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Investigation in the coupling of zirconocene complexes and trimethylsilyl(diphenylphosphino)acetylene. P–C bond cleavage chemistry from protonolysis reactions

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Abstract

The regioselectivity of the coupling reactions of the internal acetylenic derivative $Ph_2P–C{\equiv}C–SiMe_3$ (**2**) and the benzyne complex $[Cp_2Zr(\eta^2\text{-}C_6H_4)]$ (**1**) resulted preferentially in the formation of the zirconaindene metallacycle with the metal α-carbanions stabilized by the trimethylsilyl group. We have been able to structurally characterize the two regiosomers. The unusual acute Zr–C–P angle and the short Zr–P distance revealed that a significant Lewis-base/Lewis-acid σ-P–Zr interaction occurs in the α-phosphino zirconaindene metallacycle. Addition of $HCl \cdot Et_2O$ on the cyclic α-silyl zirconindene complex led to competition reactions between (i) the nucleophilic attack of the lone pair of the phosphino group followed by P–C cleavage to form Ph_2PH and $Ph–C{\equiv}C–SiMe_3$ (**7**) and (ii) protonolysis of the Zr–CSi bond to give the *Z*-vinyl silyl phosphino product $Ph_2PC(Ph){=}C(H)SiMe_3$ (**8**). When the lone electron pair of the phosphino group is engaged intramolecularly with the metal center to achieve the stable 18-electron configuration protonolysis reaction on the Zr–C bonds to give the *Z*-vinyl silyl phosphino product $Ph_2PC(H){=}C(Ph)SiMe_3$ (**9**) is the unique process observed. Protonolysis reaction on the complexes prepared in situ from the addition of **2** and zirconocene like reagents "$[Cp_2Zr]$" gave Ph_2PH, $H–C{\equiv}C–SiMe_3$, and $Ph_2PC(H){=}C(H)SiMe_3$ (**18**) which resulted from the competitive P–C and Zr–C bond cleavage processes of the transient alkyne complex $Cp_2Zr(\eta^2\text{-}Ph_2P–C{\equiv}C–SiMe_3)]$ (**14**).

Keywords: Zirconium; C–C coupling; Phosphorus; Cleavage reactions

1. Introduction

The reductive coupling of unsaturated organic molecules with low-valent group 4 complexes to yield metallacyclic compounds is well documented [1,2]. In particular, alkynes are known to act as suitable coupling partners in association with the benzyne zirconocene complex $[Cp_2Zr(\eta^2\text{-}C_6H_4)]$ **1**, to produce the corresponding zirconaindene complexes [2]. The regiochemistry of the insertion process was investigated by Buchwald and Nielsen [3], who also noted that terminal alkynes, $R–C{\equiv}C–H$, do not undergo clean coupling reactions with **1** [4], While using the trimethylsilyl group $R–C{\equiv}C–SiMe_3$ as a proton surrogate, these authors observed that the silyl fragment was ending in α-position to the metal center (Scheme 1, equation (a)) regardless of the nature of the R group. Both electronic (silyl groups are known to stabilize α-carbanions) [5] and steric factors (the α-position is probably less hindered than the β-position) [1c] were invoked to rationalize the regioselectivity of such coupling reactions. More recently, we found that addition of the terminal diphenylphosphinoacetylene $Ph_2P–C{\equiv}CH$ to the benzyne zirconocene complex **1** leads to the formation of only one regioisomer where the phosphorus fragment occupie an α position relative to the zirconocene moiety (Scheme 1, equation (b)) [6]. We proposed that the phosphino moiety $Ph_2P–$ acts as a two electrons L type ligand which directs the approach of the acetylenic

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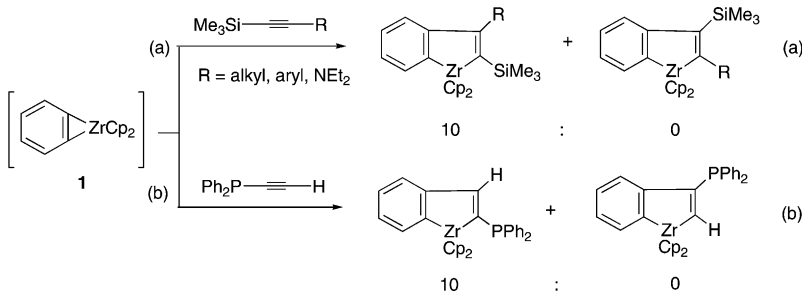


Scheme 1.

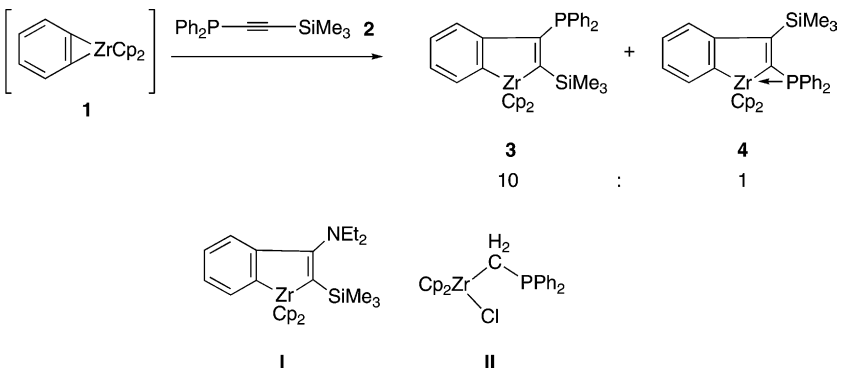
moiety, thus preventing the formation of the alternate β-regioisomer.

With the aim to gain more insight into the regio-selectivity of the insertion process, we were led to use trimetylsilyldiphenylphosphinoacetylene $Me_3Si–C{\equiv}C–PPh_2$ (**2**) as a reacting substrate for the benzyne zirconocene complex **1**. This led us to identify two isomeric zirconocene complexes whose X-ray structure analyses are reported here. In addition, protonolysis reactions carried out on such derivatives reveals the occurrence of competitive P–C and Zr–C bond cleavage reactions. These competitive P–C and Zr–C bond cleavage processes were also observed after the protonolysis reaction carried out on the complexes obtained from the addition of the internal acetylenic derivative **2** with zirconocene synthons "$[Cp_2Zr]$".

2. Results and discussion

2.1. Synthesis and X-ray crystal structure of zirconaindene complexes 3 and 4

The synthesis was carried out by direct reaction of $Me_3Si–C{\equiv}C–PPh_2$ (**2**) with the benzyne zirconocene complex **1**, generated in situ from Cp_2ZrPh_2 in refluxing toluene for 2 h, leading to two compounds in a 10:1 ratio. After their separation and purification, elemental analyses and mass spectra on pure samples were consistent with their formulation as two regioisomers, **3** and **4**, of the expected zirconaindene complexes (Scheme 2). The ^{31}P NMR spectrum of the crude reaction mixture displays a singlet at −8.5 ppm for the major isomer. By ^{1}H and ^{13}C NMR, η^5-cyclopentadienyl (Cp) and trimethylsilyl (Me_3Si) groups appear as one singlet. In addition to the signals corresponding to the aryl carbons, the deshielded chemical shift at 244.8 ($J_{CP} = 26.8$ Hz) ppm observed in the ^{13}C NMR spectrum is indicative of the occurrence of a Zr–C bond [7]. Moreover, in the $^{1}H–^{13}C\{^{31}P\}$ HMBC experiment, correlations were observed between the Zr–C sp^2-carbon atom and the protons of the silyl fragment. The signal at 152.0 ($J_{CP} = 39.8$ Hz) ppm corresponds to the carbon atom linked to the phosphorus substituent. The minor isomer exhibits characteristic signal at −67.5 ppm in the ^{31}P NMR spectrum. The ^{13}C NMR shows the sp^2-C signals linked to phosphorus and silyl fragments at 191.7 ($J_{CP} = 10.5$ Hz) and 189.9 ($J_{CP} = 11.8$ Hz) ppm, respectively. All NMR assignments are in favor of the formation of the two zirconaindenes with the major component corresponding to the complex **3** bearing the silyl fragment in α-position relative to the zirconium atom, and the minor product **4** corresponding to the reverse regioisomer. Variable temperature NMR experiments provided no evidence for any fluxional process. Addition of L type ligands (L = PMe_3, pyridine, CH_3CN) to **4** did not modify its ^{31}P NMR chemical shift. Also noteworthy in the ^{31}P NMR spectrum is a



Scheme 2.

large $\Delta\delta$ of 60 ppm observed between the two regioisomers **3** and **4** depending on whether the silyl group is placed at the α or β position relative to the zirconium center. Large chemical shift differenciations between phosphino zirconaindene regioisomers have been already observed in our earlier studies (Table 1) [6,8]. It is also noteworthy that the ^{31}P chemical shift of β-phosphino zirconaindenes, is not significantly affected by the nature of the substituent in α position to the metal center, in marked contrast with the alternate case of α-phosphino zirconaindenes, for which the ^{31}P resonance is highly dependent on the nature of the substituent placed in β position.

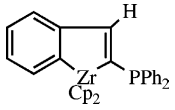
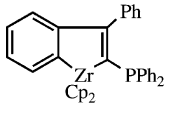
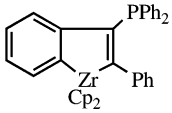
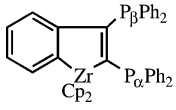
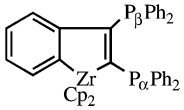
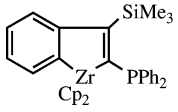
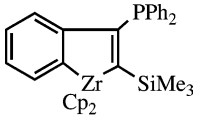
Let us specify that prolonged reflux of a mixture of the regioisomers **3** and **4** in toluene in the presence or absence of phosphines (PMe_3, $PhPMe_2$, Ph_2PMe) or pyridine as two electron donor ligands did not modify the initial ratio [3].

The X-ray structure analyses of the compounds **3** and **4** are reported (Table 2). The structural diagrams of these complexes, shown in Figs. 1 and 2, respectively, are revealing interesting features. Selected bond distances and angles are presented in Table 3. The bonding parameters at the pseudotetrahedral bent metallocene moiety for **3** and **4** are as usually observed in a number of other Zr(IV)-containing zirconocene derivatives [9]. In both structures the atoms Zr, C1–C8 are almost perfectly coplanar. The C1–C2, C2–C3, and C3–C8 bond lengths in **3** and **4** are not significantly perturbed by the nature of the substituents linked to the C1 and C2 atoms, and compare well with the other zirconaindene complexes reported in the literature ([6,10], also for phosphonium–zirconaindeneate complexes, see [11]). The Zr–C8 aromatic bond lengths measured in **3** (2.258(3) Å) is within the expected range for tetra-coordinated zirconocene complexes of the type CpZr(X)(Y) (as for example in the structurally

Table 2
Crystal data and structure refinement for **3** and **4**

	3	**4**
Formula	$C_{33}H_{33}PSiZr$	$C_{33}H_{33}PsiZr$
Formula weight	579.87	579.87
Crystal size (mm)	$0.27 \times 0.22 \times 0.07$	$0.52 \times 0.12 \times 0.07$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Temperature (K)	180	293
Wavelength (Å)	0.71073	0.71073
a (Å)	9.1354(12)	10.2451(16)
b (Å)	38.617(5)	10.3288(16)
c (Å)	8.7101(12)	14.813(3)
α (°)	90.0	70.290(19)
β (°)	113.422(15)	72.510(19)
γ (°)	90.0	82.921(18)
V (Å^3)	2819.6(7)	1407.0(4)
Z (mg m^{-3})	4	2
Calculated density (mg m^{-3})	1.366	1.369
Absorption coefficient (mm^{-1})	0.509	0.510
$F(000)$	1200	600
$2\theta_{max}$ (°)	45.2	52.5
Reflections measured	total: 12 994 unique: 3670 $R_{int} = 0.0478$	total: 13 360 unique: 5108 $R_{int} = 0.0274$
Reflections observed $[I > 2(I)]$	3670	5108
Number of variables	328	328
$T_{min} - T_{max}$	0.403–0.797	0.507–0.844
GOF on F^2	1.038	1.048
$R_1(F)[I > 2\sigma(I)]$	0.0386	0.0289
$R_1(F^2)$ (all data)	0.0530	0.0360
$wR_2(F^2)$ (all data)	0.0987	0.0780

Table 1
^{31}P NMR chemical shifts (ppm) of α- and β-phosphinozirconaindenes

α-P-zirconaindenes	δ ^{31}P	β-P-zirconaindenes	δ ^{31}P	$\Delta\delta$	Ref.
	7				[6]
	−36		−10	26	[8]
	−56(P_α)		−10(P_β)	46	[8]
 (**4**)	−67	 (**3**)	−7	60	Current

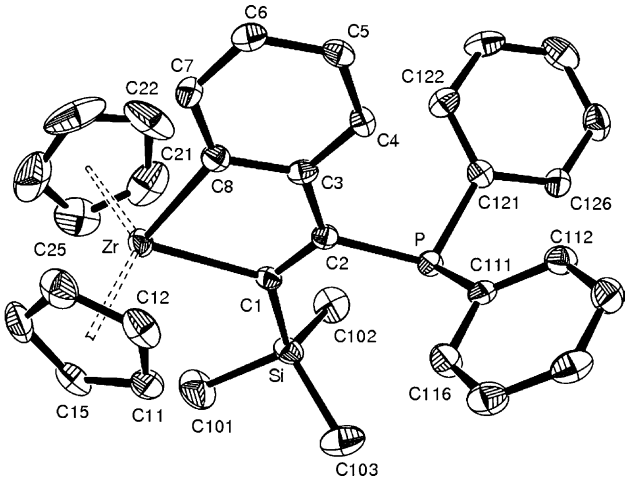


Fig. 1. Molecular structure of **3** (ORTEP drawing with thermal ellipsoids at 50% probability).

Table 3
Selected bond distances (Å) and angles (°) for **3** and **4**

	3	**4**
X	$SiMe_3$	PPh_2
Y	PPh_2	$SiMe_3$
Zr–C1	2.279(3)	2.254(2)
Zr–C8	2.258(3)	2.357(2)
C1–C2	1.345(5)	1.352(3)
C2–C3	1.502(5)	1.493(3)
C3–C8	1.414(5)	1.420(3)
C1–X	1.877(3)	1.751(2)
C2–Y	1.856(3)	1.895(2)
Zr–P	–	2.7784(6)
C1–Zr–C8	78.01(12)	68.77(7)
Zr–C1–C2	111.4(2)	126.67(15)
Zr–C8–C3	111.8(2)	116.87(14)
Zr–C1–X	123.03(16)	86.87(9)
C1–C2–Y	116.0(3)	127.09(16)
X–C1–C2	125.60(26)	144.89(18)

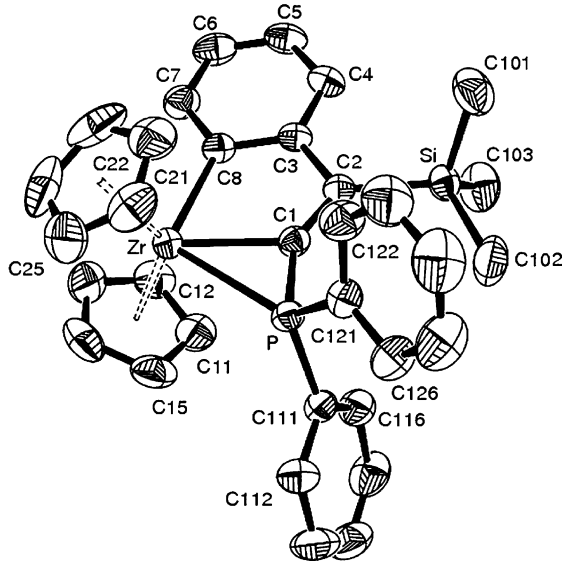


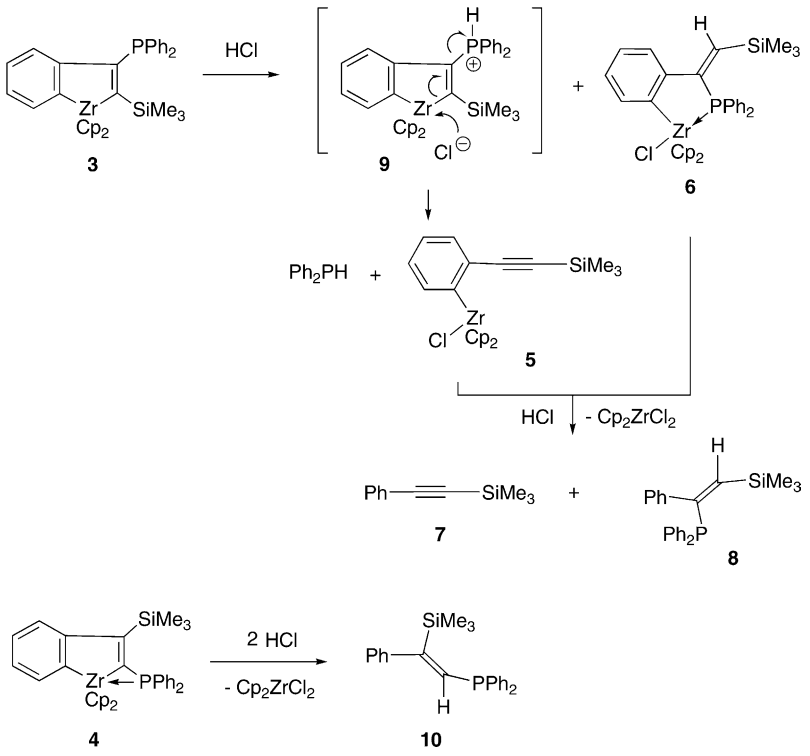
Fig. 2. Molecular structure of **4** (ORTEP drawing with thermal ellipsoids at 50% probability).

characterized zirconaindene **I**) [10]. It is in marked contrast with the Zr–C8 distance found in **4** of 2.357(2) Å which is in favor with a five-coordinated zirconocene metal fragment of the type CpZr(X)(Y)(L) [11]. Phenyl substituents at the phosphorus atom adopt an orientation as to minimize their steric interaction with the metallocene fragment. Moreover, the Zr–C1–P angle in **4** at 86.9° is unusually acute. It is much smaller than those observed in unsaturated five-membered ring zirconocenes, which are as expected around a sp^2-carbon atom as for example Zr–C1–Si angle (123.0°) in **3**. Interestingly the X-ray structure of the diphenylphosphinomethanechlorozirconocene complex $Cp_2Zr(Cl)CH_2PPh_2$ (**II**) is remarkable in revealing the degree to which the formally open-shell Zr and its phosphine substituent *avoid* interacting with one another. The Zr–C–P angle in **II** is open at 130.1° and the closest Zr–P approach in the crystal is the intramolecular distance of 3.75 Å [12]. Therefore, the Zr–P distance of 2.7784(6) Å in **4** lies in the limit of those observed in zirconocene(IV) phosphine complexes of the type $Cp_2Zr(X)(Y)(PR_3)$ (Zr–P 2.65–2.85 Å) [13,14], it is reasonable to propose that a significant Lewis-base/Lewis-acid σ-P–Zr interaction occurs in **4**.

2.2. Protonolysis reaction of zirconaindenes complexes *3* and *4*

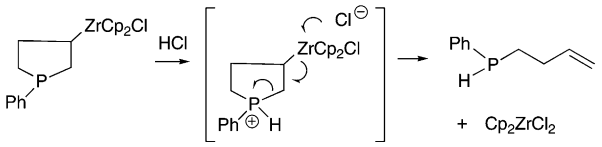
Treatment of the isolated α-trimethylsilyl zirconaindene regioisomer **3** with 2 equiv. of $HCl \cdot OEt_2$ in THF at 25 °C led to the clean formation of two phosphines which were identified by ^{31}P NMR as Ph_2PH (δ −40 ppm, $^1J_{PH} = 273$ Hz), and the vinyl phosphine **8** (δ 0.8 ppm) in 10:1 ratio, respectively. The ^1H NMR spectrum for **8** revealed the characteristic resonance of the vinylic =CH proton at δ 6.88 ppm, whereas the ^{13}C NMR spectrum showed signals at 153.5 (=CHSi) and 155.9 (PC=) ppm in the expected region for olefinic sp^2 carbon atoms. In addition, the acetylenic organic product $Me_3Si–C\equiv C–Ph$ (**7**) was also identified from the crude reaction mixture by NMR and GC–MS analysis (Scheme 3).

Clearly, the incipient alkenyl phosphine **8** is resulting from the expected protonolysis of the two Zr–C bonds of the zirconaindene complex **3** [3,14]. However, in order to rationalize the formation in the crude reaction of the primary phosphine Ph_2PH it is reasonable to propose that protonation at the phosphorus atom generates the transient phosphonium–zirconate complex **9** which rearranges after cleavage of the P–C bond to form Ph_2PH



Scheme 3.

and **5** (Scheme 3). β-Elimination reaction with halogen as leaving group in zirconacyclopentadiene complexes to afford the corresponding alkynyl zirconation product was lately observed by Takahashi and coll [15]. Moreover P–C bond cleavage in β-phosphorus zirconocene complexes was already exemplified [16]. We also proposed earlier that isolation of the homoallylic phosphine compound $PhP(H)(CH_2)_2CH{=}CH_2$ after addition of HCl to the starting β-zirconocene phospholane complex may arise from the transient formation of the corresponding phosphonium zirconocene complex followed by P–C bond cleavage (Eq. (1)) [17].



(1)

Addition of only 1 equiv. of $HCl \cdot OEt_2$ to **3** allowed us to identify from the crude solution the formation of Ph_2PH and **6** (δ ^{31}P 20 ppm). All the resonances in the ^1H and ^{13}C NMR spectra for **6** were attributed by homonuclear decoupling experiments. ^{13}C NMR assignments were confirmed by inverse gradient ^1H–$^{13}C\{^{31}P\}$ HMQC and ^{31}P–^1H INEPT NMR experiments, revealing that the Me_3Si-group in **6** is connected to the sp^2-carbon atom of the vinylic =CH fragment (δ ^1H 7.42 ppm, δ ^{13}C 142.1 ppm). The signal at 152.3 ($^1J_{CP} = 38.2$ Hz) ppm corresponds to the other olefinic sp^2-carbon atom bound to the phosphino substituent and the aryl group. Thus, ^1H and ^{13}C NMR data confirm that **6** results from the cleavage of the Zr–C(Si) bond of the starting zirconacyclopentadiene **3**. For **6**, the deshielded ^{31}P NMR chemical shift at 20 ppm strongly suggests an intramolecular σ-P–Zr interaction forming a highly favorable five-membered ring [18]. Note that these experimental conditions (1 equiv., $HCl \cdot OEt_2$) did not allow us to fully characterize the zirconocene complex **5** from the crude reaction mixture.

The vinyl phosphine derivative **10** was the unique phosphorus compound observed by ^{31}P NMR after addition of 2 equiv. of $HCl \cdot OEt_2$ on **4** (Scheme 3). Compound **10** resulted in the expected protonolysis reaction of the two Zr–C bonds of the corresponding zirconaindene complex **4** [14]. In marked contrast to the case of the α-trimethylsilyl zirconaindene **3**, it was not possible to observe the formation of any complex resulting from the mono addition of $HCl \cdot OEt_2$. It is interesting to note that it has been previously demonstrated [19] that J_{HP} coupling constants in vinyl diphenylphosphine derivatives make assignment for the the different regioisomers unambiguous as $^3J_{HP}$ (**6**: $^3J_{HP} = 29.3$ Hz, **8**: $^3J_{HP}$ 52.4 Hz) are larger than $^2J_{HP}$ (**10**: $^2J_{HP}$ 2.8 Hz).

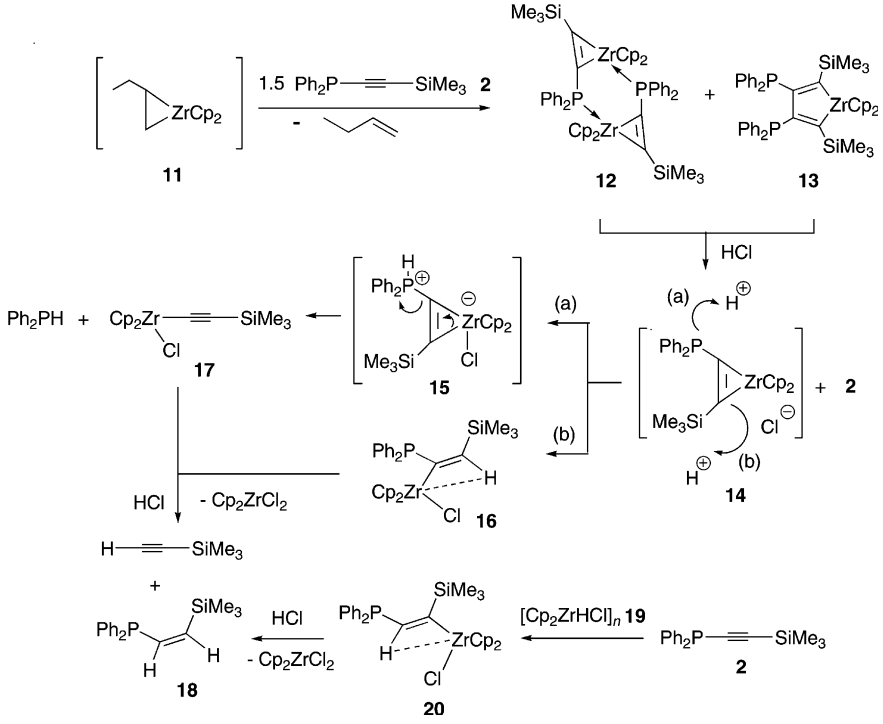
The reactivity of the α-phosphino zirconaindene complex **4** with $HCl \cdot OEt_2$ is in full agreement with

the σ-P–Zr interaction observed by X-diffraction studies. No nucleophilic attack of the lone pair of the phosphorus substituent may be envisaged in **4** as it interacts with the single acceptor $1a_1$ orbital of the zirconocene(IV) fragment to achieve the stable 18-electron configuration. Therefore, no P–C bond cleavage is observed in marked contrast to the reactivity of the reverse β-phosphino zirconaindene regioisomer **3** where the lone pair of the phosphorus atom is available for a protonation by the incoming proton H^+.

2.3. Synthesis and protonolysis reaction of zirconacycle complexes *12* and *13*

Alkynes are known to undergo dimerization at the zirconocene unit "$[Cp_2Zr]$" to give the corresponding zirconacyclopentadiene [1,20]. The zirconocene like reagent $[Cp_2Zr(\eta^2\text{-1-butene})]$ (**11**) [21] (1 equiv.) reacts with **2** (2 equiv.) in THF to yield a mixture of compounds **12** and **13** in 1:1 ratio which appear by ^{31}P NMR at $\delta = 13.6$ and 21.0 ppm, respectively (Scheme 4). Surprisingly unreacted phosphino acetylenic reagent **2** is still present in the solution. Careful control of reaction stoichiometry (**11** (1 equiv.); **2** (1.5 equiv.)) allowed us to observe the total disappearance of **2** to form the dimeric zirconacyclopropene **12** and the zirconacyclopentadiene **13** complexes in quasi quantitative yield according to NMR spectroscopy. Identical results were observed starting with $[Cp_2Zr(\eta^2\text{-}Me_3Si\text{–}C{\equiv}C\text{–}SiMe_3)(THF)]$ complex as the zirconocene "$[Cp_2Zr]$" synthon. Attempts to isolate **12** and **13** led to their decomposition with regeneration of **2** and formation of several unidentified zirconocene products. Nevertheless, **12** and **13** could be unambiguously characterized in situ by 1D and 2D (DQF-COSY, NOESY, HMQC, HMBC) NMR experiments. In addition to the signals corresponding to the diphenylphosphino substituents, ^1H NMR experiments reveal the presence for compounds **12** and **13** of η^5-cyclopentadienyl ligands and trimethylsilyl groups in 1:2 and 1:1 ratio, respectively. The deshielded chemical shifts for **12** at δ 205.5 ($J_{CP} = 68.5$ Hz) ppm and 189.7 ($J_{CP} = 9.4$ Hz) ppm observed in the ^{13}C NMR spectra are indicative of carbon atoms directly linked to the metallocene fragment [22]. These signals correspond to the ZrCP and ZrCSi carbon atoms of the cyclic zirconacyclopropene skeleton. The deshielded ^{31}P NMR resonance at δ 13.6 ppm for this α-phosphino three-membered zirconacycle may indicate the presence of a Lewis-base/Lewis-acid σ-interaction between the lone electron pair of the phosphorus atom and the vacant coordination site of the zirconium metal center to form a stable dimeric complex with a six-membered ring [23]. A number of zirconacyclopropenes have been prepared and stabilized as 18-electron metal complexes using phosphine ligands [13b,13c,22].

In the ^{13}C NMR spectra, the signal at δ 192.8 ($J_{CP} = 36.1$ Hz) ppm observed for **13** is indicative of the sp^2-CZr carbon atom of the zirconacyclopentadiene skeleton [24]. As expected, the resonance at 171.2 ppm corresponding to the carbon atom placed in β-position



Scheme 4.

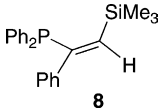
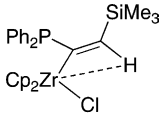
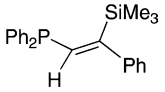
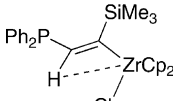
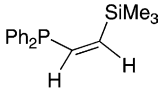
relative to the zirconium center in the five-membered ring and connected to the phosphino group appears as a doublet of doublet with coupling constants J_{CP} of 58.3 and 10.2 Hz. The deshielded ^{31}P NMR chemical shift of this unprecedented β,β′-phosphino zirconacyclopentadiene complex **13** is in accord with the deshielded chemical shift observed in β-phosphino zirconaindene complexes (Table 1). Note that no dynamic equilibrium between **12** and **13** was observed in solution by variable temperature NMR.

Protonolysis reaction of the crude reaction mixture with 2 equiv. of $HCl \cdot OEt_2$ at 25 °C of in situ generated (η^2-diphenylphosphinotrimethylsilylacetylene)zirconocene dimer **12** and the zirconacyclopentadiene complex **13** led, beside the formation of Cp_2ZrCl_2, to **2**, Ph_2PH, the vinyl phosphine **18** and trimethylsilylacetylene H–C≡C–$SiMe_3$ (Scheme 4). All these compounds were unambiguously identified by NMR spectroscopy and GC-MS analysis. ^{31}P NMR spectrum showed the presence of **2** (δ −33 ppm), Ph_2PH (δ −40 ppm), and **18** (δ −21 ppm) as the sole phosphorus products of the reaction. The vinyl phosphine compound **18** was independently prepared by hydrozirconation reaction, with the Schwartz's reagent $[Cp_2ZrHCl]_n$ (**19**), on **2** at room temperature followed by protonolysis of the Zr–C bond of the corresponding zirconocene complex **20** (Scheme 4). The ^1H and ^{13}C NMR vinyl CH resonances appear, respectively, at 6.82 and 151.2 ppm for the =CHSi fragment and at 7.24 and 147.2 ppm for the =CHP fragment and compare well with the chemical shifts obtained for **8** and **10** (Table 4).

Careful addition of 1 equiv. of $HCl \cdot OEt_2$ at 25 °C to the crude reaction mixture of **12** and **13** allowed us to observe by ^{31}P NMR the formation of Ph_2PH and the vinyl zirconocene complex **16** (Scheme 4). The ^1H NMR CHSi absorption was observed at low field (δ 8.06). ^{13}C NMR spectra showed a high field SiCH vinyl chemical shift at 106.7 ppm and a reduced $^1J_{CH}$ coupling constant of 109.0 Hz. All these NMR data are in accord with a significant agostic Zr–H–C interactions between the vinyl C–H bond and the unsaturated Zr(IV) center in complex **16** [13a,25].

According to the products resulting from the protonolysis reaction, the dimeric complex **12** and the zirconacyclopentadiene compound **13** were found to react with $HCl \cdot OEt_2$ under the monomeric form **14**. As already reported in the literature [22b,26] rapid bis(η^2-alkyne)zirconocene to zirconacyclopentadiene conversion is sometimes a readily reversible reaction despite the fact that the equilibrium lies far over on the side of the metallacycle. Reactive (η^2-alkyne)zirconocene becomes available by shifting the equilibrium by adding a suitable scavenger as for example a phosphine. This β–β′-carbon–carbon bond cleavage in five-membered zirconacycles was largely exploited synthetically [27] Such a ring-opening equilibration is facilitated by bulky alkyne substituents like the trimethylsilyl group –$SiMe_3$. Therefore, it is reasonable to propose that in the presence of $HCl \cdot OEt_2$, **13** rearranges to **14** after elimination of **2**. Then, competitive P–C and Zr–C bond cleavage reactions occurred. Nucleophilic attack of the phosphino group Ph_2P– to form a P–H phosphonium–zirconate intermediate **15** which rearranges after ring opening process following P–C bond cleavage to give **17** and Ph_2PH (Scheme 4, path (a)). Compound **16** results from the protonolysis reaction of the Zr–CSi bond of the corresponding zirconacyclopropene intermediate **14** (Scheme 4, path (b)).

Table 4
Comparison of olefinic =CH agostic and non-agostic chemical shift (ppm) and $^1J_{CH}$ (Hz) coupling constant in vinyl trimethylsilyl-phosphine derivatives

Vinyl phosphines	(=CH)			Zirconocene vinyl phosphines	(=CH)		
	δ ^1H	δ ^{13}C	δ $^1J_{CH}$		δ ^1H	δ ^{13}C	δ $^1J_{CH}$
 **8**	6.88	153.5	130	 **16**	8.06	106.7	109
 **9**	7.00	144.5	154	 **20**	8.40	110.5	129
 **18**	6.81	(=CHSi) 151.2	135				
	7.24	(=CH) 147.2	155				

Interestingly, characterization of the hydrozirconation product **20** by NMR spectroscopy revealed that the bulky trimethylsilyl substituent is located at the α-position relative to the metal fragment. The presence of a marked agostic alkenyl β-C–H–Zr interaction was obvious from the characteristic spectroscopic features. The Zr–C=C–H unit shows a ^{1}H NMR signal at rather low field (δ 8.40). The ^{13}C NMR absorption of ZrC signal is at δ 232.6, whereas the PCH signal is located upfield at δ 110.5. The low $^1J_{CH}$ coupling constant (129 Hz) is a strong indication for the presence of the agostic Zr–C–H moiety.

For zirconocenes **16** and **20** the $^1J_{CH}$ is 20–25 Hz *smaller* than in the corresponding non-metal vinyl phosphine $Ph_2PCH{=}CHSiMe_3$ (**18**). Moreover, the ^{1}H and ^{13}C NMR resonances of the =CH fragment for **16** and **20** are significantly deshielded ($\Delta\delta$ ^{1}H 1.2–1.3 ppm) and shielded ($\Delta\delta$ ^{13}C 37–45 ppm) by comparison with vinyl phosphines **8**, **10**, and **18** (Table 4). Therefore, whatever the metal fragment $ZrCp_2Cl$ is located on the carbon–carbon double bond, both of the two P, Si-heterosubstituted vinyl zirconocene regioisomers **16** and **20** showed strong evidences for Zr–H–C agostic interactions.

3. Experimental

3.1. General procedures

All manipulations were conducted under an argon atmosphere with standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker MSL 400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Positive chemical shifts are given downfield relative to Me_4Si (^{1}H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P), respectively. All the ^{1}H and ^{13}C signals were assigned on the basis of chemical shifts, spin–spin coupling constants, splitting patterns and signal intensities, and by using ^{1}H–^{1}H COSY45, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC experiments. GC–MS (electron impact, EI) analyses were carried out on a Hewlett–Packard 5890 gas chromatograph on capillary column (HP-5MS, 30 m, Ø 0.25 mm) coupled to a 5970 Hewlett–Packard mass-selective detector. Elemental analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS on a Perkin–Elmer 2400 series II instrument. Solvents were freshly distilled from sodium/benzophenone ketyl (toluene, THF), P_2O_5 (CH_2Cl_2) or lithium aluminum hydride (pentane). CD_2Cl_2, and $CDCl_3$ were treated with CaH_2, distilled, and stored under argon. Cp_2ZrCl_2, BuLi, THF-d_8 and $HCl\cdot OEt_2$ were purchased from Aldrich and used without further purification. Ph_2P–C≡C–$SiMe_3$[28], Cp_2ZrPh_2 [29], and $[Cp_2ZrHCl]_n$ [30] were prepared according to literature procedure.

3.2. Preparation of zirconaindene complexes 3 and 4

To a solution of Cp_2ZrPh_2 (0.144 g, 0.51 mmol) in toluene (2 ml) was added at room temperature Me_3Si–C≡C–PPh_2 (**2**) (0.192 g, 0.51 mmol). The mixture was heated under reflux for 2h; then the reaction mixture was allowed to cool down to room temperature. Solvents were evaporated in vacuo. ^{31}P NMR of the crude mixture showed the presence of the two regioisomers **3** and **4** in 10/1 ratio, respectively, as the sole phosphorus compounds of the reaction. The residue was dissolved in a minimum of THF (≈1 ml), then pentane was slowly added to the THF solution (≈9 ml). The precipitate formed was filtered and corresponds to **3** which was isolated as a yellow powder in 85% yield. The volatiles were removed to give **4** as a red powder in 9% yield. Recrystallization of the regioisomers in toluene/CH_2Cl_2 gave **3** as yellow crystals and **4** as red crystals. **3**. Fp: 148–150 °C. $C_{33}H_{33}PSiZr$ (579.87): *Anal.* Calc. C 68.35, H 5.73. Found: C 68.52, H 5.54%. $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ −8.5 (s) ppm. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ 0.17 (s, 9H, $SiMe_3$), 6.42 (s, 10H, Cp), 6.43–7.55 (m, 14H, CH_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$, 25 °C): δ 3.3 (s, $SiMe_3$), 112.5 (s, Cp), 123.5, 124.0, 126.8, 135.8 (s, CH_{arom}), 128.2 (s, *o*-PPh), 128.7 (s, *p*-PPh), 130.9 (d, $^3J_{CP} = 16.0$ Hz, *m*-Ph), 138.6 (d, $^1J_{CP} = 25.0$ Hz, *i*-Ph), 143.9 (s, ZrC*C*), 152.0 (d, $^1J_{CP} = 39.8$ Hz, ZrC*C*P), 188.2 (s, Zr*C*), 244.8 (d, $^2J_{CP} = 26.8$ Hz, ZrCSi) ppm. **4**. Fp: 161–163 °C. $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ −67.5 (s) ppm. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ 0.19 (s, 9H, $SiMe_3$), 5.56 (d, $^3J_{HP} = 0.8$ Hz, 10H, Cp), 6.42–7.55 (m, 14H, CH_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$, 25 °C): δ 1.1 (s, $SiMe_3$), 105.2 (s, Cp), 122.8, 126.1, 126.2, 141.8 (s, CH_{arom}), 128.6 (d, $^2J_{CP} = 7.9$ Hz, *o*-PPh), 129.2 (s, *p*-PPh), 130.9 (d, $^3J_{CP} = 11.3$ Hz, *m*-Ph), 135.0 (s, *i*-Ph), 164.3 (d, $^3J_{CP} = 43.4$ Hz,ZrC*C*), 189.9 (d, $^2J_{CP} = 11.8$ Hz, ZrC*C*Si), 191.0 (s, ZrC), 191.7 (d, $^1J_{CP} = 10.5$ Hz, ZrCP) ppm.

3.3. Addition of HCl (1 equiv.) on β-phosphino zirconaindene complex 3

To a solution of **3** (0.064 g, 0.11 mmol) in toluene (1 ml) was added 1 equiv. of HCl (0.11 ml, 1 M in Et_2O). ^{31}P, ^{1}H, and ^{13}C NMR spectra showed the presence of three products in the reaction mixture: Ph_2PH (δ ^{31}P −40 ppm, $J_{PH} = 230$ Hz), **5**, and **6** which were identified in situ. **6**. $^{31}P\{^1H\}$ NMR (101 MHz, THF-d_8, 25 °C): δ 19.9 (s) ppm. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ −0.41 (s, 9H, $SiMe_3$), 5.77 (s, 10H, Cp), 7.42 (d, $^3J_{HP} = 29.3$ Hz, 1H, =CHSi), 7.31–7.52 (m, 14H, CH_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$, 25 °C): δ 0.3 (s, $SiMe_3$), 111.9 (s, Cp), 126.1, 127.4, 133.3, 134.7 (s, CH_{aryl}), 124.7 (d, $^3J_{CP} = 8.7$ Hz, *m*-Ph), 128.1 (d, $^2J_{CP} = 8.3$ Hz, *o*-Ph), 130.3 (d, $^1J_{CP} = 11.3$ Hz, *i*-Ph),

142.1 (d, $^2J_{CP} = 3.6$ Hz, =CHSi), 142.7 (d, $^3J_{CP} = 5.8$ Hz, PCC*C* H), 152.3 (d, $^1J_{CP} = 38.2$ Hz, PC=), 157.5 (d, $^2J_{CP} = 32.3$ Hz, PC*C*), 182.1 (d, $^3J_{CP} = 2.2$ Hz, ZrC) ppm. It was not possible from the reaction mixture to unambiguously identified the carbon and proton aryl signals for complex **5**: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ 0.18 (s, 9H, $SiMe_3$), 5.94 (s, 10H, Cp); $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$, 25 °C): δ 0.6 (s, $SiMe_3$), 109.2 (s, Cp), 96.4 (s, Ph*C*C), 104.9 (s, Si*C* C) ppm.

3.4. Addition of HCl (2 equiv.) on β-phosphino zirconaindene complex 3

To a solution of **3** (0.064 g, 0.11 mmol) in toluene (1 ml) was added 2 equiv. of HCl (0.22 ml, 1 M in Et_2O). ^{31}P, ^{1}H, ^{13}C NMR spectra and GC–MS analysis on the crude reaction mixture showed the presence of Ph_2PH (δ ^{31}P −40 ppm, $J_{PH} = 230$ Hz), **7**, and **8** in 10/10/1 ratio, respectively, as the sole products of the reaction. Compounds **7** and **8** were also obtained after addition of HCl (1 equiv.) on complexes **5** and **6** obtained from the procedure described above (cf. addition of HCl (1 equiv.) on **3**). **7**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.25 (s, 9H, $SiMe_3$), 7.20–7.50 (m, 5H, Ph) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 0.0 (s, $SiMe_3$), 94.0 (s, $CSiMe_3$), 105.1 (s, CPh), 123.0, 128.1, 128.4, 131.9 (s, Ph) ppm. **8**: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 0.8 (s) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.38 (d, $^5J_{HP} = 1.2$ Hz, 9H, $SiMe_3$), 6.88 (d, $^3J_{HP} = 52.4$ Hz, 1H, CHSi), 7.25–7.58 (m, 15H, CH_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 1.1 (d, $^4J_{CP} = 7.0$ Hz, $SiMe_3$), 126.6, 127.7, 128.0, 128.5, 128.5 (s, CH_{Ph}), 133.2 (d, $^2J_{CP} = 18.1$ Hz, *o*-PPh), 137.1 (d, $^1J_{CP} = 13.2$ Hz, *i*-PPh), 153.5 (d, $^2J_{CP} = 54.3$ Hz, CHSi), 155.9 (d, $^1J_{CP} = 22.1$ Hz, P*C*Ph) ppm. GC–MS analysis (He, 1.5 ml mn^{-1}, from 35 to 80 °C (2 °C mn^{-1}) then from 80 to 280 °C (10 °C mn^{-1}); MS (EI, 70 eV) *m/z*): (**7**) 174 (M^+, 25%), 159 (100%); (Ph_2PH) 186 (M^+, 186%), 108 (100%); (**8**) 360 (M^+, 46%), 345 (20%), 175 (38%), 73 (100%).

3.5. Addition of HCl (2 equiv.) on β-phosphino zirconaindene complex 4

To a solution of **4** (0.162 g, 0.28 mmol) in toluene (3 ml) was added at room temperature 2 equiv. of HCl (0.56 ml, 1 M in Et_2O). The reaction mixture was stirred for 30 mn and the solution turned yellow. The resulting residue was extracted with pentane and filtered. Removal of the solvent in vacuo from the colourless solution gave **10** in 85% yield. $C_{23}H_{25}PSi$ (360.51): *Anal.* Calc. C 76.63, H 6.99. Found: C 77.09, H 6.72%. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ −22.0 (s) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.34 (d, $^5J_{HP} = 1.2$ Hz, 9H, $SiMe_3$), 7.00 (d, $^2J_{HP} = 2.8$ Hz, 1H, CHP), 7.25–7.58 (m, 15H, CH_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 1.8 (d, $^4J_{CP} = 8.9$ Hz, $SiMe_3$), 127.0, 128.3, 128.5, 129.0, 129.1 (s, CH_{Ph}), 133.0 (d, $^2J_{CP} = 18.3$ Hz, *o*-PPh), 140.2 (d, $^3J_{CP} = 10.1$ Hz, *i*-Ph), 144.5 (d, $^1J_{CP} = 11.8$ Hz, PCH), 148.2 (d, $^1J_{CP} = 17.1$ Hz, *i*-PPh), 165.1 (d, $^2J_{CP} = 40.2$ Hz, Si*C*Ph) ppm.

3.6. Formation of complexes [$Cp_2Zr(\eta^2$-Ph_2-PC_2Si-$Me_3)]_2$ (12) and $Cp_2ZrC(SiMe_3)$=$C(PPh_2)$–$C(PPh_2)$=$C(SiMe_3)$ (13)

To a solution of **11** (prepared from Cp_2ZrCl_2 (0.031 g, 0.11 mmol) in THF and 2 equiv. of *t*-BuLi (0.082 ml, 2.7 M) cooled to −78°C and stirred for 2 h) was added 1.5 equiv. of **2** (0.0042 g, 0.15 mmol) in THF. The reaction mixture was stirred at room temperature for 3 h. According to NMR spectroscopy complexes **12** and **13** were formed in 1:1 ratio. Attempts to isolate **12** and **13** lead to a multitude of compounds. However, they were unambiguously identified by NMR spectroscopy, in situ, following the same experimental procedure using THF-d_8. **12**: $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, −30°C): δ 13.6 (s) ppm. ^{1}H NMR (400 MHz, THF-d_8, −30°C): δ 0.10 (s, 18H, $SiMe_3$), 5.86 (s, 10H, Cp), 6.06 (s, 10H, Cp), 7.31–7.40, 7.63–7.66 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, −30°C): δ 1.2 (s, $SiMe_3$), 110.4, 111.7 (s, Cp), 127.7 (d, $^2J_{CP} = 5.4$ Hz, *m*-Ph), 133.8 (d, $^2J_{CP} = 17.2$ Hz, *o*-Ph), 144.2 (d, $^4J_{CP} = 13.0$ Hz, *i*-PPh), 189.7 (d, $^2J_{CP} = 9.4$ Hz, ZrCSi), 205.5 (d, $^1J_{CP} = 68.5$ Hz, ZrCP) ppm, *p*-Ph was not detected. **13**: $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, −30°C): δ 21.0 (s) ppm. ^{1}H NMR (400 MHz, THF-d_8, −30°C): δ 0.34 (s, 18H, $SiMe_3$), 5.38 (s, 10H, Cp), 7.31–7.40, 7.63–7.66 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8, −30°C): δ 2.3 (s, $SiMe_3$), 106.5 (s, Cp), 128.1 (d, $^3J_{CP} = 5.6$ Hz, *m*-Ph), 133.8 (d, $^2J_{CP} = 17.2$ Hz, *o*-Ph), 140.8 (d, $^4J_{CP} = 14.5$ Hz, *i*-PPh), 171.2 (dd, $^1J_{CP} = 58.3$ Hz, $^2J_{CP} = 10.2$ Hz, ZrC*C*P), 192.8 (d, $^2J_{CP} = 36.1$ Hz, ZrCSi) ppm, *p*-Ph was not detected.

3.7. Addition of HCl (1 equiv.) on 12 and 13

On the complexes **12** and **13** prepared from the above experimental procedure was added 1 equiv. of HCl (0.11 ml, 1 M in Et_2O). ^{31}P, ^{1}H, and ^{13}C NMR spectra showed the presence of three products in the reaction mixture corresponding to Ph_2PH (δ ^{31}P −40 ppm, $J_{PH} = 230$ Hz), **16**, and **17**. Complex **16** was identified in situ. Formation of complex **17** was identified after protonolysis of the Zr–C bond to give the corresponding alkyne compound H–C≡C–$SiMe_3$ (cf. following experimental procedure). **16**: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 7.3 (s) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.10 (s, 9H, $SiMe_3$), 5.85 (s, 10H, Cp), 7.40–7.42, 7.66–7.70 (m, 10H, Ph), 8.06 (d, $^3J_{HP} = 42.1$ Hz, 1H, SiCH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 0.0 (d, $^4J_{CP} = 2.9$ Hz, $SiMe_3$), 106.7 (d, $^2J_{CP} = 23.2$ Hz, SiCH), 111.0 (s, Cp), 127.7 (d,

$^2J_{CP} = 5.4$ Hz, *o*-PPh), 134.6 (d, $^3J_{CP} = 20.2$ Hz, *m*-PPh), 139.5 (d, $^1J_{CP} = 7.3$ Hz, *i*-PPh), 225.9 (d, $^1J_{CP} = 41.4$ Hz, ZrCP) ppm; *p*-PPh was not observed.

3.8. Addition of HCl (2 equiv.) on 12 and 13

On the complexes **12** and **13** prepared from the above experimental procedure was added 2 equiv. of HCl (0.22 ml, 1 M in Et_2O). ^{31}P, ^1H, and ^{13}C NMR spectra showed the total disappearance of the starting complexes and the formation in the reaction mixture of four compounds corresponding to **2**, Ph_2PH (δ ^{31}P −40 ppm, $J_{PH} = 230$ Hz), **18**, and H–C≡C–$SiMe_3$. Compounds **18** and H–C≡C–$SiMe_3$ were also formed after addition of HCl (1 equiv.) on complexes **16** and **17** prepared from the procedure described above (cf. Addition of HCl (1 equiv.) on **12** and **13**). **18**: $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ −20.7 (s) ppm. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ 0.30 (d, $^5J_{HP} = 0.6$ Hz, 9H, $SiMe_3$), 6.82 (dd, $^3J_{HP} = 45.4$ Hz, $^3J_{HH} = 15.1$ Hz, 1H, SiCH), 7.24 (dd, $^2J_{HP} = 1.6$ Hz, $^3J_{HH} = 15.1$ Hz, 1H, PCH), 7.32–7.48 (m, 10H, Ph) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$, 25 °C): δ 0.5 (d, $^4J_{CP} = 6.2$ Hz, $SiMe_3$), 128.2 (s, *p*-Ph), 132.4 (d, $^3J_{CP} = 17.8$ Hz, *m*-Ph), 128.3 (d, $^2J_{CP} = 6.1$ Hz, *o*-Ph), 139.4 (d, $^1J_{CP} = 10.1$ Hz, *i*-Ph), 147.2 (d, $^1J_{CP} = 11.2$ Hz, PCH), 151.2 (d, $^2J_{CP} = 41.9$ Hz, SiCH) ppm. GC-MS analysis (He, 1.5 ml mn^{-1}, from 35 to 80 °C (2 °C mn^{-1}) then from 80 to 280 °C (10 °C mn^{-1}); MS (EI, 70 eV) m/z): (H–C≡C–$SiMe_3$) 98 (M^+, 8%), 83 (100%), 53 (11%); (Ph_2PH) 186 (M^+, 58%), 108 (100%); (**18**) 284 (M^+, 85%), 269 (50%), 100 (100%).

3.9. Preparation of Z–$Ph_2PC(H)$=$C(ZrCp_2Cl)SiMe_3$ (20)

A solution of **2** (0.226 g, 0.80 mmol) in THF (10 ml) was added at −20°C to a suspended solution of $[Cp_2ZrHCl]_n$ (**19**) (0.206 g, 0.80 mmol) in THF (10 ml). The reaction mixture was stirred at room temperature for 2 h. Removal of the solvent in vacuo from the yellow solution gave **20** in nearly quantitative yield. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ −21.0 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.44 (s, 9H, $SiMe_3$), 6.00 (s, 10H, Cp), 7.38–7.43, 7.64–7.67 (m, 10H, Ph), 8.40 (s, 1H, PCH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 1.8 (d, $^4J_{CP} = 5.1$ Hz, $SiMe_3$), 110.5 (d, $^1J_{CP} = 40.9$ Hz, PCH), 111.7 (s, Cp), 128,1 (s, *p*-PPh), 129.0 (d, $^2J_{CP} = 5.4$ Hz, *o*-PPh), 133.3 (d, $^3J_{CP} = 18.4$ Hz, *m*-PPh), 139.3 (d, $^1J_{CP} = 14.3$ Hz, *i*-PPh), 232.6 (d, $^2J_{CP} = 8.6$ Hz, ZrCSi) ppm.

3.10. Preparation of Z–$Ph_2PC(H)$=$C(H)SiMe_3$ (18) from 20

To a solution of **20** (0.184 g, 0.34 mmol) in THF (4 ml) was added 1 equiv. of HCl (0.34 ml, 1 M in Et_2O). The reaction mixture was stirred at room temperature for 1 h and then evaporated to dryness. The resulting residue was extracted with pentane and filtered. Removal of the solvent in vacuo from the colourless solution gave **18** in 90% yield. *Anal.* Calc. for $C_{17}H_{21}PSi$ (284.41): C, 71.79; H, 7.44. Found: C, 71.96; H, 7.28%.

3.11. X-ray analysis of zirconaindene complexes 3 and 4

For complexes **3** and **4** data collection have been collected on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford cryosystems cryostream cooler device and using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), at low temperature for **3** and room temperature for **4**. Final unit cell parameters were obtained by means of a least-squares refinement of a set of 5000 well-measured reflections, and a crystal decay was monitored in the course of data collection by measuring 200 reflections by image, any significant fluctuations of intensities have been observed during measurements. Structures have been solved by means of direct methods using the program SIR92 [31] and subsequent differences Fourier maps, then refined by least-squares procedures on a F^2 by using the program SHELXL-97 [32]; atomic scattering factors were taken from International Tables for X-ray crystallography [33]. All hydrogen atoms were located on a difference Fourier maps, but introduced in the refinement as fixed contributors by using a riding model and with an isotropic thermal parameter fixed at 20% higher than those of the C-sp^2 atoms and 50% for the C-sp^3 atoms to which they were connected, the methyl groups were refined with the torsion angle as free variable. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement weighting schemes have been used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Criteria for a satisfactory complete analysis were the ratios of root mean square shift standard deviation being less than 0.1 and no significant features in final difference Fourier maps. Drawings of molecules are performed by using the program ORTEP3 [34] with 50% probability displacement ellipsoids for non-hydrogen atoms.

4. Conclusions

We have demonstrated that coupling reactions of the internal acetylenic derivative Ph_2P–C≡C–$SiMe_3$ (**2**) with both the benzyne complex **1** and the zirconocene like reagent, take place regioselectively to produce primarily metallacyclic derivatives where the α-carbanion is stabilized by the trimethylsilyl group. Quite surprisingly, this regiochemical outcome appears to be much more favourable than the alternate situation where the

chemically unsaturated metal fragment is yet stabilized by the lone pair of the phosphino group Ph_2P–. Nevertheless, we have been able to isolate and structurally characterize the two regioisomers **3** and **4**. The structure of **4** represents the first reported example of an α-phosphino zirconacycle. Significantly, the existence of a Lewis-base/Lewis-acid σ-P–Zr interaction is confirmed here by the occurrence of an unusually acute Zr–C–P angle.

Interestingly, further protonation reactions follow different pathways depending on the nature of the initial regioisomer. Typically, when the phosphino substituent is placed in β-position relative to the metal center, addition of HCl leads to a competition between (i) protonation at the lone pair of the phosphino group followed by P–C cleavage, and (ii) protonolysis of the Zr–CSi bond. Alternatively, when the lone electron pair of the phosphino group is protected by interaction with the metal center thus achieving a stable 18-electron configuration, protonolysis takes place exclusively at the Zr–C bonds thus releasing the corresponding organic moiety.

Our future research efforts in this area will examine the synthetic utility of the phosphorus–carbon bond cleavage in metallacyclic group 4 complexes for the specific synthesis of unsaturated organic derivatives that are difficult to prepare by alternate procedures.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 215453 and 215454 compounds for **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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