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Versatile Behavior of a New Class of Bicyclic Compounds: Zirconacyclopentadiene Phosphiranes

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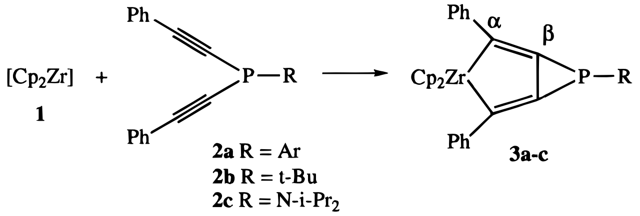
Summary: Diacetylenic phosphanes are cleanly transformed when reacted with zirconocene into zirconacyclopentadiene phosphiranes. These new cyclic systems are the source of a variety of unsaturated phosphorus compounds like phospharadialene or alkenyl alkynyl phosphanes.

Interactions between unsaturated phosphorus compounds and zirconium species usually initiate a totally different chemistry[1−3] than that generally observed when the same zirconium compounds are reacted with the corresponding unsaturated organic or inorganic derivatives.[4] Moreover, the chemical behavior of the resulting metalated phosphorus moieties is also unexpected. Thus, we have already shown that phosphorus placed in a β position to a zirconium fragment induces original rearrangement processes leading, for example, to a large variety of α-functionalized substituted phosphanes: when phosphorus is included in a ring, an unprecedented ring-opening reaction is observed.[1]

Several recent papers describe oxidative alkyne coupling using [Cp_2Zr] leading to a variety of metallacyclic complexes which act as excellent sources of [Cp_2Zr] or give rise to a number of metallacycles when they are reacted with unsaturated organic species.[5] Therefore, taking into account observations mentioned before, investigations concerning coupling reactions involving phosphorus alkynes and [Cp_2Zr] (**1**) should lead to different reactions and unexpected derivatives. Indeed, we report here the synthesis of a new class of compounds, the zirconacyclopentadiene phosphiranes **3a**−**c**. Preliminary experiments on the reactivity of these species toward halogenated compounds demonstrate their versatile behavior.[6]

Scheme 1. Synthesis of Zirconacyclopentadiene-phosphiranes 3 (Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$)



Treatment of phosphanes **2a**−**c** with freshly prepared [Cp_2Zr] (**1**) synthon in THF at −78 °C leads to the ziconacyclopentadiene phosphiranes **3a**−**c** isolated as powders in 90% yield (Scheme 1).[7] These derivatives exhibit remarkably shielded ^{31}P chemical shifts at −300.5 (**3a**) −299.7 (**3b**), and −244.2 (**3c**) ppm which fit well with a phosphirane-type structure. Indeed, the δ ^{31}P value for **3a** is one of the highest reported for a molecule containing strained-membered rings and is apparently exceeded among phosphirane derivatives only by the parent phosphirane compound (δ: −341

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) See, for example: (a) Cénac, N.; Zablocka, M.; Igau, A.; Majoral, J.-P.; Skowronska, A. *Organometallics* **1996**, *15*, 1208. (b) Zablocka, M.; Igau, A.; Cénac, N.; Donnadieu, B.; Dahan, F.; Majoral, J.-P.; Pietrusiewicz, K. M. *J. Am. Chem. Soc.* **1995**, *117*, 8083. (c) Igau, A.; Dufour, N.; Mahieu, A.; Majoral, J.-P.; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 95 and references cited herein.

(2) Reactivity of ^{t}*BuC*≡P with zirconocene derivatives, see: (a) Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergstrasser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207 and references cited herein.

(3) Reactivity of $R_3P{=}CH_2$ with group 4 metallocene derivatives, see, for example: (a) Binger, P.; Glase, G.; Gabor, B.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 81 and references cited herein. (b) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668 and references cited herein. (c) Schmidbaur, H.; Pichl, R. *Z. Naturforsch.* **1985**, *40b*, 352 and references cited herein.

(4) Tetrahedron Symposia in print No. 57: Negishi, E. *Tetrahedron* **1995**, *51*, 4255. For reviews, see for example: (a) Annby, U.; Karlson, S. *Acta Chem. Scand.* **1993**, *47*, 425. (b) Labinger, J. A. *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, p 667. (c) Negishi, E. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: New York, 1991; Vol. 8, p 1163.

(5) For an overview concerning the reaction of zirconocene with bis(alkynyl) derivatives, see, for example: (a) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. **1995**, *117*, 2665. (b) Warner, B. P.; Davis, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5471. (c) Metzler, N.; Nöth, H.; Thomann, M. *Organometallics* **1993**, *12*, 2423. (d) Negishi, E. I.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788.

(6) Part of this work was presented at IVème Journée Grand Sud-Ouest, Toulouse-France, November 25, 1994, and at XIIIth International Conference on Phosphorus Chemistry, Jerusalem-Israel, July 16−21, 1995.

(7) General procedure for the synthesis of **3**: To a solution of dichlorozirconocene [Cp_2ZrCl_2] (0.292 g, 1.0 mmol) in THF (5 mL) at −78 °C was added BuLi in hexane (0.8 mL, 2.5 M). The mixture was stirred for 2 h at −78 °C, then 1 equiv of bis(acetylenic)phosphine in THF (5 mL) was added via canula. The reaction mixture was warmed slowly to room temperature and stirred for a further 3 h. The resulting solution was evaporated to dryness. Successive extractions of the residue with pentane (2 × 30 mL) gave compound **3** as a powder. Satisfactory elemental analysis for **3a**−**c**. **3a**: brown powder, $^{31}P\{^1H\}$ NMR (C_6D_6) δ −300.5 ppm. ^1H NMR (C_6D_6): δ 7.62 (d, $^4J(H,P) = 3.1$ Hz, 2H, CH_{Ar}), 7.35−7.33 (m, 6H, CH_{Ph}), 7.10−7.07 (m, 4H, CH_{Ph}), 5.40 (s, 5H, Cp), 5.38 (s, 5H, Cp), 1.30 (s, 18H, *o*-*t*Bu), 1.19 (s, 9H, *p*-*t*Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 168.7 (d, $^2J(C,P) = 4.0$ Hz, CZr), 159.1 (d, $^1J(C,P) = 5.0$ Hz, *i*-C_{Ar}), 150.8 (s, *o*-C_{Ar}), 149.3 (s, *m*-C_{Ar}), 145.3 (s, *i*-C_{Ar}), 130.3 (d, $^3J(C,P) = 15.6$ Hz, *i*-C_{Ph}), 129.5 (s, *o*-C_{Ph}), 128.9 (s, *m*-C_{Ph}), 123.1 (s, *p*-C_{Ph}), 107.3 (s, Cp), 106.9 (s, Cp), 88.5 (d, $^1J(C,P) = 62.7$ Hz, $P\mathit{C}{=}C$), 39.7 (s, *p*-$\mathit{C}CH_3$), 34.6 (d, $^3J(C,P) = 8.6$ Hz, *o*-$\mathit{C}CH_3$), 32.3 (s, *o*-$CC\mathit{C}H_3$), 32.0 (s, *p*-$C\mathit{C}H_3$). **3b**: yellow powder, $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −299.7. ^1H NMR (CD_2Cl_2): δ 8.29−8.26 (m, 4H, Ph), 7.52−7.46 (m, 6H, Ph), 5.65 (s, 5H, Cp), 5.34 (s, 5H, Cp), 0.98 (d, $^3J(H,P) = 12.5$ Hz, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 165.7 (d, $^2J(C,P) = 6.0$ Hz, CZr), 139.7 (s, *i*-C_{Ph}), 128.8 (s, *o*-C_{Ph}), 128.1 (s, *m*-C_{Ph}), 127.7 (s, *p*-C_{Ph}), 105.2 (s, Cp), 105.1 (s, Cp), 79.1 (d, $^1J(C,P) = 64.5$ Hz, $P\mathit{C}{=}C$), 33.9 (d, $^1J(C,P) = 42.2$ Hz, $CH_3\mathit{C}$), 26.6 (d, $^2J(C,P) = 15.7$ Hz, $\mathit{C}H_3C$). **3c**: red powder, $^{31}P\{^1H\}$ NMR (C_6D_6) δ −244.2. ^1H NMR (C_6D_6): δ 8.13−8.09 (m, 4H, CH_{Ph}), 7.53−7.26 (m, 6H, CH_{Ph}), 5.65 (s, 5H, Cp), 5.43 (s, 5H, Cp), 2.75 (sept, $^3J(H,H) = 6.7$ Hz, 2H, $CH_3C\mathit{H}$), 1.08 (d, $^3J(H,H) = 6.7$ Hz, 12H, $C\mathit{H}_3CH$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 168.9 (d, $^2J(C,P), = 7.6$ Hz, CZr), 134.1 (s, *i*-C_{Ph}), 129.7 (s, *m*-C_{Ph}), 129.5 (s, *p*-C_{Ph}), 129.2 (s, *o*-C_{Ph}), 106.0 (s, Cp), 105.9 (s, Cp), 85.5 (d, $^1J(C,P) = 71.3$ Hz, $P\mathit{C}{=}C$), 46.1 (d, $^2J(C,P) = 7.4$ Hz, $CH_3\mathit{C}H$), 24.2 and 24.1 (s, $\mathit{C}H_3CH$).

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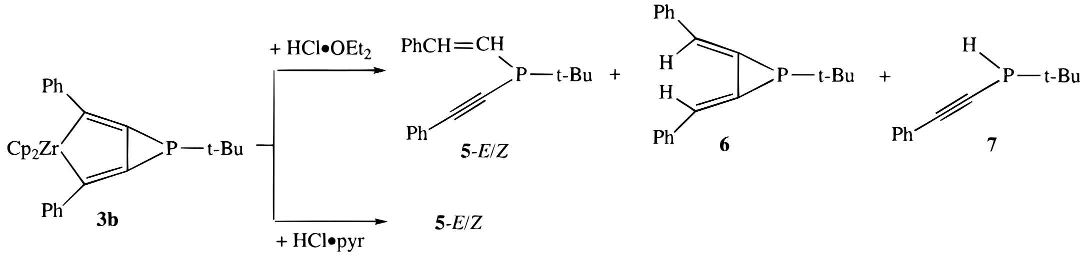
Scheme 2. Reactivity of 3b with Electrophile H$^+$



ppm).[8] Cp groups are inequivalent and appear as two singlets both in the ^{1}H and ^{13}C NMR spectra. ^{13}C NMR spectra show a doublet at 165.7−168.9 ppm ($^2J_{CP}$, 4.0−7.6 Hz) characteristic for sp^2 carbon atoms bound to zirconium[9] and a doublet at 79.1−88.5 ppm ($^1J_{CP}$, 62.7−71.3 Hz) characteristic for sp^2 carbon atoms bound to phosphorus. These data agree with the proposed structure. While compounds **3b** and **3c** are found to be stable at room temperature for several days, in contrast, **3a** is transformed into a new derivative not yet fully characterized overnight at room temperature.[10]

Attempts to get suitable crystals for X-ray structure determinations of compounds **3a**−**c** have failed up to now. Therefore, in order to have a better insight of the structure and properties of these new metalated phosphorus species, a preliminary study of their reactivity was undertaken. Addition of HCl·OEt$_2$ to the phosphirane **3b** in THF at −78 °C leads to a mixture of four products: the alkenyl−alkynyl phosphanes *E*/*Z*-**5** (35%) in a 1/1 ratio, the phospharadialene **6** (35%), and the secondary phosphane **7** (30%) (Scheme 2). All of these compounds are fully characterized by NMR[11] and mass spectrometry. The molecular structure of *Z*-5 (as its sulfide adduct **8**) is also established by X-ray crystallography studies[12] (Figure 1), which confirms that a selective monoreduction of one of the two alkenyl groups of the starting phosphane **2b** takes place. Interestingly, such a selective monoreduction occurs when **3b** is reacted with HCl·pyridine: products *E*/*Z*-5 (1/1 ratio) are obtained in quantitative yield.

NMR data for **6** fit well with the values given for the few phospharadialenes already reported in the literature.[13] The ^{31}P NMR spectrum exhibits a singlet at high field ($\delta = -131.1$ ppm), and classical ^{13}C resonances for the cyclic ($\delta = 119.5$, $^1J_{CP} = 40.9$ Hz) and acyclic ($\delta = 122.8$, $^2J_{CP} = 4.6$ Hz) sp^2 carbon atoms are detected. The radialene structure of **6** is unambiguously determined by X-ray analysis[12] (Figure 2) and compares well with the unique structure of this type, **9**, characterized by X-ray analysis.[14] Slightly longer intracylic P−C bonds (1.825−1.827 Å for **6**; 1.816 Å for **9**) and a slightly shorter intracyclic C−C bond (1.413 Å for **6**; 1.422 Å for **9**) are found for **6**.

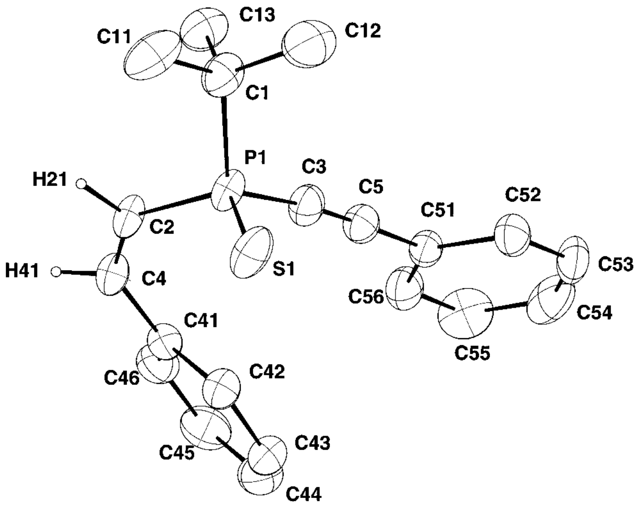
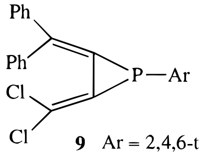


Figure 1. Molecular structure of **8** in the crystal. Selected distances (Å) and angles (deg): P(1)−S(1) 1.951(1), P(1)−C(1) 1.827(4), P(1)−C(2) 1.804(4), P(1)−C(3) 1.743(4), C(2)−C(4) 1.307(5), C(3)−C(5) 1.204(5), C(4)−C(41) 1.462(5), C(5)−C(51) 1.433(6), S(1)−P(1)−C(1) 113.7(1), S(1)−P(1)−C(2) 115.2(1), P(1)−C(2)−C(4) 129.9(3), P(1)−C(3)−C(5) 173.5(4), C(1)−P(1)−C(2) 104.1(2), C(1)−P(1)−C(3) 104.8(2), C(2)−P(1)−C(3) 105.6(2), C(2)−C(4)−C(41) 131.9(4), C(3)−C(5)−C(51) 178.1(4).

Formation of *E*/*Z*-**5**, **6**, and **7** can be easily explained via the transient generation of the complex **10** resulting from the cleavage of a zirconium−carbon bond and subsequent protonation (Scheme 3). Such an intermediate can react with a second equivalent of HCl to give *E*/*Z*-**5** via phosphirane ring opening and **6** via substitution of the remaining zirconium fragment.[15]



9 Ar = 2,4,6-t-Bu$_3$C$_6$H$_2$

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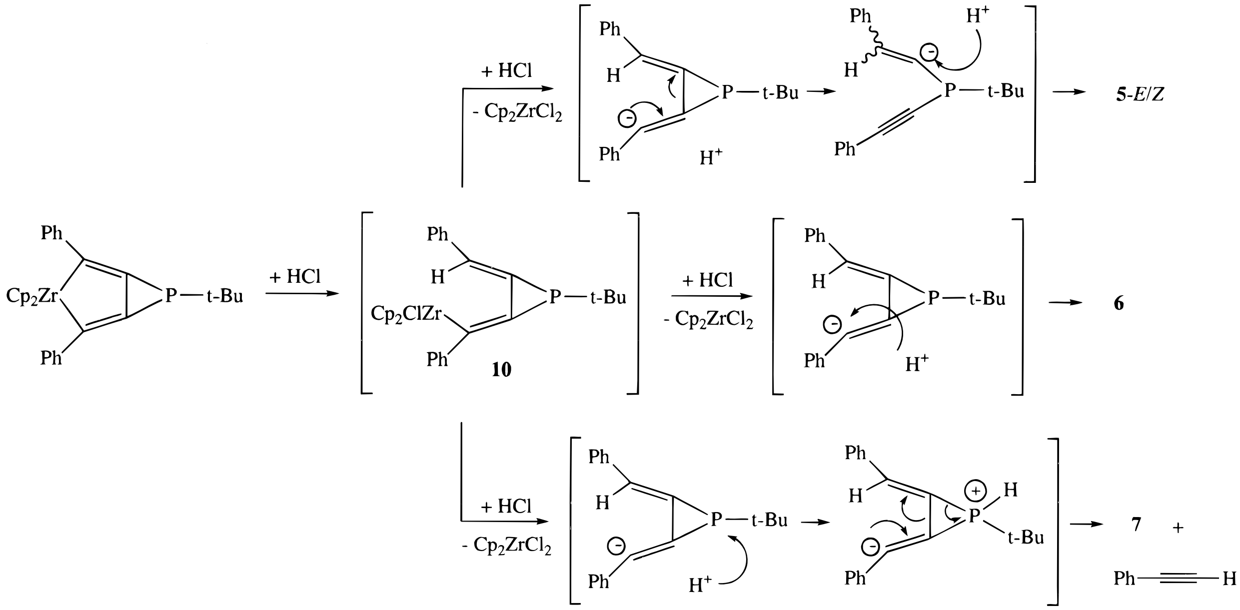
[8] (a) Mathey, F. *Chem. Rev.* **1990**, 997−1025. (b) Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *25*, 1097.

[9] Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65.

[10] This transformation can be easily monitored by ^{31}P NMR since a $\Delta\delta$ of 584 ppm is detected! ^{13}C and ^{1}H NMR data for this new species are not informative enough to propose, unambiguously, a structure. Attempts to get suitable crystals for an X-ray structure determination have failed up to now.

[11] Selected NMR data for componds *E*/*Z*-**5** and **6**. *E*-**5**: ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −16.4. ^{1}H NMR (C$_6$D$_6$): δ 7.72−7.65 (m, 4H, CH$_{Ph}$), 7.39−7.24 (m, 6H, CH$_{Ph}$), 7.21 (dd, ^3J(H,P) = 13.5 Hz, ^3J(H,H) = 16.9 Hz, 1H, =CHPh), 6.75 (dd, ^2J(H,P) = 14.5 Hz, ^3J(H,H) = 16.9 Hz, 1H, PCH=), 1.30 (d, ^3J(H,P) = 13.6 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 143.7 (d, ^2J(C,P) = 26.0 Hz, =CHPh), 135.0 (d, ^3J(C,P) = 7.2 Hz, *i*-C$_{Ph}$), 131.9 (s, *o*-C$_{Ph}$), 129.8 (s, *p*-C$_{Ph}$), 127.9 (s, *m*-C$_{Ph}$), 122.5 (d, ^1J(C,P) = 13.2 Hz, PCH=), 106.2 (s, ≡CPh), 86.2 (d, ^1J(C,P) = 16.2 Hz, PC≡), 31.4 (d, ^1J(C,P) = 4.4 Hz, CH$_3$*C*), 27.4 (d, ^2J(C,P) = 13.1 Hz, *C*H$_3$C). *Z*-**5**: ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −35.3. ^{1}H NMR (C$_6$D$_6$): δ 7.72−7.65 (m, 4H, CH$_{Ph}$), =C*H*Ph resonance hidden by phenyl signals, 7.39−7.24 (m, 6H, CH$_{Ph}$), 6.39 (dd, ^2J(H,P) = 2.5 Hz, $^3J_{HH}$ = 12.7 Hz, 1H, PCH=), 1.28 (d, ^3J(H,P) = 13.5 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 144.6 (d, ^2J(C,P) = 19.5 Hz, =CHPh), 136.9 (d, ^3J(C,P) = 2.2 Hz, *i*-C$_{Ph}$), 131.9 (s, *o*-C$_{Ph}$), 128.3 (s, *p*-C$_{Ph}$), 127.9 (s, *m*-C$_{Ph}$), 124.9 (d, ^1J(C,P) = 17.3 Hz, PCH=), 104.1 (s, ≡CPh), 87.3 (d, ^1J(C,P) = 29.4 Hz, PC≡), 31.5 (d, ^1J(C,P) = 4.3 Hz, CH$_3$*C*), 27.2 (d, ^2J(C,P) = 15.2 Hz, *C*H$_3$C). **6**: recrystallized from THF as yellow crystals. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = −131.1. ^{1}H NMR (C$_6$D$_6$): δ 7.72−7.65 (m, 4H, CH$_{Ph}$), 7.55 (d, ^3J(H,P) = 9.6 Hz, 2H, =CHPh), 7.39−7.24 (m, 6H, CH$_{Ph}$), 1.13 (d, ^3J(H,P) = 12.7 Hz, 9H, *t*Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 137.7 (d, ^3J(C,P) = 2.3 Hz, *i*-C$_{Ph}$), 128.3 (s, *p*-C$_{Ph}$), 127.9 (s, *m*-C$_{Ph}$), 127.2 (d, ^4J(C,P) = 2.4 Hz, *o*-C$_{Ph}$), 122.8 (d, ^2J(C,P) = 4.6 Hz, =CHPh), 119.5 (d, ^1J(C,P) = 40.9 Hz, PC=), 35.6 (d, ^1J(C,P) = 39.1 Hz, CH$_3$*C*), 29.2 (d, ^2J(C,P) = 14.3 Hz, *C*H$_3$C). Satisfactory analysis were found for *E*/*Z*-**5** and **6**.

Scheme 3. Proposed Mechanism for the Formation of *E*/*Z*-5, 6, and 7



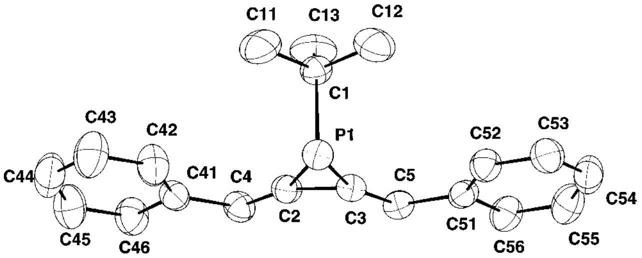
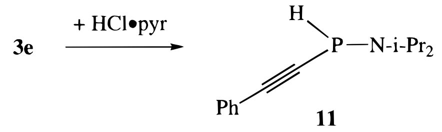


Figure 2. Molecular structure of **6** in the crystal. Selected distances (Å) and angles (deg): P(1)−C(1) 1.884(3), P(1)−C(2) 1.827(3), P(1)−C(3) 1.825(3), C(2)−C(3) 1.413(4), C(2)−C(4) 1.330(4), C(3)−C(5) 1.327(4), C(4)−C(41) 1.454(4), C(5)−C(51) 1.457(4), P(1)−C(2)−C(4) 150.8(2), P(1)−C(2)−C(3) 67.1(2), P(1)−C(3)−C(2) 67.3(2), P(1)−C(3)−C(5) 151.9(2), C(1)−P(1)−C(2) 107.1(1), C(1)−P(1)−C(3) 107.2(1), C(2)−P(1)−C(3) 45.5(1), C(2)−C(4)−C(41) 128.5(3), C(3)−C(5)−C(51) 128.8(3), C(2)−C(3)−C(5) 140.8(3), C(3)−C(2)−C(4) 142.0(3).

The formation of the secondary phosphane **7** (δ ^{31}P = −55.1, $^{1}J_{PH}$ = 216.7 Hz) might involve first the protonation on the phosphorus atom of the complex **10**, concomitant cleavage of the zirconium−carbon bond, then ring opening and phosphorus carbon bond cleavage. Such a mechanism should be favored for a species like **3e** possessing a donor group bonded to phosphorus. Indeed, addition of HCl·pyridine to **3e** gives rise exclusively to the secondary phosphane **11** (δ ^{31}P = −129.0, $^{1}J_{PH}$ = 249.9 Hz) (Scheme 4).

Scheme 4. Synthesis of the Secondary Phosphane 11



It has been already reported that zirconacyclopentadienes react with a dichlorophosphane, such as $PhPCl_2$, to give the corresponding phosphole.[16] This metallacycle transfer is not observed when, for example, **3b** is treated with $RPCl_2$ (R = C_6H_5 or 2,4,6(tBu)$_3$C$_6$H$_2$). In this case, the bis(alkynyl)phosphane **2b** is formed in addition to either the cyclic polyphosphane $(PhP)_5$ or the diphosphene (tBu)$_3$C$_6$H$_2$—P=P—C$_6$H$_2$(tBu)$_3$. Compound **2b** is also recovered when **3b** is reacted with (trimethylsilyl)trifluoromethane sulfonate.

Work is in progress to extend these reactions to other bis(alkynyl)phosphanes and to study the chemical reactivity of phosphirane zirconacyclopentadienes species.

Acknowledgment. We thank the CNRS for financial support.

Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **6** and **8** (18 pages). Ordering information is given on any current masthead page.

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(12) Crystal data for *Z*-**5** (as the sulfide adduct **8**) and **6**. ENRAF-NONIUS CAD4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å); graphite monochromator. Crystal data for **6**: crystal dimensions (mm) 0.9 × 0.5 × 0.125, monoclinic space group $P2_1/n$, a = 10.809(2) Å, b = 6.125(2) Å, c = 25.442(8) Å, V = 1674 Å^3, Z = 4, ρ_{calcd} = 1.16 g cm^{-3}, $F(000)$ = 624.45; 3811 reflections with $3 < 2\theta < 52°$, 1875 reflections with $I > 3.0\sigma(I)$. Structure solution and refinement for 3284 independent reflections with $I > 3.0\sigma(I)$ and 191 parameters. R = 0.038; R_w = 0.038. Residual electron density max 0.189, min −0.177 e Å^{-3}. Crystal data for **8**: crystal dimensions mm 0.3 × 0.4 × 0.2, orthorhombic space group $P2_12_12_1$, a = 6.037(3)Å, b = 14.887(3) Å, c = 20.049(8) Å, V = 1674 Å^3, Z = 4, ρ_{calcd} = 1.19 g cm^{-3}, $F(000)$ = 689.88; 1845 reflections with $3 < 2\theta < 50°$, 1457 reflections with $I > 3.0\sigma(I)$. Structure solution and refinement for 1682 independent reflections with $I > 3.0\sigma(I)$ and 201 parameters. R = 0.027; R_w = 0.029. Residual electron density max 0.189, min −0.165 e Å^{-3}. The structures were solved by direct methods (SHELXS86) and refined according to the CRYSTALS program. The positions of all hydrogen atoms were determined from difference Fourier maps but introduced in calculated positions (C−H = 0.98 Å) and thermal parameters fixed 20% higher than those of the carbon atoms to which they were attached. All non-hydrogen atoms were anisotropically refined. Corrections for Lorentz polarization effects and semi-empirical absorption corrections were applied.

(13) Maerker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933.

(14) Miyahara, I.; Hayashi, A.; Hirotsu, K.; Yoshifuji, M.; Yoshimura, H.; Toyota, K. *Polyhedron* **1992**, *3*, 385.

(15) Such results can be compared with those recently reported concerning the treatment of zirconacyclopentadiene derivatives with HCl: cleavage of the carbon−zirconium bond was also observed with formation either of (*E,E*) butadiene compounds[5c] or alkenyl-alkynyl derivatives.[5b]

(16) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.