 18-electron, complexes of the type $[Cp_2MX_2L]$ (X = H, R, halides, etc.; L = neutral $2e^-$ donor) are important species in organic and organometallic reactions.[4] Over the last twenty years, efforts devoted to research in the preparation of cationic group 4 metallocene complexes, due to their properties in olefin polymerization, have been substantial.[5] It appeared that cationic $[Cp_2MXL_2]^+$ and dicationic $[Cp_2ML_3]^{2+}$ five-coordinate complexes are reactive catalysts in olefin polymerization reactions.[6] Despite their potential use as catalytic or stoichiometric reagents,[7] anionic five-coordinate group 4 metal complexes of the general formula $[Cp_2MX_3]^-$ (X = H, R, halides) are rare.[8] It is only very recently that the first group 4 anionic trihydride complex **I** has been structurally characterized by Stephan and co-workers.[9] No general routes for the preparation of stable anionic organo five-coordinate complexes of the type $[Cp_2MR_3]^-$ (R = alkyl, aryl, alkenyl, alkynyl) have been yet described. To the best of our knowledge, except for the complex **II** spectroscopically identified by Negishi and co-workers,[10] group 4 d^0-ate complexes $[Cp_2MR_3]^-$ in which all atoms directly linked to the Zr center are carbon atoms appear to be extremely unstable, and therefore their chemistry remains largely unexplored. Herein we report the extension of the synthesis of stable 18-electron zirconate complexes[11] using both (i) the Lewis acid character of 16-electron coordinatively unsaturated zirconium(IV) complexes and (ii) the regioselective nucleophilic attack of a tertiary phosphine at sp-carbon atoms of acetylenic systems. We also comment on the X-ray crystal structures obtained for the zwitterionic complexes **3** and **12a**.

Results and Discussion

Using both the nucleophilic properties of tertiary phosphines and the ability of 16-electron d^0-zirconocene

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† E-mail: majoral@lcc-toulouse.fr.

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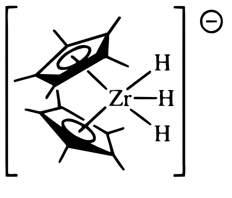
10.1021/om990436r CCC: $19.00
Publication on Web 12/09/1999



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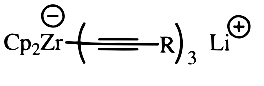

$[Cp_2Zr(-C\equiv C-R)_3]^{-} Li^{+}$

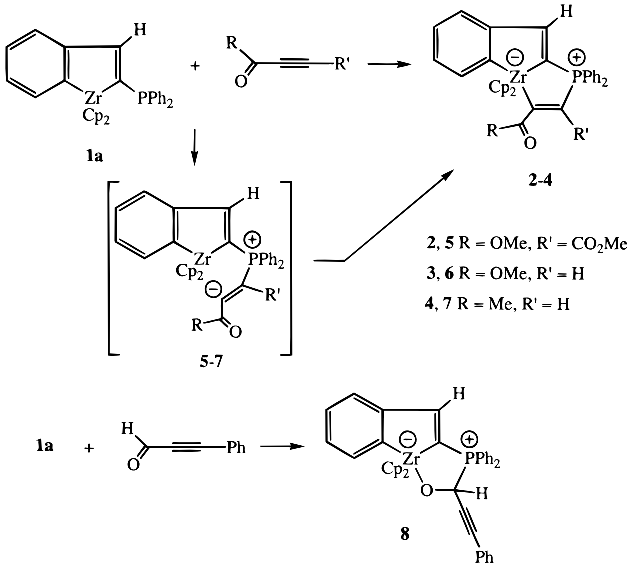
II

complexes to coordinate two electron donor ligands, we recently prepared and structurally characterized the first stable zirconocene-ate complexes **2** and **3** from treatment at room temperature of 2-phosphino-1-zirconaindene **1a**[12] with 1 equiv of alkyne reagent, namely, dimethyl acetylenedicarboxylate (DMAD) and methyl propiolate (Scheme 1).[11] Extension of this reaction to 3-butyn-2-one, H−C≡C−C(O)Me, gave the corresponding zwitterionic complex **4** in quantitative yield (Scheme 1). The ^{31}P NMR chemical shift at 39.8 ppm is in accord with a four-coordinate phosphorus derivative. In addition to the signal corresponding to the η^5-cyclopentadienyl ligands, the ^{1}H NMR spectrum revealed the presence of the proton of the five-membered ring of the indene moiety [doublet at 7.92 ppm with $J_{HP} = 29.3$ Hz]. The deshielded chemical shifts at 194.9 and 236.2 ppm observed in ^{13}C NMR are indicative of the lateral Zr−C bonds (Table 1). In marked contrast, the signal of the central sp^2-carbon atom linked to zirconium and phosphorus is shifted to high field with a low carbon−phosphorus coupling constant [δ 158.4 ($J_{CP} = 2.9$ Hz) ppm; to be compared with δ 191.5 ppm and $J_{CP} = 49.0$ Hz for **1a**]. All of these characteristic spectroscopic ^{1}H and ^{13}C NMR data are consistent with a zwitterionic pentavalent structure for the zirconocene complex **4** (Table 1).[11,13,14] It is reasonable to postulate that the first step of the reaction in the preparation of compounds **3** and **4** is the nucleophilic attack of phosphorus(III) on the unsubstituted acetylenic carbon atom with formation of the corresponding transient zwitterions **6** and **7**. In the second step an intramolecular cyclization of the carbanionic center of the betaïne species **6** and **7** on the zirconium metal fragment occurs to form stable zirconate products **3** and **4** (Scheme 1). No reaction occurred on **1a** with nonactivated terminal acetylenic systems such as *tert*-butyl-, phenyl-, and trimethylsilyl acetylene. Thus, organo-zirconocene-ate complexes are obtained with **1a** when functional groups linked to the acetylenic moiety provide sufficient activation by conjugation with the carbon−carbon triple bond.

Interestingly the nucleophilic attack of the phosphine unit in **1a** on Ph−C≡C−C(O)H took place selectively at the carbon atom of the aldehyde function to quantitatively give the anionic zirconocene complex **8** after cyclization (Scheme 1).[14]

To expand the scope of the formation of anionic organo-zirconocene-ate complexes, we investigated the reaction of **1a** with heteroacetylene reagents. Indeed, calculations and experimental studies have shown that the regioselectivity of nucleophilic additions of tertiary phosphines on terminal heteroacetylene derivatives depends on the nature of the heteroatom directly bonded to the unsaturated system (Chart 1).[15] In a first approach an acetylenic system directly substituted with a first-row element as the terminal ethynyl ether EtO−C≡C−H was reacted with **1a** in toluene at room temperature. After 5 h complex **9** was isolated in 85% yield and fully characterized (Scheme 2). As for the other zirconate complexes, ^{1}H and ^{13}C NMR assignments were unambiguously confirmed by inverse gradient δ^1H−δ^{13}C{^{13}C,^{31}P} HMQC and ^{31}P−^{1}H INEPT NMR experiments. Thus, the proton of the five-membered ring of the indene moiety appeared in the expected region at 7.99 ppm with $J_{HP} = 28.8$ Hz. In ^{13}C NMR, the deshielded chemical shift at 194.3 is typical for Zr−C$_1$-sp^2 aromatic carbon atom (Table 1). As previously observed for the organo-zirconocene-ate complexes **2**,[11] **3**,[11] and **4**, the chemical shift of the central carbon atom linked to zirconium is shifted to high field with a low carbon−phosphorus coupling constant [δ 154.2 ppm, $J_{CP} = 17.6$ Hz]. Note that the displacement of the lateral Zr−C$_{10}$H carbon atom at 167.1 ppm [compared to δ Zr−C$_{10}$ in **2**,[11] **3**,[11] and **4**: 220−240 ppm, Table 1] is due to the β-shielding effect of the methoxy group.[16] The regioselective formation of **9** is in accord with the nucleophilic attack of the phosphine moiety in **1a** on the acetylenic carbon atom linked to the methoxy group to form the intermediate **10**, which gives after cyclization complex **9** (Scheme 2).

Scheme 1. Addition of Acetylenic Systems on 1a



In a second approach, an acetylenic system directly substituted with a second-row element as the phosphorus atom was added on the phosphino−zirconaindene **1a**. At room temperature in toluene, diphenylphosphino acetylene **11a** did not react with **1a**; however complex **12a** was formed in quantitative yield as only one regioisomer under refluxing conditions after 16 h (Scheme

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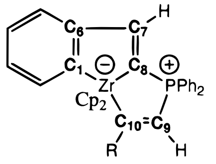
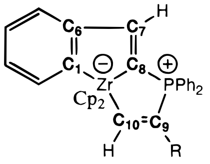
Table 1. Selected NMR Spectroscopic Data for Anionic Zirconocene Complexes 3, 4, 9, 12a, 12b, and 24−26 Prepared from Terminal Acetylenic and Propargylic Systems[a]

		^{31}P	C_1	C_6	C_7	C_8	C_9	C_{10}
1a		6.9	184.9	165.7	142.7 (130.0)	191.5 (49.0)		
3	R = CO_2Me	33.4	194.4 (5.6)	157.9 (31.5)	170.4	156.9 (7.3)	122.8 (118.6)	222.3 (51.6)
4	R = COMe	39.8	194.9 (5.6)	158.3 (37.0)	170.7	158.4 (2.9)	118.6 (118.4)	236.2 (47.2)
9	R = OEt	29.3	194.3 (4.5)	156.9 (32.8)	170.6	154.2 (17.6)	142.2 (160.5)	167.1 (70.1)
12a	R = PPh_2	34.5, 8.7 (43.3)	195.6 (6.1)	158.2 (31.3)	170.9	158.5 (8.8, 2.4)	134.5 (105.6, 9.4)	235.2 (106.3, 49.5)
12b	R = PEt_2	38.9, −6.2 (44.9)	194.4 (5.8)	157.7 (29.7)	166.6 (1.0)	157.2 (11.2, 1.0)	134.5 (105.6, 9.4)	239.6 (97.6, 43.2)
22	R = CH_2OMe	41.1	193.7 (4.8)	158.6 (31.7)	169.3 (1.4)	160.8 (12.1)	132.9 (107.1)	225.4 (56.0)
23	R = CH_2OCH_2CCH	41.3	193.6 (4.7)	158.5 (31.8)	169.4 (1.6)	160.5 (12.4)	132.1 (111.9)	227.1 (55.9)
24	R = CH_2NMe_2	37.6	192.2 (4.8)	157.0 (31.5)	168.1 (1.3)	159.8 (12.9)	131.1 (106.8)	221.1 (56.7)

[a] Chemical shifts in ppm, couplings (between parentheses) in Hz. The numbering system is as follows:

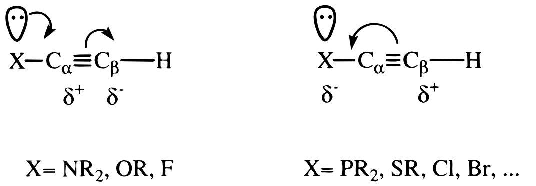


3,4, 12a, 12b

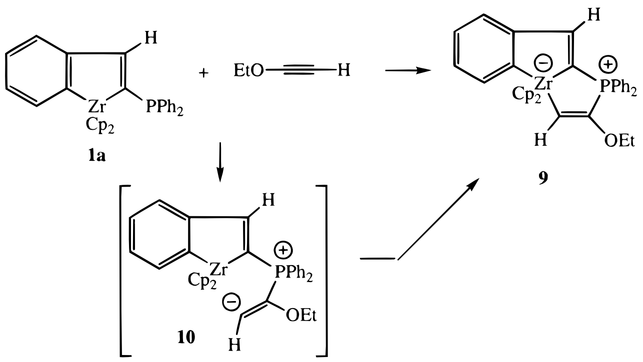


9, 22-24

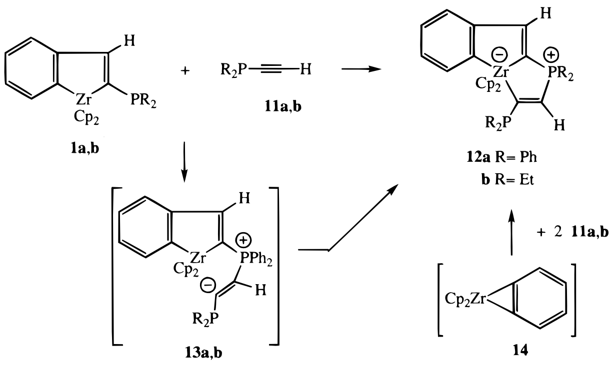
Chart 1



Scheme 2. Addition of a First-Row Heteroelement Substituted Terminal Acetylenic System on 1a



Scheme 3. Addition of Phosphorus Terminal Acetylenic Phosphines 11a,b on 1a,b



3). **12a** was also conveniently prepared starting from zirconabenzyne **14**,[17] generated in situ at 80 °C, and 2 equiv of the corresponding alkynylphosphine **11a**. ^{31}P, ^{1}H, and ^{13}C NMR data of **12a** exhibit the same characteristic features as for the zirconate complexes **2**,[11] **3**,[11] and **4** (Table 1). The ^{1}H NMR spectrum exhibits (besides the signals corresponding to the protons of the aromatic rings) one doublet at δ 7.91 (J_{HP} = 20.0 Hz) and a doublet of doublet at 7.16 (J_{HP} = 43.8 and 19.5 Hz) ppm assigned respectively to the vinylic protons $=C_7H$ and $=C_9H$; Cp groups' resonances appear as one singlet at δ 5.58 ppm. ^{13}C NMR indicates that the carbon atoms coming from the starting phosphino alkynyl moiety are coupled with both phosphorus atoms of the complex: two doublets of doublets are detected at 134.5 (J_{CP} = 105.6 and 9.4 Hz) and 235.2 (J_{CP} = 106.3 and 49.5 Hz) ppm. The marked deshielded chemical shift observed for the latter carbon strongly suggests that this carbon is directly linked to the zirconium atom and is in full agreement with those observed for zirconate **2**,[11] **3**,[11] and **4** (Table 1). The doublet observed at 195.6 (J_{CP} = 6.1 Hz) ppm is typical for the $Zr-C_1$-sp^2 aromatic carbon atom of the zirconaindene framework. Interestingly, the central carbon atom directly linked to the zirconium fragment exhibits the characteristic shielded chemical shift (δ 158.5 ppm) and appears as a doublet of doublets with, as observed for the other zirconate complexes, low J_{CP} coupling constants (8.8 and 2.4 Hz). Under the same experimental conditions the zirconocene-ate complex **12b** was obtained as one regioisomer and displays the same ^{31}P, ^{1}H, and ^{13}C NMR features as for **12a** (Scheme 3, Table 1). Thus transient formation of intermediate **13a**,**b**, from the nucleophilic attack of **1a** on terminal heteroacetylenes **11a**,**b**, may be envisaged in the formation of **12a**,**b**. With the phosphine sulfide acetylene derivative $Ph_2P(S)-C\equiv CH$, **15**, the corresponding anionic zirconocene complex **16** was formed along with phosphorus side products due to the thermal instability of **15** under the reaction conditions used to allow the reaction to go to completion (Scheme 4). The same product **16** was quantitatively obtained by another route via addition of elemental sulfur S_8 on **12a** (Scheme 4). Interestingly, the nucleophilic attachment of the phos-

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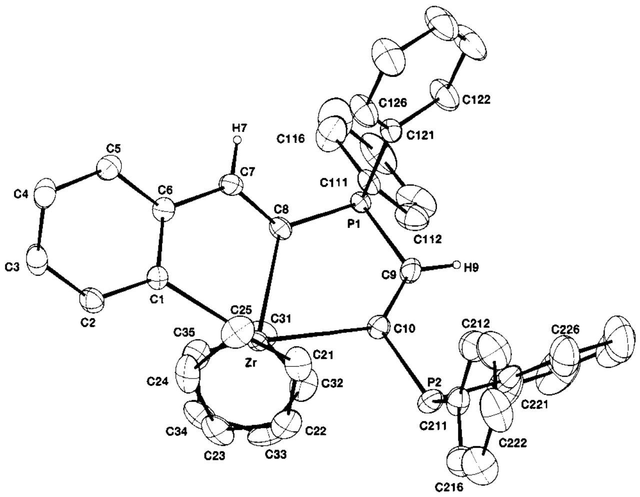
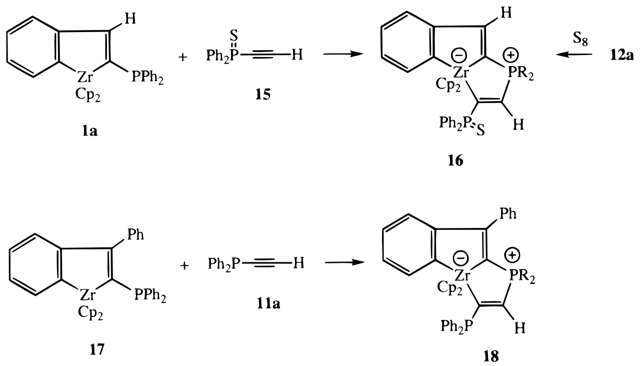


Figure 1. X-ray crystal structure of **12a** (CAMERON drawing with thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg) are given in Table 3.

Scheme 4. Preparation of Zirconates 16 and 18



phine unit Ph_2P in **1a** does not depend on the valence number of the phosphorus atom in conjugation with the triple bond of the heteroacetylene reagents **11a**,**b** and **15**. Moreover addition of **11a** on the new phosphino zirconaindene **17**[18] gave the expected zirconocene-ate complex **18** in almost quantitative yield (Scheme 4). Thus, we have illustrated that in the reaction sequence leading to the synthesis of the zirconate complexes **9**, **12a,b**, **16**, and **18** an oxygen atom in conjugation with the triple bond of a terminal acetylenic system acts as a donor, while a heteroatom below the first-row elements, such as a phosphorus atom, acts as an acceptor.

Table 2. Crystallographic Parameters for 12a

chem formula	$C_{44}H_{36}P_2Zr$, C_4H_8O
fw	791.05
cryst syst	triclinic
space group	$P\bar{1}$ (2)
Z	2
T, K	180
a, Å	10.020(2)
b, Å	12.213(2)
c, Å	19.022(3)
α, deg	93.37(2)
β, deg	90.08(2)
γ, deg	114.16(2)
V, Å^3	2119.40
D_{calc}, g cm^{-3}	1.24
μ(Mo Kα), cm^{-1}	3.60
2θ range, deg	2.9-48.4
no. of unique data	6125
R_{av}	0.07
no. of reflns used	5482 [$I > \sigma(I)$]
no. of params varied	523
S	0.96
$R(F_o)$	0.058
$R_w(F_o)$	0.069
$(\Delta/\rho)_{\max}$	0.99
$(\Delta/\rho)_{\min}$, e Å^{-3}	−0.76

Table 3. Selected Bond Distances (Å) and Angles (deg) for 12a

	Distances		
Zr−C(1)	2.400(3)	Zr−C(8)	2.362(3)
Zr−C(10)	2.465(3)	P(1)−C(8)	1.749(3)
P(1)−C(9)	1.766(3)	C(1)−C(6)	1.410(4)
C(7)−C(8)	1.344(4)	C(9)−C(10)	1.340(4)
	Angles		
C(1)−Zr−C(10)	140.8(1)	C(8)−Zr−C(10)	72.4(1)
Zr−C(1)−C(6)	117.8(2)	Zr−C(8)−C(7)	120.2(2)
Zr−C(10)−C(9)	124.9(2)	Zr−C(8)−P(1)	119.55(15)
C(8)−P(1)−C(9)	104.59(14)	C(6)−C(7)−C(8)	117.9(3)

It is important to note that no reaction occurs upon addition of nonterminal phosphino acetylenic sytems such as $Ph_2P-C\equiv C-R$ (R = Ph, $SiMe_3$) with **1a** and **17**. To confirm the spectroscopic assignments and to have a better insight into the structure of the organo-ate complexes prepared, X-ray diffraction studies were carried out on **3**[11] and **12a** (Figure 1, Table 2). The zirconium atom in both structures is coordinated to two η^5-cyclopentadienyl ligands and three different sp^2-carbon atoms arranged around the central metal in a pseudo-tetrahedral geometry.[19] Features at the Cp_2Zr unit are typical for bent metallocene complexes.[20] The Zr−C(Cp) distances are in a narrow range between 2.499(3) and 2.561(3) Å, and the bond angle between the centroids of the Cp rings D(1)−Zr−D(2) are 132.4° and 130.8° for **3**[11] and **12a**, respectively. The remaining bonding sites around the zirconium atom are used to coordinate three sp^2-carbon atoms. All the atoms [from C(1) to C(10), and Zr] involved in the composition of the metallapolycycle lie in the same plane that bisects the Cp_2Zr fragment, with a maximum deviation from the ideal plane for the phosphorus atom P(1) of 0.35 (**3**) and 0.25 (**12a**) Å. The geometry around the C-sp^2 carbons linked to zirconium is not distorted to any great extent. P(1) is tetrahedrally coordinated with angles near the ideal tetrahedral angle. The bond lengths and angles around P(1) are consistent with a four-coordinate cyclic phosphonium salt.[21] The large value of the [C(1)−Zr−C(10)] angle and the extraordinarily long external Zr−C bond lengths represent the truly outstanding structural features in **3**[11] and **12a** (Table 3). The unprecedented large ligand angle respectively of 140.22(2)° and 140.8(1)° is due to the necessity of achieving good orbital overlap with the single acceptor 1a$_1$ orbital available in **1a** for bonding of a fifth ligand, as well as the resolving of the steric requirements of the ligands. The

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[20] For a comparison with typical examples of other d^0-configurated early transition metal bent metallocene complexes see ref 1 and: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974, and references therein.

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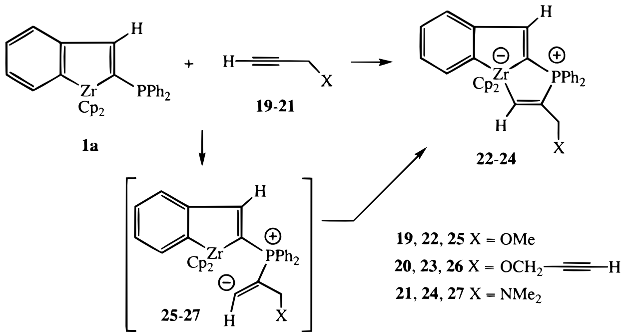
Zr−C-sp^2 external bond lengths in **3** and **12a** are halfway from typical neutral Cp$_2$Zr(IV)−C σ-bonds and Cp$_2$Zr(IV)−olefin π-type interaction.[22] Compared to bis-(η^5-cyclopentadienyl)zirconacyclopentadiene(IV) and bis-(η^5-cyclopentadienyl)zirconaindene(IV) units, the three independent Zr−C σ-bonds in **3** and **12a** are longer.[1,20] These elongations for the Zr−C-sp^2 bonds in **3** and **12a** are consistent with the results from Lauher and Hoffmann's work,[23] which predicts that filling of the metal-based LUMO (through the sp^2-carbon atom coming from the acetylenic substrate in this case) will result in lengthening of the remaining metal−ligand bonds compared to those in 16-electron [Cp$_2$MX$_2$] complexes. It illustrates the effect of the zirconium atom achieving an 18-electron configuration, which suggests that the metal−ligand bonding situation in **3** and **12a** is best described as consisting of three different σ-bonds. Moreover the lengthening of the Zr−C-sp^2 bonds is also possibly the result of the lower Lewis acidity of the anionic metal center in this zwitterionic five-coordinate metallocenes. Interestingly the Zr−C-sp^2 bond in the central position is shorter than the ones in the outside. This trend deviates significantly from the theoretical calculations on the [Cp$_2$TiH$_3$]$^-$ model[23] and from X-ray analysis on neutral five-coordinate zirconocene complexes of the type [Cp$_2$ZrR$_2$L].[24] The Zr−C(7) and Zr−C(9) distances are about 0.8 Å (or 32%) longer than the Zr−C(η^5) bond [average Zr−C(η^5) bond length: 2.526 (3) Å] to carbon atoms of the Cp rings; this suggests that no π-interaction is involved between the different carbon atoms of the cycles and the metal in the structures **3** and **12a**. Both the carbonyl and methoxy oxygen atoms of the carboxylic function in **3**[11] and the phosphine moiety in **12a** are turned away from the zirconium center. The final result is an 18-electron zirconate complexes since all the three sp^2-carbon atoms linked to zirconium are two-electron donors and the two η^5-C$_5$H$_5$ rings each provide six electrons to the d^0 Zr(IV) center.

Scheme 5. Addition of First-Row Heteroelements Substituted Terminal Propargylic Systems 19−21 on 1a



Coupling reactions involving zirconocene complexes and propargylic systems lead generally to mixtures of products with low yields.[25] Even though these reagents are apparently not the ideal compounds incorporating an acetylenic function to react with group 4 complexes to give regioselective reactions, we decided to test their reactivity toward **1a**. No reaction was observed with propargyl reagents H−C≡C−CH$_2$R (R = Ph, SiMe$_3$) on **1a**. However, addition of heterosubstituted propargyl derivatives **19**−**21** to **1a** gave regioselectively and quantitatively the anionic zirconocene complexes **22**−**24** (Scheme 5). Mass spectra for **22**−**24** are in accord with a 1:1 [**1a**·propargyl reagent] adduct. ^{31}P, ^{1}H, and ^{13}C NMR exhibit the characteristic features as for the zirconate complexes described previously (Table 1). Assignments for ^{1}H and ^{13}C chemical shifts for **22**−**24** were also unambiguously confirmed by inverse gradient δ^{1}H−δ^{13}C{^{13}C,^{31}P} HMQC and ^{31}P−^{1}H INEPT NMR experiments. Information can be retrieved from ^{13}C NMR data (Table 1) since we observed the classical deshielded displacements of the lateral Zr−C carbon atoms [δ Zr−C$_1$ 192−194 and Zr−C$_{10}$H 221−227 ppm] and the shielded chemical shift for the central Zr−C$_8$ carbon atom [δ 159−161 ppm] typical for these anionic organo-zirconocene complexes. Up to now, it is difficult to rationalize the synthesis of **22**−**24** by the transient formation of **25**−**27** since to the best of our knowledge no nucleophilic attacks of tertiary phosphines on propargyl derivatives have been reported in the literature.[26] Nevertheless, it is interesting to note that, in the final products **22**−**24**, the orientation of the acetylenic function of the propargyl reagent followed the same orientation observed in the formation of zirconate **9**. All of these alkyne reagents, namely the ethynyl ethoxy acetylene and the propargyl systems **19**−**21**, bear a first-row element as the heterosubstituted atom.

Organometallocene group 4 complexes [Cp$_2$MR$_1$R$_2$]^{IV} are useful intermediates in organic synthesis since various procedures for the cleavage of carbon−zirconium bonds using electrophiles have been reported.[27] Up to now the reactivity of zirconate complexes of the type [Cp$_2$MR$_1$R$_2$R$_3$]$^-$ with electrophiles has not been investigated. Thus in a first approach we have tested the chemical behavior of **12a** with H$^+$. The isolated final products result from the cleavage of the three Zr−C bonds to give the divinyl phosphonium compound **28** and an another isomer in approximately a 95:5 ratio (Scheme 6). Addition of MeI as electrophile reagent on **12a** showed the quantitative formation of the stable bis-phosphonium zirconate compound **29** (Scheme 6). Even in the presence of an excess (8 equiv) of MeI no electrophilic cleavage of one of the three Zr−C bonds in **12a** was observed.

In summary, we have prepared and isolated via formal [3+2] cycloaddition reactions a large variety of

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(22) For Zr−C σ/π-bonding situation see: Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W. *J. Am. Chem. Soc.* **1980**, *102*, 6346−48. Erker, G.; Engel, K. *Organometallics* **1984**, *3*, 128.

(23) Laugher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

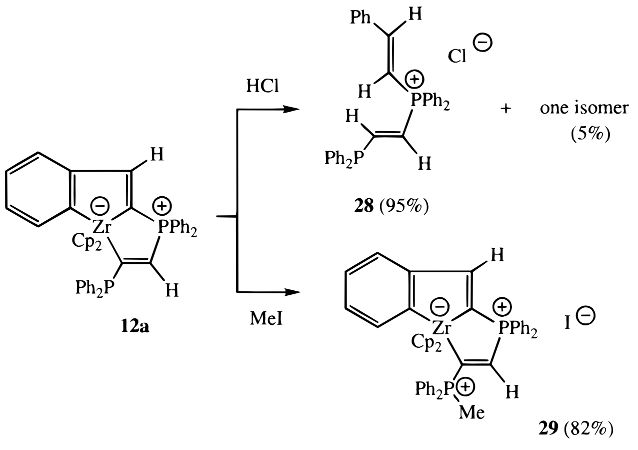
(24) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 373. Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burkalov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193.

(25) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870.

(26) An intramolecular nucleophilic attack of phosphorus(III) on an acetylenic carbon atom in the rearrangement of *N*-propargylamino-phosphines has been observed: Angelov, C. M.; Dahl, O. *Tetrahedron Lett.* **1983**, *24*, 1643.

(27) Tetrahedron Symposia in print No. 57, Guest Ed. Negishi E.: *Tetrahedron* **1995**, *51*, 4255. For reviews see for example: Annby, U.; Karlsson, S. *Acta Chem. Scand.* **1993**, *47*, 425. Labinger, J. A. In *Comprehensive Organic Chemistry*; Fleming, I., Ed.; Pergamon Press: New York, 1991; Vol. 3, Chapter 3, p 667. Negishi, E. *Ibid.* Chapter 5, Paquette L. A., Ed. Erker, G.; Aulbach, M.; Mena, M.; Pfaff, R.; Sosna, F. *Chem. Scr.* **1989**, *29*, 451. Negishi, E. *Chem. Scr.* **1989**, *29*, 457. Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

Scheme 6. Reactivity of the Anionic Five-Coordinate Zirconocene Complex 12a



anionic five-coordinate zirconocene-ate complexes as the result of the nucleophilic attack of the phosphine unit in **1a**,**b** on activated acetylenic systems. We have illustrated with phosphino−zirconocene systems **1a**,**b** that the nucleophilic reaction of the phosphine(III) moiety follows the proposed rule that a heteroelement in conjugation with the triple bond of a terminal acetylene orientates nucleophilic attack on C_α for first-row elements and on C_β for elements of the second period (Chart 1). X-ray crystallography studies on complexes **3** and **12a** showed that the large value of the [C(1)−Zr−C(10)] angle and the very long external Zr−C bond lengths are typical features of five-coordinate zirconate complexes. General preparation of stable zirconate species via similar or different reaction pathways and the studies of the chemical properties and reactivity of these species are currently under active investigation.

Experimental Section

All manipulations were performed under an argon atmosphere, either on a vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, toluene, benzene, diethyl ether), lithium aluminum hydride (pentane, *n*-hexanes), or CaH_2 (CH_2Cl_2, $CHCl_3$). Deuterated NMR solvents were treated with $LiAlH_4$ (C_6D_6, THF-d_8) and CaH_2 (CD_2Cl_2), distilled, and stored under argon. Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker MSL-400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Chemical shifts are given downfield relative to Me_4Si (^1H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P), respectively. ^{13}C NMR assignments were confirmed by inverse gradient $\delta^1H{-}\delta^{13}C\{^{13}C,^{31}P\}$ HMQC and $^{31}P{-}^1H$ INEPT NMR experiments. For the NMR data of the compounds **4**, **8**, **9**, **12a**,**b**, **16**, **18**, **22-24**, and **29** the numbering system is as given in Table 1. Elemental and mass spectrum analyses obtained on a Nermag R10-10H were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Cp_2ZrPh_2,[17] $H{-}C{\equiv}C{-}PPh_2$,[28] $Ph{-}C{\equiv}C{-}PPh_2$,[28] and $H{-}C{\equiv}C{-}PEt_2$[28] were prepared according to literature procedures. $H{-}C{\equiv}C{-}C(O)Me$, $Ph\text{-}C{\equiv}C{-}C(O)H$, $H{-}C{\equiv}C{-}OEt$, $H{-}C{\equiv}C{-}CH_2OMe$, $(H{-}C{\equiv}C{-}CH_2)_2O$, and $H{-}C{\equiv}C{-}CH_2NMe_2$ were purchased from Aldrich and used without further purification.

Typical Procedure for the Preparation of Zirconates 4, 8, and 9. To a solution of **1a** (0.249 g, 0.49 mmol) in toluene (6 mL) at room temperature was added a stoichiometric amount of the corresponding reagent ($H{-}C{\equiv}C{-}C(O)Me$ (**4**), $Ph{-}C{\equiv}C{-}C(O)H$ (**8**), $H{-}C{\equiv}C{-}OEt$ (**9**)). The resulting solution was stirred for 5 h, leading to the formation of zirconate complexes **4**, **8**, and **9**, respectively, in almost quantitative yield as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The solvent was evaporated to dryness. The brown solid residue was dissolved in a minimum of THF (≈1−2 mL) and then poured into pentane (20 mL). The resulting precipitate was washed twice with 20 mL of pentane and vaccum-dried, leading to **4** (brown powder, 73%), **8** (brown powder, 55%), and **9** (brown powder, 85%), respectively.

Data for 4: ^1H (C_6D_6, 200.1 MHz) δ 2.31 (s, 3H, CH_3), 5.65 (s, 10H, CH_{Cp}), 6.67 (d, J_{HP} = 40.6 Hz, 1H, C_9H), 7.64−7.22 (m, 14H, Ph), 7.92 (d, J_{HP} = 29.3 Hz, 1H, C_7H) ppm; $^{13}C\{^1H\}$ (C_6D_6, 62.9 MHz) δ 31.4 (s, CH_3), 107.3 (s, CH_{Cp}), 123.1 (d, $^3J_{CP}$ = 1.0 Hz, *m*-Ph), 125.6, 126.1 (s, CH_{arom}), 130.4 (d, $^1J_{CP}$ = 68.6 Hz, *i*-Ph), 130.5 (d, $^2J_{CP}$ = 10.6 Hz, *o*-Ph), 133.1 (d, $^3J_{CP}$ = 2.6 Hz, *m*-Ph), 133.4 (d, $^2J_{CP}$ = 9.0 Hz, *o*-Ph), 142.9 (s, CH_{arom}), 212.8 (d, J_{CP} = 35.9 Hz,*C*OMe) ppm. Anal. Calcd for $C_{34}H_{29}O_2PZr$: C, 70.92; H, 5.07. Found: C, 70.67; H, 4.76.

Data for 8: $^{31}P\{^1H\}$ (CD_2Cl_2, 32.4 MHz) 27.8 (s) ppm; ^1H (CD_2Cl_2, 200.1 MHz) δ 5.79 (d, $^3J_{HP}$ = 5.9 Hz, 1H, CHO), 5.87 (s, 10H, CH_{Cp}), 6.91−8.01 (m, 19H, Ph), 8.25 (d, J_{HP} = 26.2 Hz, 1H, C_7H) ppm; $^{13}C\{^1H\}$ (CD_2Cl_2, 62.9 MHz) δ 73.0 (d, J_{CP} = 76.7 Hz, PCOH), 86.6 (d, J_{CP} = 9.6 Hz, *C*CPh), 87.7 (s, C*C*Ph), 107.5, 108.7 (s, CH_{Cp}), 121.5, 124.5, 125.2, 127.7, 128.0, 139.3 (s, CH_{arom}), 121.9 (d, J_{CP} = 3.1 Hz, *i*-CCPh), 123.7 (d, J_{CP} = 68.0 Hz, *i*-PPh), 124.1 (d, J_{CP} = 57.6 Hz, *i*-PPh), 128.1 (d, $^2J_{CP}$ = 10.7 Hz, *o*-Ph), 128.7 (d, $^2J_{CP}$ = 10.4 Hz, *o*-Ph), 130.8 (d, $^3J_{CP}$ = 2.8 Hz, *m*-Ph), 131.8 (d, $^3J_{CP}$ = 2.7 Hz, *m*-Ph), 132.0 (d, $^3J_{CP}$ = 2.6 Hz, *m*-Ph), 132.7 (d, $^2J_{CP}$ = 7.8 Hz, *o*-Ph), 133.1 (d, $^2J_{CP}$ = 7.9 Hz, *o*-Ph) ppm. Anal. Calcd for $C_{39}H_{31}OPZr$: C, 73.44; H, 4.90. Found: C, 73.17; H, 4.84. MS (DCI/CH_4): *m*/*z* 637 [$M^+ + 1$].

Data for 9: ^1H (THF-d_8, 200.1 MHz) δ 1.19 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 3.93 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2), 5.51 (s, 10H, CH_{Cp}) 7.07 (d, J_{HP} = 48.6 Hz, 1H, $C_{10}H$), 7.68−6.76 (m, 14H, Ph), 7.99 (d, J_{HP} = 28.8 Hz, 1H, C_7H) ppm; $^{13}C\{^1H\}$ (THF-d_8, 62.9 MHz) δ 57.9 (s, CH_3), 76.7 (d, J_{CP} = 25.3 Hz, OCH_2), 106.6 (s, CH_{Cp}), 123.1, 125.4, 125.6, 127.5, 128.2, 128.4 (s, CH_{arom}), 130.4 (d, $^1J_{CP}$ = 66.9 Hz, *i*-Ph), 130.0 (d, $^2J_{CP}$ = 10.6 Hz, *o*-Ph), 132.7 (d, $^3J_{CP}$ = 2.2 Hz, *m*-Ph), 133.9 (d, $^2J_{CP}$ = 9.4 Hz, *o*-Ph), 139.9, 141.8 (s, CH_{arom}) ppm. Anal. Calcd for $C_{34}H_{31}OPZr$: C, 70.67; H, 5.41. Found: C, 70.30; H, 5.50. MS (DCI/CH_4): *m*/*z* 577 [$M^+ + 1$].

Typical Procedure for the Preparation of Zirconates 12a,b. To a solution of **1a** (0.254 g, 0.50 mmol) in toluene (6 mL) at room temperature was added a stoichiometric amount of the phosphinoacetylene $H{-}C{\equiv}C{-}PPh_2$ (0.105 g, 0.50 mmol). The resulting solution was heated under reflux for 16 h. Then the solvent was removed under vacuum. Residue was taken up in THF (2 mL) and poured into pentane (40 mL). The precipitate was collected by filtration, washed with additional pentane (2 × 5 mL), and dried under vacuum to give **12a** (brown powder, 55%). In an identical procedure, **12b** (brown powder, 62%) was obtained from **1b** (0.320 g, 0.78 mmol) and 1 equiv of $H{-}C{\equiv}C{-}PEt_2$.

Alternative Route to 12a,b. A Schlenk flask was charged with Cp_2ZrPh_2 (0.188 g, 0.50 mmol), $H{-}C{\equiv}C{-}PR_2$ (1.00 mmol), toluene (6 mL), and a stir bar. The mixture was heated under reflux for 16 h and worked up in a manner analogous to the preceding procedure to give **12a,b** in respectively 85 and 78% isolated yield.

Data for 12a: $^{31}P\{^1H\}$ (THF-d_8, 32.4 MHz) 34.5 (d, J_{PP} = 43.3 Hz, Ph_2P^+), 8.7 (d, J_{PP} = 43.3 Hz, Ph_2P) ppm; ^1H (THF-d_8, 200.1 MHz) δ 5.58 (s, 10H, CH_{Cp}), 6.76−7.54 (m, 24H, Ph), 7.16 (dd, J_{HP} = 43.8 Hz, J_{HP} = 19.5 Hz, 1H, C_9H), 7.91 (d, J_{HP} = 20.0 Hz, 1H, C_7H) ppm; $^{13}C\{^1H\}$ (THF-d_8, 62.9 MHz) δ 107.6

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(28) Charier, C.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, *167*, 1002.

(d, $J_{\mathrm{CP}} = 3.4$ Hz, $\mathrm{CH_{Cp}}$), 122.9, 125.5, 126.0, 129.2, 142.7 (s, $\mathrm{CH_{arom}}$), 129.4 (d, $^{2}J_{\mathrm{CP}} = 10.4$ Hz, *o*-Ph), 130.4 (d, $^{2}J_{\mathrm{CP}} = 10.4$ Hz, *o*-Ph), 132.9 (d, $^{3}J_{\mathrm{CP}} = 2.2$ Hz, *m*-Ph), 133.2 (d, $^{2}J_{\mathrm{CP}} = 8.6$ Hz, *o*-Ph), 135.2 (d, $^{2}J_{\mathrm{CP}} = 19.0$ Hz, *o*-Ph), 142.0 (d, $J_{\mathrm{CP}} = 25.4$ Hz, *i*-Ph), 161.5 (d, $J_{\mathrm{CP}} = 28.3$ Hz, $\mathrm{PC}\mathit{C}\mathrm{O_2Me}$) ppm. Anal. Calcd for $\mathrm{C_{44}H_{25}P_2Zr}$: C, 73.61; H, 5.05. Found: C, 73.37; H, 4.82. MS (DCI/$\mathrm{NH_3}$): *m*/*z* 717 [$\mathrm{M^+} + 1$].

Data for 12b: $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 32.4 MHz) 38.9 (d, $J_{\mathrm{PP}} = 44.9$ Hz, $\mathrm{Ph_2P}$), −6.2 (d, $J_{\mathrm{PP}} = 44.9$ Hz, $\mathrm{Et_2P}$) ppm; $^{1}\mathrm{H}$ ($\mathrm{C_6D_6}$, 200.1 MHz) δ 0.62−1.81 (m, 10H, Et), 5.88, 5.92 (s, 5H, $\mathrm{CH_{Cp}}$), 6.53 (dd, $J_{\mathrm{HP}} = 45.2$ Hz, $J_{\mathrm{HP}} = 18.6$ Hz, 1H, $\mathrm{C_9H}$), 7.25−7.82 (m, 14H, $\mathrm{CH_{Ar}}$), 7.98 (d, $J_{\mathrm{HP}} = 28.6$ Hz, 1H, $\mathrm{C_7H}$) ppm; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 62.9 MHz) δ 7.3 (d, $J_{\mathrm{CP}} = 3.3$ Hz, $\mathrm{CH_3}$), 11.3 (d, $J_{\mathrm{CP}} = 14.0$ Hz, $\mathrm{CH_3}$), 19.2 (d, $J_{\mathrm{CP}} = 40.5$ Hz, $\mathrm{CH_2}$), 21.4 (d, $J_{\mathrm{CP}} = 22.8$ Hz, $\mathrm{CH_2}$), 107.3 (d, $J_{\mathrm{CP}} = 2.0$ Hz, $\mathrm{CH_{Cp}}$), 112.7 (s, $\mathrm{CH_{Cp}}$), 125.5, 127.9, 130.2, 138.9 (s, $\mathrm{CH_{arom}}$), 129.4 (d, $^{2}J_{\mathrm{CP}} = 10.4$ Hz, *o*-Ph), 130.4 (d, $^{2}J_{\mathrm{CP}} = 10.4$ Hz, *o*-Ph), 132.9 (d, $^{3}J_{\mathrm{CP}} = 2.2$ Hz, *m*-Ph), 133.2 (d, $^{2}J_{\mathrm{CP}} = 8.6$ Hz, *o*-Ph), 135.2 (d, $^{2}J_{\mathrm{CP}} = 19.0$ Hz, *o*-Ph), 142.0 (d, $J_{\mathrm{CP}} = 25.4$ Hz, *i*-Ph) ppm. Anal. Calcd for $\mathrm{C_{36}H_{36}P_2Zr}$: C, 63.96; H, 6.90. Found: C, 63.22; H, 6.72.

Synthesis of Zirconate 16. To a solution of **1a** (0.254 g, 0.50 mmol) in toluene (6 mL) at room temperature was added a stoichiometric amount of the thiophosphinoacetylene $\mathrm{H{-}C{\equiv}C{-}P(S)Ph_2}$. The resulting solution was heated under reflux. After 8 h, as monitored by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy, formation of the zirconate complex **16** as the major reaction product along with other unidentified phosphorus derivatives coming from the thermal decomposition of the thiophosphaacetylene $\mathrm{H{-}C{\equiv}C{-}P(S)Ph_2}$ was observed. Treatment of the resulting reaction mixture did not allow separation of **16** from the side products.

Alternative Route to 16. To a stirred solution of **12a** (0.318 g, 0.40 mmol) in THF (10 mL) was added a stoichiometric amount of sulfur at room temperature. After 2 h, the resulting reaction mixture was poured into 20 mL of pentane. The precipitate was washed respectively with pentane (2 × 5 mL) and toluene (2 × 5 mL) to give **16** as a brown powder in 92% yield. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ (THF-d_8, 32.4 MHz): 59.7 (d, $J_{\mathrm{PP}} = 133.6$ Hz, $\mathrm{Ph_2PS}$), 36.8 (d, $J_{\mathrm{PP}} = 133.6$ Hz, $\mathrm{Ph_2P}$) ppm. $^{1}\mathrm{H}$ (THF-d_8, 200.1 MHz): δ 5.68 (s, 10H, $\mathrm{CH_{Cp}}$), 7.27 (dd, $J_{\mathrm{HP}} = 42.0$ Hz, $J_{\mathrm{HP}} = 38.0$ Hz, 1H, $\mathrm{C_9H}$), 6.74−7.71 (m, 25H, $\mathrm{CH_{Ar}}$), 7.96 (d, $J_{\mathrm{HP}} = 30.4$ Hz, 1H, $\mathrm{C_7H}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ (THF-$\mathrm{D_8}$, 62.9 MHz): δ 108.2 (s, $\mathrm{CH_{Cp}}$) 122.8, 126.2, 129.4, 138.9, 142.1 (s, $\mathrm{CH_{arom}}$), 129.3 (d, $^{2}J_{\mathrm{CP}} = 11.0$ Hz, *o*-Ph), 129.7 (d, $^{1}J_{\mathrm{CP}} = 67.6$ Hz, *i*-Ph), 130.7 (d, $^{2}J_{\mathrm{CP}} = 10.5$ Hz, *o*-Ph), 131.5 (d, $^{3}J_{\mathrm{CP}} = 2.7$ Hz, *m*-Ph), 133.2 (d, $^{2}J_{\mathrm{CP}} = 8.9$ Hz, *o*-Ph), 133.4 (d, $^{2}J_{\mathrm{CP}} = 9.1$ Hz, *o*-Ph), 133.5 (d, $^{3}J_{\mathrm{CP}} = 2.4$ Hz, *m*-Ph), 138.5 (d, $J_{\mathrm{CP}} = 69.8$ Hz, *i*-Ph), 140.6 (dd, $J_{\mathrm{CP}} = 107.0$ Hz, $J_{\mathrm{CP}} = 2.9$ Hz, $\mathrm{C_9H}$), 155.6 (dd, $J_{\mathrm{CP}} = 7.8$ Hz, $J_{\mathrm{CP}} = 1.5$ Hz, $\mathrm{ZrC_8P}$), 157.2 (d, $J_{\mathrm{CP}} = 31.4$ Hz, $\mathrm{C_6}$), 172.0 (s, $\mathrm{C_7H}$), 197.1 (d, $J_{\mathrm{CP}} = 6.8$ Hz, $\mathrm{ZrC_1}$), 221.9 (dd, $J_{\mathrm{CP}} = 54.0$ Hz, $J_{\mathrm{CP}} = 42.0$ Hz, $\mathrm{ZrC_{10}}$) ppm. Anal. Calcd for $\mathrm{C_{44}H_{25}P_2SZr}$: C, 71.52; H, 3.41. Found: C, 71.40; H, 3.32.

Synthesis of Zirconate 18. To a solution of **17** (0.292 g, 0.50 mmol) in toluene (3 mL) at room temperature was added a stoichiometric amount of the phosphinoacetylene $\mathrm{Ph{-}C{\equiv}C{-}PPh_2}$. The resulting solution was heated under reflux for 23 days for the reaction to go to completion to give as the unique product of the reaction **18** as monitored by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. The mixture was worked up in a manner analogous to the preceding procedure for compound **4** to isolate **18** as a brown powder in 70% yield. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ (THF-d_8, 32.4 MHz): 33.5 (d, $J_{\mathrm{PP}} = 41.0$ Hz, $\mathrm{Ph_2P^+}$), 8.4 (d, $J_{\mathrm{PP}} = 41.0$ Hz, $\mathrm{Ph_2P}$) ppm. $^{1}\mathrm{H}$ (THF-d_8, 200.1 MHz): δ 5.68 (s, 10H, $\mathrm{CH_{Cp}}$), 6.20−7.56 (m, 25H, $\mathrm{CH_{Ar}}$), 6.94 (dd, $J_{\mathrm{HP}} = 44.0$ Hz, $J_{\mathrm{HP}} = 19.4$ Hz, 1H, $\mathrm{C_9H}$) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ (THF-d_8, 62.9 MHz): δ 108.1 (d, $J_{\mathrm{CP}} = 3.7$ Hz, $\mathrm{CH_{Cp}}$), 122.6, 125.5, 126.8, 126.9, 128.6, 129.1 (s, $\mathrm{CH_{arom}}$), 129.3 (d, $^{3}J_{\mathrm{CP}} = 5.7$ Hz, *m*-Ph), 129.8 (d, $^{2}J_{\mathrm{CP}} = 10.5$ Hz, *o*-Ph), 130.7 (d, $^{1}J_{\mathrm{CP}} = 66.3$ Hz, *i*-Ph), 132.1 (d, $^{3}J_{\mathrm{CP}} = 2.5$ Hz, *m*-Ph), 133.5 (d, $^{2}J_{\mathrm{CP}} = 9.1$ Hz, *o*-Ph), 135.1 (d, $^{2}J_{\mathrm{CP}} = 18.8$ Hz, *o*-Ph), 138.5 (dd, $J_{\mathrm{CP}} = 107.4$ Hz, $J_{\mathrm{CP}} = 9.5$ Hz, $\mathrm{C_9H}$), 142.3 (d, $^{1}J_{\mathrm{CP}} = 27.2$ Hz, *i*-Ph), 144.3 (d, $^{1}J_{\mathrm{CP}} = 15.8$ Hz, *i*-Ph), 154.4 (d, $J_{\mathrm{CP}} = 1.8$ Hz, $\mathrm{ZrC_8P}$), 159.7 (d, $J_{\mathrm{CP}} = 31.4$ Hz, $\mathrm{C_6}$), 181.7 (s, $\mathrm{C_7}$), 195.1 (d, $J_{\mathrm{CP}} = 6.8$ Hz, $\mathrm{ZrC_1}$), 228.3 (dd, $J_{\mathrm{CP}} = 45.8$ Hz, $J_{\mathrm{CP}} = 104.8$ Hz, $\mathrm{ZrC_{10}}$) ppm. Anal. Calcd for $\mathrm{C_{50}H_{40}P_2Zr}$: C, 75.63; H, 5.08. Found: C, 75.39; H, 5.15.

Typical Procedure for the Preparation of Zirconates 22−24. To a solution of **1a** (0.250 g, 0.49 mmol) in toluene (6 mL) at room temperature was added a stoichiometric amount of the propargyl reagent ($\mathrm{H{-}C{\equiv}C{-}CH_2OMe}$ (**19**), $\mathrm{(H{-}C{\equiv}C{-}CH_2)_2O}$ (**20**), and $\mathrm{H{-}C{\equiv}C{-}CH_2NMe_2}$ (**21**)). The resulting solution was heated under reflux for 16 h (**22**), 3 days (**23**), and 10 days (**24**), respectively. The reaction mixture was then allowed to cool to room temperature, and the solvent was removed under vacuum. The residue taken up in THF (2 mL) was poured into pentane (40 mL). The precipitate was collected by filtration, washed with pentane (2 × 10 mL), and dried under vacuum to give respectively **22** (brown powder, 75%), **23** (brown powder, 56%), and **24** (brown powder, 72%).

Data for 22: $^{1}\mathrm{H}$ (THF-d_8, 200.1 MHz) δ 3.04 (s, 3H, $\mathrm{OCH_3}$), 3.99 (d, $J_{\mathrm{HP}} = 10.9$ Hz, 2H, $\mathrm{CH_2O}$), 5.49 (s, 10H, $\mathrm{CH_{Cp}}$), 6.75−7.70 (m, 14H, Ph), 7.89 (d, $J_{\mathrm{HP}} = 28.5$ Hz, 1H, $\mathrm{C_7H}$), 9.21 (d, $J_{\mathrm{HP}} = 60.5$ Hz, 1H, $\mathrm{ZrC_{10}H}$) ppm; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ (THF-d_8, 62.9 MHz) δ 57.9 (s, $\mathrm{OCH_3}$), 76.7 (d, $J_{\mathrm{CP}} = 25.3$ Hz, $\mathrm{CH_2O}$), 106.6 (s, $\mathrm{CH_{Cp}}$), 123.1, 125.4, 125.6, 127.5, 128.2, 128.4, 139.9, 141.8 (s, $\mathrm{CH_{arom}}$), 130.0 (d, $^{2}J_{\mathrm{CP}} = 10.6$ Hz, *o*-Ph), 130.4 (d, $J_{\mathrm{CP}} = 66.9$ Hz, *i*-Ph), 132.7 (d, $^{3}J_{\mathrm{CP}} = 2.2$ Hz, *m*-Ph), 133.9 (d, $^{2}J_{\mathrm{CP}} = 9.4$ Hz, *o*-Ph) ppm. Anal. Calcd for $\mathrm{C_{36}H_{31}O_4PZr}$: C, 70.67; H, 5.41. Found: C, 70.45; H, 5.22. MS (DCI/$\mathrm{CH_4}$): *m*/*z* 577 [$\mathrm{M^+} + 1$].

Data for 23: $^{1}\mathrm{H}$ (THF-d_8, 200.1 MHz) δ 2.77 (t, $J_{\mathrm{HH}} = 2.4$ Hz, 1H, CCH), 3.85 (d, $J_{\mathrm{HH}} = 2.4$ Hz, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CCH}$), 4.15 (d, $J_{\mathrm{HP}} = 11.2$ Hz, 2H, $\mathrm{PCC}\mathit{H}_2$), 5.44 (s, 10H, $\mathrm{CH_{Cp}}$), 6.71−7.70 (m, 14H, Ph), 7.86 (d, $J_{\mathrm{HP}} = 28.6$ Hz, 1H, $\mathrm{C_7H}$), 9.28 (d, $J_{\mathrm{HP}} = 60.1$ Hz, 1H, $\mathrm{ZrC_{10}H}$) ppm; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ (THF-d_8, 62.9 MHz) δ 57.4 (s, $\mathrm{C}\mathit{H}_2\mathrm{CCH}$), 73.5 (d, $J_{\mathrm{CP}} = 25.3$ Hz, $\mathrm{PC}\mathit{C}\mathrm{H_2}$), 76.1 (s, $\mathrm{CH_2}\mathit{C}\mathrm{CH}$), 80.9 (s, $\mathrm{CH_2C}\mathit{C}\mathrm{H}$), 106.6 (s, $\mathrm{CH_{Cp}}$), 123.0, 125.4, 125.6, 142.7 (s, $\mathrm{CH_{arom}}$), 130.0 (d, $^{2}J_{\mathrm{CP}} = 10.6$ Hz, *o*-Ph), 132.7 (d, $^{3}J_{\mathrm{CP}} = 2.6$ Hz, *m*-Ph), 134.0 (d, $^{2}J_{\mathrm{CP}} = 9.4$ Hz, *o*-Ph) ppm. Anal. Calcd for $\mathrm{C_{36}H_{31}O_4PZr}$: C, 71.84; H, 5.19. Found: C, 71.62; H, 4.92. MS (DCI/$\mathrm{CH_4}$): *m*/*z* 601 [$\mathrm{M^+} + 1$].

Data for 24: $^{1}\mathrm{H}$ ($\mathrm{CDCl_3}$, 200.1 MHz) δ 2.10 (s, 6H, $\mathrm{NCH_3}$), 3.05 (d, $J_{\mathrm{HP}} = 8.8$ Hz, 2H, $\mathrm{CH_2N}$), 5.63 (s, 10H, $\mathrm{CH_{Cp}}$), 6.97−7.71 (m, 14H, Ph), 7.94 (d, $J_{\mathrm{HP}} = 28.4$ Hz, 1H, $\mathrm{C_7H}$), 9.17 (d, $J_{\mathrm{HP}} = 62.7$ Hz, 1H, $\mathrm{ZrC_{10}H}$) ppm; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ ($\mathrm{CDCl_3}$, 62.9 MHz) δ 45.1 (s, $\mathrm{NCH_3}$), 63.6 (d, $J_{\mathrm{CP}} = 26.7$ Hz, $\mathrm{CH_2N}$), 105.5 (s, $\mathrm{CH_{Cp}}$), 122.3, 124.3, 124.4, 141.2 (s, $\mathrm{CH_{arom}}$), 128.4 (d, $^{2}J_{\mathrm{CP}} = 11.4$ Hz, *o*-Ph), 129.0 (d, $J_{\mathrm{CP}} = 57.0$ Hz, *i*-Ph), 131.4 (d, $^{3}J_{\mathrm{CP}} = 2.2$ Hz, *m*-Ph), 132.6 (d, $^{2}J_{\mathrm{CP}} = 9.1$ Hz, *o*-Ph) ppm. Anal. Calcd for $\mathrm{C_{35}H_{34}NPZr}$: C, 71.15; H, 5.80. Found: C, 71.02; H, 5.72.

Synthesis of Compound 28. To a solution of **12a** (0.250 g, 0.35 mmol) in THF (6 mL) at 0 °C was added 3 equiv of HCl in solution in ether (1.05 mL, 1 M). The resulting solution was then stirred at room temperature for 2 h. After filtration and removal of the solvents, the residue was washed with pentane (2 × 10 mL). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy showed the formation of compound **28** and the other isomer (5%) at $\delta^{31}\mathrm{P}$ 48.4 and 1.5 ($J_{\mathrm{PP}} = 10.4$ Hz) ppm which could not be separated from **28**. The stereochemistry of this isomer could not be assigned due to overlap of the different vinylic protons by the aromatic signals.

Data for 28: $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$, 32.4 MHz) 19.9 (d, $J_{\mathrm{PP}} = 7.4$ Hz, $\mathrm{Ph_2P^+}$), 2.5 (d, $J_{\mathrm{PP}} = 7.4$ Hz, $\mathrm{Ph_2P}$) ppm; $^{1}\mathrm{H}$ ($\mathrm{CD_2Cl_2}$, 200.1 MHz) δ 6.12 (ddd, $J_{\mathrm{HH}} = 18.0$ Hz, $J_{\mathrm{HP}} = 23.5$ Hz, $J_{\mathrm{HP}} = 5.2$ Hz, 1H, $\mathrm{Ph_2PCH{=}CH}$), 7.05 (dd, $J_{\mathrm{HH}} = 17.1$ Hz, $J_{\mathrm{HP}} = 23.2$ Hz, 1H, $\mathrm{PhCH{=}}$), 7.15−7.81 (m, 25H, $\mathrm{CH_{Ph}}$), 7.69 (m, $J_{\mathrm{HH}} = 18.0$ Hz, 1H, $\mathrm{Ph_2PCH{=}}$), 7.92 (dd, $J_{\mathrm{HH}} = 17.1$ Hz, $J_{\mathrm{HP}} = 18.5$ Hz, 1H, $\mathrm{PhCH{=}C}\mathit{H}$) ppm; $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$, 62.9 MHz) δ 104.3 (d, $J_{\mathrm{CP}} = 90.0$ Hz, $\mathrm{PhCH{=}}\mathit{C}\mathrm{H}$), 116.9 (d, $J_{\mathrm{CP}} = 92.4$ Hz, $\mathrm{Ph_2PCH{=}}\mathit{C}\mathrm{H}$),), 128.9 (d, $^{2}J_{\mathrm{CP}} = 13.9$ Hz, *o*-Ph), 129.0, 130.3, 131.9, 135.0 (s, $\mathrm{CH_{Ph}}$), 130.0 (d, $^{3}J_{\mathrm{CP}} = 13.9$ Hz, *o*-Ph), 131.4 (d, $^{3}J_{\mathrm{CP}} = 6.4$ Hz, *m*-Ph), 132.8 (d, $^{2}J_{\mathrm{CP}} = 20.4$ Hz, *o*-Ph), 133.1 (d, $^{2}J_{\mathrm{CP}} = 10.7$ Hz, *m*-Ph), 133.9 (d, $^{2}J_{\mathrm{CP}} = 20.7$ Hz, *o*-Ph), 155.0 (d, $J_{\mathrm{CP}} = 3.9$ Hz, $\mathrm{Ph}\mathit{C}\mathrm{H}$), 164.3 (d, $J_{\mathrm{CP}} = 32.1$ Hz, $\mathrm{Ph_2P}\mathit{C}\mathrm{H}$)

ppm. After addition of an excess of sulfur, **28** was isolated as the corresponding thiophosphino compound **28′**. The reaction mixture was stirred for 16 h at room temperature in THF; then **28′** was purified on column chromatography over Florisil with pentane followed by methanol as a brown powder in 65% yield. $^{31}P\{^{1}H\}$ ($CDCl_3$, 32.4 MHz): 15.9 (d, $J_{PP} = 59.0$ Hz, Ph_2P^+), 39.3 (d, $J_{PP} = 59.0$ Hz, Ph_2PS) ppm. ^{1}H ($CDCl_3$, 200.1 MHz): δ 6.73−8.18 (m, 27H, CH═ and CH_{Ph}), 8.92 (m, 1H, ═CH),), 9.21 (dd, $J_{HH} = 19.2$ Hz, $J_{HP} = 40.8$ Hz, 1H, ═CH) ppm. $^{13}C\{^{1}H\}$ ($CDCl_3$, 62.9 MHz): δ 104.3 (d, $J_{CP} = 88.6$ Hz, PhCH═*C*H), $Ph_2P(S)CH═$*C*H hidden by aromatic carbons, 116.9, 118.4, 129.5, 130.9, 133.2, 133.5 (C_{Ph}), 129.1, 129.2, 129.3, 129.9, 130.6, 130.8, 131.6, 131.8, 132.4,132.6, 133.6, 135.7 (CH_{Ph}), 153.4 (d, $J_{CP} = 60.9$ Hz, $Ph_2P(S)$*C*H), 157.5 (d, $J_{CP} =$ 5.7 Hz, Ph*C*H) ppm. Anal. Calcd for $C_{34}H_{29}ClP_2S$: C, 72.01; H, 5.15. Found: C, 71.89; H, 5.28.

Synthesis of Zirconate 29. A Schlenk flask was charged with **12a** (0.250 g; 0.35 mmol), methyl iodide (22 μL, 0.35 mmol), THF (6 mL), and a stir bar. The resulting solution was stirred at room temperature for 3 h. The precipitate formed along the course of the reaction was collected after filtration. **29** was obtained as a brown powder after extraction with CH_2Cl_2 (10 mL) in 82% yield. $^{31}P\{^{1}H\}$ (CD_2Cl_2, 32.4 MHz): 36.5 (d, $J_{PP} = 134.5$ Hz, Ph_2P), 27.3 (d, $J_{PP} = 134.5$ Hz, Ph_2PMe) ppm. ^{1}H (CD_2Cl_2, 200.1 MHz): δ 2.96 (d, $^{2}J_{HP} = 12.2$ Hz, 3H, CH_3), 5.64 (s, 10H, CH_{Cp}), 6.94−7.79 (m, 25H, CH_{Ar}), 7.70 (dd, $J_{HP} = 33.3$ Hz, $J_{HP} = 44.0$ Hz, 1H, C_9H), 8.04 (dd, $J_{HP} = 30.6$ Hz, $J_{HP} = 1.0$ Hz, 1H, C_7H) ppm. $^{13}C\{^{1}H\}$ (CD_2Cl_2, 62.9 MHz): δ 12.2 (d, $^{1}J_{CP} = 57.7$ Hz, PCH_3), 106.1 (s, CH_{Cp}), 121.9, 126.8, 129.7, 138.1, 140.3 (s, CH_{arom}), 122.6 (d, $^{1}J_{CP} = 75.7$ Hz, *i*-Ph), 125.3 (d, $^{1}J_{CP} = 70.6$ Hz, *i*-Ph), 129.3 (d, $^{2}J_{CP} = 11.0$ Hz, *o*-Ph), 129.7 (d, $^{2}J_{CP} = 11.5$ Hz, *o*-Ph), 131.5 (d, $^{2}J_{CP} = 9.3$ Hz, *o*-Ph), 133.5 (d, $^{2}J_{CP} = 8.9$ Hz, *o*-Ph), 133.6 (d, $^{3}J_{CP} = 2.6$ Hz, *m*-Ph), 133.7 (d, $^{3}J_{CP} = 2.7$ Hz, *m*-Ph), 148.6 (dd, $J_{CP} = 105.0$ Hz, $J_{CP} = 3.4$ Hz, C_9H), 149.9 (dd, $J_{CP} = 6.7$ Hz, $J_{CP} = 2.5$ Hz, ZrC_8P), 155.1 (d, $J_{CP} = 26.2$ Hz, C_6), 172.2 (s, C_7H), 193.0 (d, $J_{CP} = 5.4$ Hz, ZrC_1), 198.3 (dd, $J_{CP} = 59.1$ Hz, $J_{CP} = 58.9$ Hz, ZrC_{10}) ppm. Anal. Calcd for $C_{45}H_{28}IP_2Zr$: C, 63.68; H, 3.32. Found: C, 63.59; H, 3.24. MS (FAB/MNBA): *m*/*z* 731 [M^+].

X-ray Analysis of 12a. Single crystals of **12a** were obtained by layering pentane on top of a saturated dichloromethane solution of the corresponding complexes. X-ray diffraction analysis were carried out at 160 K on a STOE IPDS (imaging plate diffraction system) equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 80 mm with the crystal oscillated in φ. The structure coverage of the unique set was close to 98% complete to at least $2\theta = 48.4°$. Crystal decay was monitored by measuring 200 reflections per image. The final unit cell was obtained by the least-squares refinement of 5000 reflections using a Mo Kα radiation. ($\lambda = 0.71073$ Å). Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. Numerical absorption corrections were applied. Relevant crystal data are given in Table 2. The structure was solved by direct methods SIR92[29] and refined by least-squares procedures on F_{obs}. H atoms were located on difference Fourier maps, but they were introduced in calculation in idealized positions (d(C−H) = 0.96 Å), and their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are connected. Concerning the specific hydrogen atoms H(71) and H(91), they were isotropically refined. All non hydrogen atoms were refined anisotropically. Least-squares refinements were carried out by minimizing the function $\sum w(||F_o| - F_c||)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was used. Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. The calculations were carried out with the aid of the CRYSTALS programs[30] running on the PC. The drawing of the molecule was realized with CAMERON[31] with thermal ellipsoids at the 50% probability level. The atomic scattering factors were taken from International Tables for X-ray Crystallography.

Acknowledgment. Thanks are due to CNRS (France) for financial support. V.C. thanks the Spanish Ministerio de Educacion y Cultura for a postdoctoral fellowship.

Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3** and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990436R

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