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Intramolecular coupling of acetylenic groups of bis(alkynyl)phosphanes and silanes mediated by benzynezirconocene: a route to new mono- and tricyclic heterocycles

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Abstract—Benzo-zirconacyclohexadiene-phospha or silacyclobutene fused ring systems are easily prepared via a benzynezirconocene intermediate by means of thermolysis of Cp_2ZrPh_2 in the presence of bis(alkynyl)phosphanes or silanes. These polyunsaturated systems are the source of a variety of new mono- or tricyclic heterocycles incorporating either one or two heteroatoms.

1. Introduction

The development of new and practical methods for the formation of carbon–carbon bonds is currently among the main goals of a number of research groups throughout the world. In recent years much attention has been paid to the chemistry of group 4 elements and especially zirconium species to reach this objective.[1] Zirconocene complexes have shown a versatile behavior for such reactions. It was well demonstrated that the zirconocene fragment [Cp_2Zr] promoted the intramolecular coupling of alkynyl groups with formation of cyclic derivatives[2] or coupling of diynes with formation of zirconacyclic cumulenes[3,4] to quote a few examples. Some of the resulting metallacycles were found to be useful starting reagents for the synthesis of a variety of carbo- and heterocycles with carbon–carbon bond formation.[5] As an example, azazirconacyclopentadienes or zirconacyclopentadienes are a source of pyridine or benzene derivatives when reacted with alkynes.[6] Insertion of isocyanide[7,8] or carbon monoxide[8,9] on zirconacyclopentadienes and related species allowed the preparation of the corresponding cyclic imines or ketones. Insertion of acetylenic or olefinic systems into benzynezirconocene has also been described[10–12] leading via carbon–carbon bond formation to new metallafused rings.

A few years ago we reported a novel intramolecular coupling reaction of a bis(alkynyl)phosphane *t*BuP($C{\equiv}CPh)_2$ mediated by benzynezirconocene which provided a quite unexpected tricyclic zircona-1,2-dihydrophosphete which treated with HCl or $PhSbCl_2$ gave access to unprecedented mono- or tricyclic 1,2-dihydrophosphetes.[13] This was the first example, to our knowledge, of a reaction of dialkynes with arynezirconocene complexes. Therefore there was a need to check whether the cleavage of zirconium–carbon bonds with HCl, or transmetallation with various dihalogenated derivatives, of various zircona polyunsaturated heterocycles should allow us to propose a general and convenient procedure for the regioselective synthesis of a variety of new mono- or tricyclic heterocycles incorporating either one or two heteroatoms.

This paper affords a positive answer to these interrogations with the synthesis, using this methodology, of a variety of polyunsaturated systems incorporating one or two of the following elements: zirconium, phosphorus, silicon, germanium, tin, antimony and arsenic. None of these families of polycycles are accessible using known procedures. X-Ray diffraction studies of three of these

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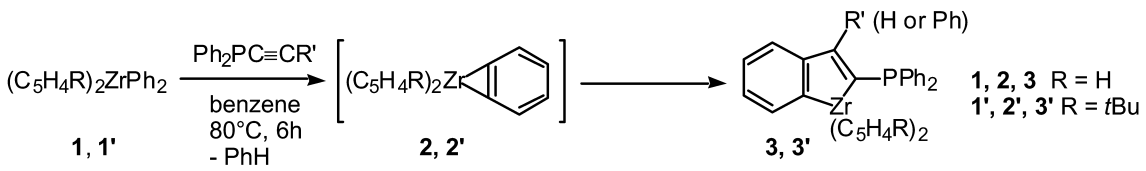


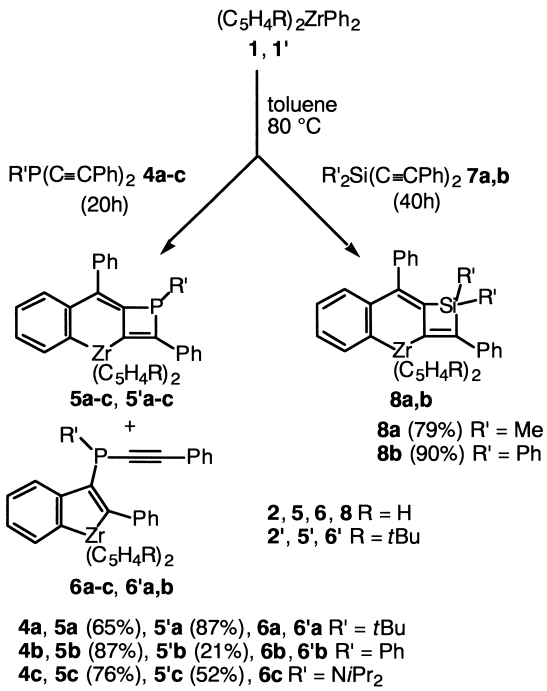
Scheme 1.

derivatives corroborated their structure and brought arguments for the mechanism of formation of these compounds.

2. Results and discussion

Thermolysis of $(\eta^5\text{-}C_5H_4R)_2ZrPh_2$ **1**, **1′** in the presence of mono(alkynyl)phosphanes $Ph_2PC{\equiv}CR'$ has previously been shown to produce 2-phosphino-1-zirconaindenes **3**, **3′** arising from the regiospecific insertion of the carbon–carbon triple bond of the acetylenic group into the zirconium–carbon bond of the in situ-generated benzyne-zirconocenes **2**, **2′** (Scheme 1).[11b]

A similar reaction was undertaken with bis(alkynyl)-phosphanes and diphenylzirconocene. Treatment of $R'P(C{\equiv}CPh)_2$ (**4a**: R′=*t*Bu, **4b**: R′=Ph, **4c**: R′=N*i*Pr$_2$) with $(\eta^5\text{-}C_5H_5)_2ZrPh_2$ **1** in toluene at 80 °C over 20 h did not afford the expected 2-(alkynyl)phosphino-1-zirconaindenes. Surprisingly, trapping of the transient benzyne complex $Cp_2Zr(\eta^2\text{-}C_6H_4)$ **2** by the diacetylenic phosphanes resulted in the formation of fused benzo-zirconacyclohexadiene-phosphacyclobutene rings **5a-c** (Scheme 2). ^{31}P NMR spectra of crude products displayed a largely major signal (>85%) at 59.9 (**5a**), 21.3 (**5b**) and 46.3 (**5c**) ppm beside a minor peak at −11.8, −30.1 and 4.2 ppm, respectively. A simple wash with pentane allowed the isolation of the zirconacycles **5a-c** in 65, 87, and 76% yield, respectively. The $\delta\,^{31}P$ values for **5a-c** are deshielded compared with those of starting phosphanes (**4a**: −38.9 ppm; **4b**: −62.8 ppm; **4c**: −16.6 ppm) indicating that the phosphorus atom is no more bonded to a sp carbon atom. The side complexes were identified as 3-(alkynyl)phosphino-1-zirconaindenes **6a-c** and will be discussed later.



Scheme 2. Synthesis of zirconacycles **5a-c**, **5′a-c** and **8a**,**b**.

Complexes **5a-c** were further characterized by the usual spectroscopic and analytical methods: ^1H NMR (two signals around 6 ppm for the two unequivalent cyclopentadienyl ligands) and ^{13}C NMR (no classical acetylenic carbon resonances in the 70–110 ppm range), IR (no characteristic C≡C absorption band around 2100 cm^{-1}), mass spectrometry and elemental analyses. Nevertheless identification based only on spectroscopic data was uncertain. However, an X-ray structural analysis of **5a** established the molecular structure of these tricyclic zircona-1,2-dihydrophosphetes and demonstrated the intramolecular coupling reaction of dialkynylphosphanes and zirconabenzyne. The solid-state structure of **5a** has already been reported in a preliminary communication.[13]

The same reaction performed with the more hindered bis(*tert*-butylcyclopentadienyl)diphenyl zirconium **1′** and the bis(phenylalkynyl)phosphanes **4a-c** led to the fully characterized *t*BuCp-substituted tricyclic complexes **5′a-c** (Scheme 2). These zirconacycles presented similar spectroscopic data to those of **5a-c** ($\delta\,^{31}P$=61.7 (**5′a**), 22.9 (**5′b**), 46.4 (**5′c**) ppm). In some cases, the side complexes namely 3-(alkynyl)phosphino-1-zirconaindenes **6′a**,**b** were also detected in the ^{31}P NMR spectra of the crude products (**6′a**: −12.6; **6′b**: −30.7 ppm).

Thermolysis of diphenylzirconocene in the presence of bis(alkynyl)silanes was investigated, in order to check if such a quite unusual intramolecular carbon bond formation involving *gem*-alkynyl groups can or cannot be extended to other *gem*-diacetylenic systems.

Addition of $R'_2Si(C{\equiv}CPh)_2$ (**7a**: R′=Me, **7b**: R′=Ph) to the transient benzynezirconocene **2** in toluene at 80 °C over 40 h provided the fused benzo-zirconacyclohexadiene-silacyclobutenes **8a**,**b** isolated as powders in 79 and 90% yield, respectively, after work-up (Scheme 2). Their ^1H NMR spectra showed one cyclopentadienyl signal at δ=5.99 (**8a**) and δ=6.05 (**8b**) ppm. IR and ^{13}C NMR data corroborated the absence of a Si–C≡C–Ph group indicating that the 2-(alkynyl)sila-1-zirconaindenes were not formed. All the other NMR data were in agreement with the tricyclic structure of **8**. Nevertheless, an X-ray structure determination of **8a** was undertaken in order to complete the characterization of these zirconacycles. The molecular view of **8a** is shown in Figure 1, and the most representative bond lengths and angles are summarized. This clearly shows that

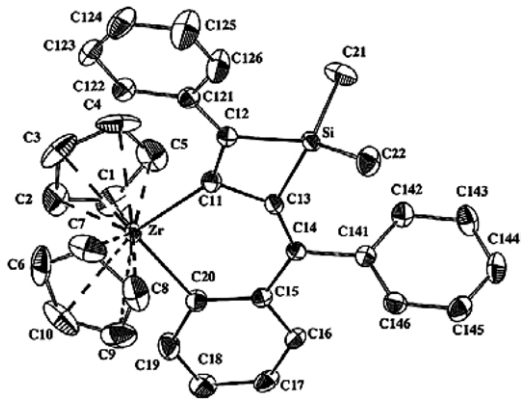
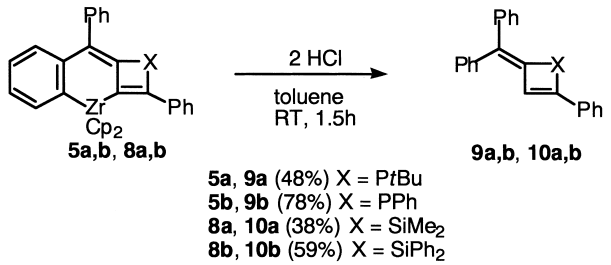


Figure 1. Molecular structure of **8a** (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°): Zr–C20 2.267(2), C20–C15 1.416(3), C15–C14 1.483(3), C14–C13 1.357(3), C13–C11 1.522(3), Zr–C11 2.241(2), C11–C12 1.374(3), Si–C12 1.860(2), Si–C13 1.869(2); C20–Zr–C11 94.97(8), Zr–C11–C13 111.03(14), Zr–C11–C12 145.92(15), C12–C11–C13 103.05(17), C11–C13–Si 88.33(13), C11–C12–Si 93.32(14), C13–Si–C12 74.92(9).

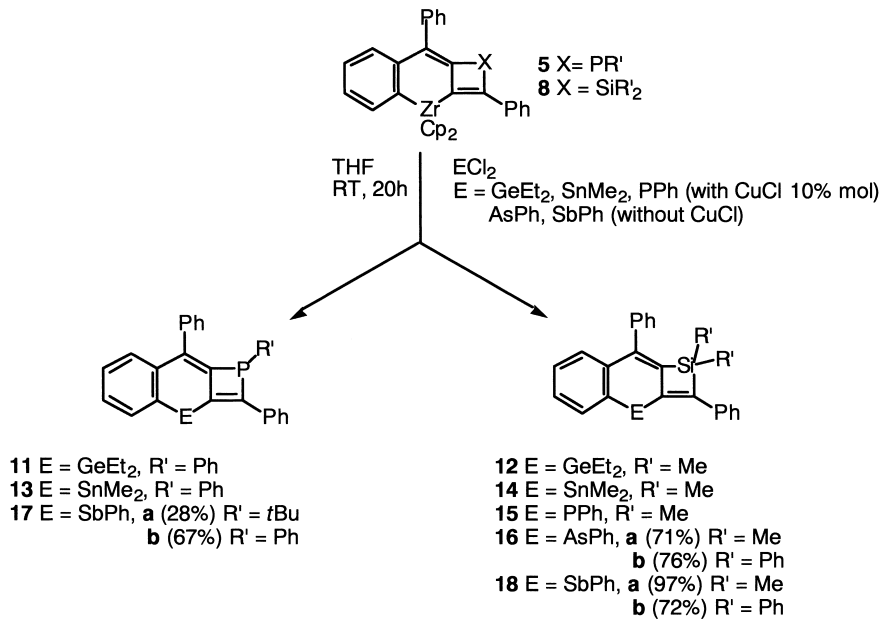
a fused benzo-zirconacyclohexadiene-silacyclobutene ring system is present in the structure. Interestingly only a few examples of metallacyclohexadienes of group 4 are known.[13,14] The molecular structure reveals a characteristic bent metallocene arrangement of the ligands around zirconium. Distances from the metal to the cyclopentadienyl ring centers are both 2.223 Å. The angle between the geometrical centers of both Cp rings and the zirconium is 134.36°. The bond lengths of the two Zr–C(sp^2) are 2.267(2) Å and 2.241(2) Å for Zr–C20 and Zr–C11, respectively. The C20–Zr–C11 angle is 94.97(8)°. These data are in good agreement with those of previously described zirconocenes. Indeed the molecular structures of **8a** and **5a** closely resemble each other, differences coming only from the four-membered ring.



Scheme 3. Reactivity of benzo-zirconacyclohexadiene-phospha or -sila-cyclobutenes towards HCl.

Amazingly, these new zirconacyclic complexes were found to be stable on exposure to air during several weeks in the solid state. Two types of reaction were performed with these zirconacycles: addition of HCl, and exchange reactions with a variety of dihalogenated main group element species. The cleavage of the two covalent zirconium–carbon bonds in **5** or **8** was achieved upon treatment with HCl leading to (*exo*-alkylidene)phospha- or silacyclobutene derivatives (Scheme 3), thus offering a new preparative method of these four-membered rings.[15] After appropriate work-up, the compounds **9** (X=PR′) and **10** (X=SiR'_2) were obtained as coloured oils in good to moderated yields (38–78%). They were characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectral analysis.

Exchange of the Cp_2Zr moiety was also attempted with group 14 and 15 elements by the way of a metallacycle transfer reaction of the carbon fragment from the six-membered zirconacycle to a main group halide (Scheme 4).[16] Complexes **5**, **8** did not react with Et_2GeCl_2 or Me_2SnCl_2 to give the corresponding six-membered germa- or stannacycles, even under prolonged reaction times or as high temperature. However, expected derivatives were obtained when the reaction was conducted in the presence of 10 mol% of CuCl.[17] The compounds **11**–**14** could not be isolated in pure form since a small amount of Cp_2ZrCl_2 always remained even after several column chromatographies, but mass spectrometry (parent ion $[M]^+$ and fragmentation peaks $[M-Et_2Ge]^+$ or $[M-Me_2Sn]^+$) was in



Scheme 4. Exchange reactions from benzo-zirconacyclohexadiene-phospha or -silacyclobutenes.

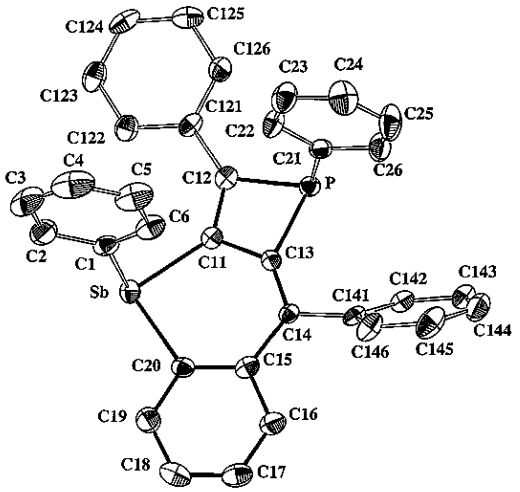
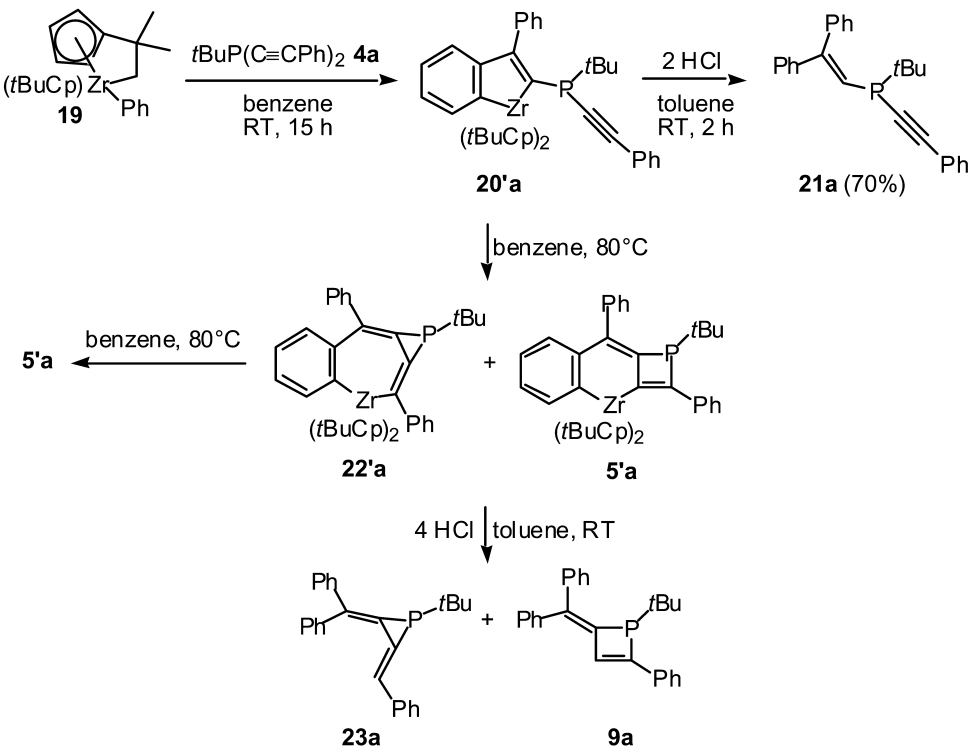


Figure 2. Molecular structure of **17b** (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°): Sb–C1 2.155(4), Sb–C20 2.159(4), C20–C15 1.416(6), C15–C14 1.483(6), C14–C13 1.358(6), C13–C11 1.450(5), Sb–C11 2.122(4), C11–C12 1.364(6), P–C12 1.851(4), P–C13 1.858(4); C20–Sb–C1 98.14(15), C11–Sb–C1 92.25(16), C20–Sb–C11 90.64(15), Sb–C11–C13 121.3(3), Sb–C11–C12 137.0(3), C12–C11–C13 101.0(4), C11–C13–P 91.9(3), C11–C12–P 95.1(3), C13–P–C12 71.69(18).

agreement with the general formula of **11**–**14** and the other NMR data corroborated the proposed structure. Similarly the phosphorus tricyclic compound **15** contaminated by traces of Cp_2ZrCl_2 was obtained from the reaction of **8** with $PhPCl_2$. In marked contrast the treatment of **5** with $PhPCl_2$ gave rise to several phosphorus species as indicated by ^{31}P NMR. The six-membered arsacycles **16** were prepared from **8** and $PhAsCl_2$ and fully characterized; interestingly, it was not necessary to use CuCl in this case. The best results were obtained when $PhSbCl_2$ was used. The six-membered stibacycles **17**, **18** were isolated in quite good yield after work-up and characterized by usual spectroscopic and analytical methods. For the heterocycles incorporating phosphorus and antimony atoms, the transformation was diastereoselective as indicated by the singlet in the ^{31}P NMR spectrum of the crude product (δ ^{31}P=73.7 **17a**, 42.2 **17b** ppm). Confirmation of the identity of **17b** and as a consequence of the other tricyclic systems was achieved by a single-crystal X-ray study. The representation of the structure of **17b** is shown in Figure 2, and the relevant bond lengths and angles are summarized. The molecular structure shows that the compound **17b** has the expected [6,6,4]-fused ring system and is very similar to that of the previously described zirconacycle **5a**.[13] In the six-membered stibacyclic ring, the three Sb–C(sp^2) distances are identical in length to those found in known tertiary stibines,[18] e.g. Ph_3Sb 2.155 Å; $(C_4H_3S)_3Sb$ 2.129 Å. The phenyl groups linked to antimony and phosphorus atoms are in *trans* position.

Therefore, zirconatricyclic complexes appear to be useful reagents allowing, via reactions involving selective Zr–C bond cleavage or Zr-groups 14–15 exchanges, the formation of a variety of new polyunsaturated mono or tricyclic systems.

In order to gain a deeper understanding of the unusual intramolecular coupling of acetylenic groups of bis(phenylalkynyl)phosphanes or silanes using benzynezirconocene complexes, we investigated the reaction mechanism. When the bis(alkynyl)phosphane **4a** was allowed to react with $(\eta^5\text{-}C_6H_4t\text{Bu})_2ZrPh_2$ **1′** in benzene at 80 °C for only 4 h, the formation of several phosphorus species can be detected. The ^{31}P NMR spectrum of the crude product showed a major peak at δ=−16.5 ppm in addition to four minor peaks at δ=61.6 (**5′a**), δ=−12.6, δ=−38.9 (**4a**) and δ=−181.9 ppm. Further reaction time (16 h) at 80 °C resulted

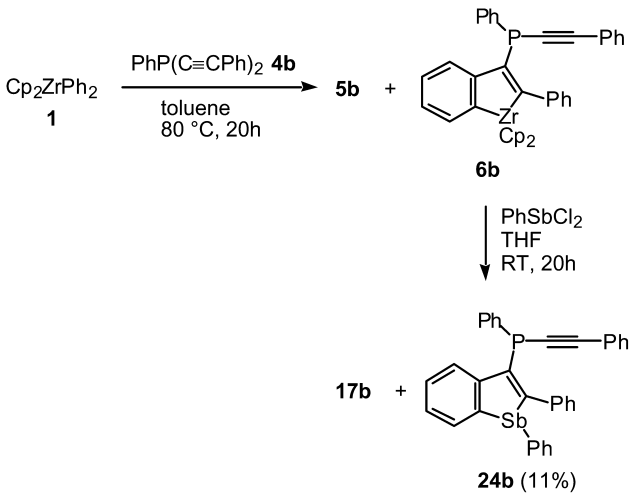


Scheme 5. Chemical evidence for the formation of a 2-(alkynyl)phosphinozirconaindene complex.

in the disappearance of the signals of the two intermediate complexes at −16.5 and −181.9 ppm as well as of the signal of the starting phosphane **4a**. The *t*BuCp-substituted tricyclic complex **5′a** was isolated after removal of the side product responsible of a signal at −12.6 ppm in ^{31}P NMR with pentane. In order to avoid the twofold insertion reaction of the bis(alkynyl)phosphane with the zirconium species, and to characterize the intermediates (δ^{31}P= −16.5, −181.9 ppm), we performed a similar reaction with the cyclometallated complex **19**. This compound, as a consequence of C–H bond activation of the methyl substituent of a *tert*-butyl group, often reacts at lower temperatures than benzynezirconocene.[19] Treatment of a freshly prepared solution of **19** in benzene at room temperature with **4a** afforded only one compound (δ^{31}P=−16.5 ppm) formed in near quantitative yield after stirring for 15 h (Scheme 5). It could not be isolated in pure form since a small amount of (*t*BuCp)$_2$ZrPh$_2$ **1′** always remained even after several treatments. Attempts to get suitable crystals for X-ray structure determination have failed up to now. The ^{31}P chemical shift is in the expected range for a P–C≡C unit. IR data are also instructive, as one characteristic absorption band appeared at 2172 cm^{-1} which can be assigned to the P–C≡C stretching mode of **20′a**. Surprisingly, the regioisomeric complex **6′a** (see Scheme 2) was not observed in the crude product. Thermolysis of **20′a** for 20 h at 80 °C in benzene gave **5′a** (Scheme 5). The reaction was monitored by ^{31}P NMR spectroscopy which showed the disappearance of the signal due to **20′a** which was replaced by the signal of the zirconacycle **5′a** along with a small signal at −181.9 ppm. Such a shielded signal is in favor of a constrained three-membered phosphorus ring, i.e. phosphirane.[20] This assumption is supported by the following experiment: addition of HCl 1N to the mixture of compounds obtained after heating **4a** and **1′** at 80 °C for 4 h, gave rise to the known compounds **9a**, **21a** and to the phospharadialene **23a** (δ^{31}P=−143.5 ppm)[20] (Scheme 5). Therefore, the structure of the intermediate at −181.9 ppm can be reasonably formulated as a zirconacycloheptatriene–phosphacyclopropane **22′a**.

The cleavage of the two covalent zirconium–carbon bonds of **20′a** was achieved upon treatment with HCl leading to the (alkenyl)(alkynyl)phosphane **21a** in 70% isolated yield as a coloured oil (Scheme 5). Mass spectrometry analysis (parent ion at 368 [M]$^+$) was in agreement with the general formula for **21a**. The δ^{31}P (−34.8 ppm) was in the expected range,[20] and the IR spectrum showed an absorption band at 2163 cm^{-1} clearly indicating the presence of a P–C≡C group. The ^{1}H and ^{13}C NMR data agreed with the proposed phosphane structure.

The last uncertainty is related to the structure of the compound responsible of the signal at −12.6 ppm which was postulated to be the regioisomeric complex **6′a**. A similar compound, i.e. **6b** was observed also when **4b** was directly heated in the presence of **1**. In order to have a better indirect knowledge of the structure of these derivatives, an exchange reaction with dichloro phenylstibine was attempted on the mixture **5b**+**6b** (Scheme 6). Addition of $PhSbCl_2$ to a solution of Cp_2ZrPh_2 **1** and $PhP(C{\equiv}CPh)_2$ **4b** in toluene afforded the two stibacyclic compounds **17b** and



Scheme 6. Chemical evidence for the formation of a 3-(alkynyl)phosphinozirconaindene complex.

24b. ^{31}P NMR spectrum exhibited as expected two singlets with very different chemical shifts (δ^{31}P=42.2 (**17b**) and −57.4 (**24b**) ppm). The 3-(alkynyl)phosphinostibaindene **24b** was isolated by fractional recrystallization as orange crystals in a very low yield. Full characterization by usual spectroscopic and analytical methods was completed by successful X-ray diffraction analysis. The molecular structure of the 3-substituted stibole **24b** is represented in Figure 3 and important bond lengths and angles are summarized. Therefore, these results clearly demonstrated that the two (alkynyl)phosphinozirconaindenes **20** or **20′** (major) and **6** or **6′** (minor) are formed when a diacetylenic phosphane is treated with zirconabenzyne: the strong interaction between the phosphorus lone pair and zirconium explains the high regioselectivity observed.

Therefore on the basis of NMR experiments and X-ray diffraction studies, we can propose the mechanism outlined in Scheme 7 for the preparation of **5** (i) formation of an

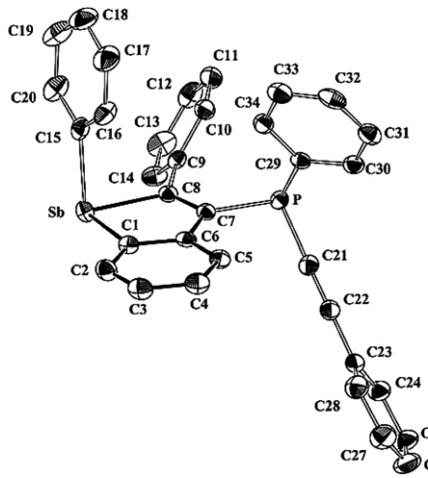
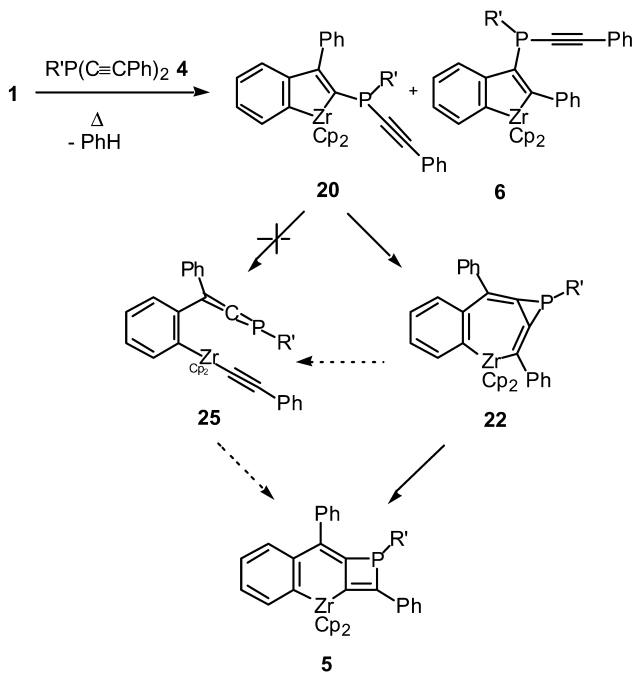


Figure 3. Molecular structure of **24b** (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°): Sb–C15 2.1593(18), Sb–C1 2.1235(19), Sb–C8 2.1594(16), P–C7 1.8436(16), P–C29 1.8431(17), P–C21 1.7654(19), C21–C22 1.208(3), C22–C23 1.434(3); C15–Sb–C8 88.29(6), C1–Sb–C15 95.48(7), C1–Sb–C8 80.30(7), C29–P–C7 100.96(7), C21–P–C29 100.70(8), C21–P–C7 102.25(8), C22–C21–P 173.69(15), C21–C22–C23 177.78(19).



Scheme 7. Multistep insertion mechanism involved in the formation of fused zirconacycles **5**.

2-(alkynyl)phosphino-1-zirconaindene **20** arising from insertion reaction of one of the C≡C triple bond of **4** into a Zr–C bond of the transient zirconabenzyne **2** (ii) intramolecular insertion reaction of the second alkynyl group into a Zr–C bond of the intermediate **20** providing zirconacycloheptatriene **22** with a phosphacyclopropane side ring (iii) 1,2-migration of the phosphanyl group leading to zirconacycle **5**. In this case it is noteworthy that it is not possible to further transform complex **6** because of its regiochemistry. In addition the transient formation of the intermediate **25** from **22** which might give **5** cannot be completely ruled out even if no evidence of the formation of a phosphaallene species[21] was found in ^{31}P NMR spectra in any experiments (δ ^{31}P in the range 39–93 ppm). A similar mechanism was already proposed by Takahashi in the case of intramolecular coupling of acetylenic groups of bis-(alkynyl)silanes promoted by zirconocene [Cp_2Zr] or $Cp_2Zr(\eta^2$-$C_2H_2)$.[14b]

3. Conclusion

Thermolysis of Cp_2ZrPh_2 in the presence of bis(alkynyl)-phosphanes or silanes provides new tricyclic systems, namely benzo-zirconacyclohexadiene-phospha or -silacyclo-butenes. A three step mechanism can explain the unusual regioselective formation of these polycyclic compounds leading to new mono or tricyclic derivatives incorporating one or two group 14–15 elements. Studies on the reactivity and properties of these new families of heterocycles are underway.

4. Experimental

4.1. General data

All manipulations were carried out under an argon atmosphere. Mass spectra were determined by using a Kratos concept IS or a Nermag R10-10H spectrometer while NMR spectra were obtained by using a Bruker AC200 or DRX500 instrument at 300 K (chemical shifts are given in ppm relative to TMS for ^{1}H, ^{13}C nuclei and to H_3PO_4 for ^{31}P nucleus). IR spectra were recorded on a Bruker IFS66V spectrometer (only significant IR bands are reported). Combustion analyses were performed by the analytical service of LSEO of the Université de Bourgogne.

The diphenylzirconocene **1**[22] and the bis(*tert*butylcyclo-pentadienyl)diphenyl zirconium **1′**[23] were synthesized as described in literature.

4.2. Preparation of zirconacycles 5, 5′ and 8

A solution of $(C_5H_4R)_2ZrPh_2$ **1** (R=H) or **1′** (R=*t*Bu) and bis(phenylalkynyl)phosphane **4** or silane **7** in toluene was heated to 80 °C for 20 h (phosphane) to 40 h (silane). After removal of the solvent in vacuo, the resulting solid was washed with pentane (**5**, **5′**) or ether (**8**) to afford the expected complex.

4.2.1. Complex 5a. (η^5-$C_5H_5)_2ZrPh_2$ (1.195 g, 3.184 mmol) and *t*BuP(C≡CPh)$_2$ (0.923 g, 3.184 mmol) gave **5a** as orange crystals after recrystallization in toluene/pentane. Yield: 65% (1.210 g, 2.058 mmol).

^{31}P{^{1}H} NMR (81 MHz, C_6D_6): δ=59.9 (s); ^{1}H NMR (200 MHz, C_6D_6): δ=7.39–6.63 (m, CH_{arom}), 6.56 and 6.26 (d, J(H,P)=0.6 Hz, 5H, CH_{Cp}), 0.74 (d, J(H,P)=11.3 Hz, 9H, (CH_3)$_3$CP); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ= 214.4 (d, J(C,P)=4.3 Hz, C_{quat}), 184.5 (s, C_{quat}), 163.9 (d, J(C,P)=2.4 Hz, C_{quat}), 150.1 (d, J(C,P)=6.2 Hz, C_{quat}), 143.1 (d, J(C,P)=6.2 Hz, C_{quat}), 142.2 (d, J(C,P)=10.1 Hz, C_{quat}), 140.9 (d, J(C,P)=6.7 Hz, C_{quat}), 140.0 (d, J(C,P)= 13.9 Hz, C_{quat}), 138.3, 131.7, 131.5, 129.5, 128.7, 128.4, 127.4, 127.0, 125.8, 125.7, 125.0 and 123.2 (s, CH_{arom}), 112.7 and 112.6 (s, CH_{Cp}), 33.2 (d, J(C,P)=29.8 Hz, (CH$_3$)$_3$CP), 28.2 (d, J(C,P)=12.0 Hz, (CH_3)$_3$CP); MS (DCI/CH_4): *m*/*z* (%): 587 (100) [M+1]$^+$. Anal. calcd for $C_{36}H_{33}PZr$ (587.9): C 73.55, H 5.66; found: C 73.76, H 5.86.

4.2.2. Complex 5b. (η^5-$C_5H_5)_2ZrPh_2$ (0.490 g, 1.300 mmol) and PhP(C≡CPh)$_2$ (0.400 g, 1.300 mmol) gave **5b** as an orange powder. Yield: 87% (0.690 g, 1.135 mmol).

^{31}P{^{1}H} NMR (81 MHz, C_6D_6): δ=21.3 (s); ^{1}H NMR (200 MHz, C_6D_6): δ=7.03–6.85 (m, CH_{arom}), 6.08 and 5.94 (s, 5H, CH_{Cp}); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ=235.2 (s, C_{quat}), 184.2 (s, C_{quat}), 162.5 (d, J(C,P)=6.1 Hz, C_{quat}), 150.7 (d, J(C,P)=6.1 Hz, C_{quat}), 142.5 (d, J(C,P)=5.0 Hz, C_{quat}), 139.4 (d, J(C,P)=4.4 Hz, C_{quat}), 138.0 (d, J(C,P)= 14.4 Hz, C_{quat}), 137.5 (s, C_{quat}), 136.7 (d, J(C,P)=6.6 Hz, C_{quat}), 133.0, 132.7, 132.4, 131.8, 131.4, 130.7, 130.1, 129.9, 128.4, 127.9, 127.5, 124.8 and 118.1 (s, CH_{arom}), 112.3 and 111.9 (s, CH_{Cp}); MS (70 eV): *m*/*z* (%): 606 (20) [M]$^+$. Anal. calcd for $C_{38}H_{29}PZr$ (607.9): C 75.09, H 4.81; found C 74.88, H 5.03.

4.2.3. Complex 5c. (η^5-$C_5H_5)_2ZrPh_2$ (0.143 g, 0.390 mmol) and (*i*Pr)$_2$NP(C≡CPh)$_2$ (0.130 g, 0.390 mmol) gave **5c** as an orange powder. Yield: 76% (0.186 g, 0.295 mmol).

$^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ=46.3 (s); ^1H NMR (200 MHz, C_6D_6, 343 K): δ=7.49–6.45 (m, CH_{arom}), 6.18 and 5.90 (d, J(H,P)=2.7 Hz, 5H, CH_{Cp}), 3.39 (m, 2H, $(CH_3)_2CHNP$), 1.06 (d, J(H,H)=5.9 Hz, 6H, $(CH_3)_2CHNP$), 0.52 (d, J(H,H)=5.7 Hz, 6H, $(CH_3)_2CHNP$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=217.4 (d, J(C,P)=10.4 Hz, C_{quat}), 184.2 (s, C_{quat}), 172.0 (s, C_{quat}), 151.5 (d, J(C,P)=5.5 Hz, C_{quat}), 148.3 (s, C_{quat}), 142.0 (d, J(C,P)=6.5 Hz, C_{quat}), 139.8 (d, J(C,P)=10.1 Hz, C_{quat}), 138.8 (d, J(C,P)=15.7 Hz, C_{quat}), 132.0, 131.9, 131.8, 130.5, 128.2, 127.6, 127.0, 126.4, 125.4, 125.3, 123.8 and 122.7 (s, CH_{arom}), 111.9 and 111.5 (s, CH_{Cp}), 25.3 (s, $(CH_3)_2CHNP$), 15.0 (s, $(CH_3)_2CHNP$); MS (70 eV): m/z (%): 629 (87) $[M]^+$. Anal. calcd for $C_{38}H_{38}NPZr$ (630.9): C 72.34, H 6.07, N 2.22; found C 72.58, H 6.01, N 2.11.

4.2.4. Complex 5′a. (η^5-C_5H_4tBu)$_2$ZrPh$_2$ (0.241 g, 0.496 mmol) and tBuP(C≡CPh)$_2$ (0.143 g, 0.493 mmol) gave **5′a** as a yellow powder. Yield: 87% (0.301 g, 0.430 mmol).

$^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ=61.7 (s); ^1H NMR (200 MHz, C_6D_6) δ=7.53–6.79 (m, CH_{arom}), 6.62–6.57 (m, 2H, CH_{arom}+CH_{tBuCp}), 6.41, 6.28, 6.21, 5.95, 5.87, 5.79 and 5.74 (pseudo-q, 1H, CH_{tBuCp}), 1.13 and 1.02 (s, 9H, $(CH_3)_3C_{tBuCp}$), 0.93 (d, J(H,P)=10.8 Hz, 9H, $(CH_3)_3CP$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=214.2 (d, J(C,P)=4.6 Hz, C_{quat}), 184.8 (s, C_{quat}), 164.1 (s, C_{quat}), 150.5 (s, C_{quat}), 145.7 (s, C_{quat}), 143.5 (d, J(C,P)=5.5 Hz, C_{quat}), 142.7 (d, J(C,P)=10.2 Hz, C_{quat}), 142.0 (d, J(C,P)=4.6 Hz, C_{quat}), 141.2 (s, C_{quat}), 140.9 (d, J(C,P)=13.8 Hz, C_{quat}), 132.1, 131.8, 131.4, 128.3, 127.1, 126.9, 126.0, 125.8, 125.5 and 122.5 (s, CH_{arom}), 118.6, 114.0, 113.2, 111.3, 110.6, 106.1, 105.3 and 103.4 (s, CH_{tBuCp}), 33.9 (s, $(CH_3)_3C_{tBuCp}$), 33.6 (d, J(C,P)=31.4 Hz, $(CH_3)_3CP$), 33.3 (s, $(CH_3)_3C_{tBuCp}$), 31.6 and 30.9 (s, 2$(CH_3)_3C_{tBuCp}$), 28.5 (d, J(C,P)=12.0 Hz, $(CH_3)_3CP$); MS (DCI/CH_4): m/z (%): 699 (100) $[M+1]^+$. Anal. calcd for $C_{44}H_{49}PZr$ (700.1): C 75.49, H 7.05, P 4.42; found C 75.71, H 7.36, P 4.10.

4.2.5. Complex 5′b. (η^5-C_5H_4tBu)$_2$ZrPh$_2$ (0.502 g, 1.070 mmol) and PhP(C≡CPh)$_2$ (0.330 g, 1.070 mmol) gave **5′b** as a yellow powder. Yield: 21% (0.206 g, 0.286 mmol).

$^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ=22.9 (s); ^1H NMR (200 MHz, $CDCl_3$) δ=7.32–6.80 (m, CH_{arom}), 6.38 and 6.29 (dd, 4H, CH_{tBuCp}), 1.16 (s, 18H, $(CH_3)_3C_{tBuCp}$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=216.6 (d, J(C,P)=5.3 Hz, C_{quat}), 184.4 (s, C_{quat}), 161.0 (d, J(C,P)=6.9 Hz, C_{quat}), 150.9 (d, J(C,P)=6.1 Hz, C_{quat}), 144.3 (s, C_{quat}), 142.6 (s, C_{quat}), 142.0 (d, J(C,P)=10.7 Hz, C_{quat}), 141.6 (d, J(C,P)=7.6 Hz, C_{quat}), 138.3 (d, J(C,P)=15.2 Hz, C_{quat}), 137.8 (s, C_{quat}), 137.1 (s, C_{quat}), 133.2, 132.8, 132.6, 131.1, 128.6, 128.5, 127.8, 127.7, 127.4, 126.4, 125.2, 125.1 and 122.6 (s, CH_{arom}), 114.8, 112.8, 111.2, 110.6, 109.8, 107.9, 107.8 and 105.3 (s, CH_{tBuCp}), 33.7 and 33.5 (s, $(CH_3)_3C_{tBuCp}$), 31.5 and 31.1 (s, $(CH_3)_3C_{tBuCp}$); MS (70 eV): m/z (%): 718 (93) $[M]^+$. Anal. calcd for $C_{46}H_{45}PZr$ (720.1): C 76.73, H 6.30; found C 76.85, H 6.49.

4.2.6. Complex 5′c. (η^5-C_5H_4tBu)$_2$ZrPh$_2$ (0.206 g, 0.424 mmol) and (iPr)$_2$NP(C≡CPh)$_2$ (0.141 g, 0.423 mmol) gave **5′c** as orange powder. Yield: 52% (0.163 g, 0.219 mmol).

$^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ=46.4 (s); ^1H NMR (200 MHz, C_6D_6, 345 K): δ=7.47–7.42 (m, 2H, CH_{arom}), 7.34–6.63 (m, CH_{arom}), 6.45 and 6.22 (pseudo-q, 1H, CH_{tBuCp}), 6.18–6.14 (m, 2H, CH_{tBuCp}), 5.95–5.85 (m, 4H, CH_{tBuCp}), 3.42 (m, 2H, $(CH_3)_2CHNP$), 1.16 (s, 9H, $(CH_3)_3C_{tBuCp}$), 1.06 (d, J(H,H)=6.2 Hz, 6H, $(CH_3)_2CHNP$), 1.01 (s, 9H, $(CH_3)_3C_{tBuCp}$), 0.76 (d, J(H,H)=6.6 Hz, 6H, $(CH_3)_2CHNP$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=217.5 (d, J(C,P)=9.6 Hz, C_{quat}), 184.9 (s, C_{quat}), 171.6 (s, C_{quat}), 151.7 (d, J(C,P)=5.7 Hz, C_{quat}), 149.7 (s, C_{quat}), 144.7 (s, C_{quat}), 142.6 (d, J(C,P)=7.6 Hz, C_{quat}), 142.0 (s, C_{quat}), 140.6 (d, J(C,P)=10.5 Hz, C_{quat}), 139.1 (d, J(C,P)=16.3 Hz, C_{quat}), 132.1, 131.9, 131.1, 128.4, 127.9, 127.3, 126.6, 125.9, 125.7, 125.2 and 122.4 (s, CH_{arom}), 115.3, 114.2, 110.9, 110.8, 110.1, 108.9, 107.8 and 105.4 (s, CH_{tBuCp}), 33.5 and 33.4 (s, $(CH_3)_3C_{tBuCp}$), 31.7 and 31.0 (s, $(CH_3)_3C_{tBuCp}$)—NMR resonances for $(CH_3)_2CHNP$ moiety were not observed; MS (DCI/CH_4): m/z (%): 742 (100) $[M+1]^+$. Anal. calcd for $C_{46}H_{54}NPZr$ (743.1): C 74.34, H 7.42, N 1.88, P 4.16; found C 74.45, H 7.37, N 1.81, P 4.15.

4.2.7. Complex 8a. (η^5-C_5H_5)$_2$ZrPh$_2$ (0.900 g, 0.240 mmol) and Me_2Si(C≡CPh)$_2$ (0.620 g, 0.240 mmol) gave **8a** as a yellow powder. Yield: 79% (1.060 g, 0.190 mmol).

^1H NMR (200 MHz, C_6D_6) δ=7.35–6.85 (m, CH_{arom}), 5.99 (s, 10H, CH_{Cp}), 0.19 (s, 6H, $(CH_3)_2Si$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=230.4, 185.6, 175.0, 153.1, 152.1, 147.1, 142.9 and 141.4 (s, C_{quat}), 134.0, 131.2, 129.9, 128.3, 128.0, 127.0, 126.7, 125.8, 124.5 and 122.8 (s, CH_{arom}), 111.4 (s, CH_{Cp}), −0.3 (s, $(CH_3)_2Si$); MS (DCI/CH_4): m/z (%): 557 (12) $[M]^+$. Anal. calcd for $C_{34}H_{30}SiZr$ (557.9): C 73.20, H 5.42; found C 73.22, H 5.52.

4.2.8. Complex 8b. (η^5-C_5H_5)$_2$ZrPh$_2$ (1.190 g, 3.170 mmol) and Ph_2Si(C≡CPh)$_2$ (1.220 g, 3.170 mmol) gave **8b** as a yellow powder. Yield: 90% (1.940 g, 2.850 mmol).

^1H NMR (200 MHz, C_6D_6) δ=6.57–8.14 (m, CH_{arom}), 6.05 (s, 10H, CH_{Cp}); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=235.6, 185.9, 172.3, 152.5, 150.2, 146.2, 144.1 and 140.9 (s, C_{quat}), 135.6 and 135.1 (s, CH_{arom}), 134.9 (s, C_{quat}), 133.5 (s, CH_{arom}), 133.2 (s, C_{quat}), 132.5, 131.7, 130.5, 129.6, 128.5, 128.4, 128.3, 127.8, 127.4, 125.8, 124.6 and 123.0 (s, CH_{arom}), 111.9 (s, CH_{Cp}); MS (70 eV): m/z (%): 680 (8) $[M]^+$. Anal. calcd for $C_{44}H_{34}SiZr$ (682.1): C 77.53, H 4.99; found C 77.24, H 5.24.

4.3. Preparation of heterocycles 9 and 10

A solution of toluene (20 mL) saturated with HCl was added dropwise at 0 °C to a solution of zirconacycles **5** or **8** in toluene (20 mL) and stirred for 1.5 h at room temperature. The volatile components were then removed in vacuo and the resulting oil was extracted with pentane (20 mL) and filtered. The crude product was purified by column chromatography (SiO_2, pentane/ether: 99/1) to afford the expected compound as coloured oil.

4.3.1. Compound 9a. From 0.826 g of complex **5a** (1.400 mmol) was isolated 0.250 g (0.680 mmol, 48%) of **9a** as a yellow oil.

$^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ=39.7 (s); ^1H NMR (200 MHz, C_6D_6) δ=7.59–6.90 (m, CH_{arom} and =C*H*), 0.92 (d, *J*(H,P)=11.7 Hz, 9H, (CH_3)$_3$CP); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ=154.6 (d, *J*(C,P)=5.5 Hz, C_{quat}), 142.3 (s, C_{quat}), 140.9 (d, *J*(C,P)=5.5 Hz, C_{quat}), 138.1 (d, *J*(C,P)=6.5 Hz, C_{quat}), 136.6 (d, *J*(C,P)=10.2 Hz, =*C*H), 136.3 (d, *J*(C,P)=10.2 Hz, C_{quat}), 135.5 (s, C_{quat}), 131.0, 130.9, 130.7, 128.8, 128.6, 128.4, 128.3, 127.9, 127.7, 126.7 and 126.6 (s, *C*H$_{arom}$), 32.4 (d, *J*(C,P)=27.0 Hz, (CH$_3$)$_3$*C*P), 27.8 (d, *J*(C,P)=12.3 Hz, (*C*H$_3$)$_3$CP); MS (70 eV): *m*/*z* (%): 368 (8) $[M]^+$.

4.3.2. Compound 9b. From 0.600 g of complex **5b** (0.990 mmol) was isolated 0.300 g (0.770 mmol, 78%) of **9b** as a yellow oil.

$^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ=13.2 (s); ^1H NMR (200 MHz, C_6D_6) δ=7.59 (s, 1H, =C*H*), 7.58–6.52 (m, CH_{arom}); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=154.5 (s, C_{quat}), 140.5 (d, *J*(C,P)=1.5 Hz, C_{quat}), 140.0 (d, *J*(C,P)=6.1 Hz, C_{quat}), 136.8 (s, C_{quat}), 136.7 (d, *J*(C,P)=11.4 Hz, =*C*H), 136.5 (d, *J*(C,P)=3.0 Hz, C_{quat}), 136.4, 135.9 and 136.8 (s, C_{quat}), 136.6, 132.8, 132.4, 130.3, 129.8, 129.7, 128.9, 128.7, 128.5 and 128.1 (s, *C*H$_{arom}$), 127.7 (d, *J*(C,P)=3.0 Hz, *C*H$_{arom}$); MS (70 eV): *m*/*z* (%): 388 (100) $[M]^+$.

4.3.3. Compound 10a. From 0.200 g of complex **8a** (0.360 mmol) was isolated 0.045 g (0.130 mmol, 38%) of **10a** as an orange oil.

^1H NMR (200 MHz, C_6D_6) δ=7.91 (s, 1H, =CH), 7.46–7.01 (m, CH_{arom}), 0.45 (s, 6H, (CH_3)$_2$Si); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ=160.1 (s, C_{quat}), 148.1 (s, =*C*H), 144.6, 144.3, 141.7, 140.5 and 137.7 (s, C_{quat}), 131.1, 130.7, 129.0, 128.9, 128.6, 128.5, 128.2, 128.1, 127.4 and 127.3 (s, *C*H$_{arom}$), −0.51 (s, (*C*H$_3$)$_2$Si); MS (70 eV): *m*/*z* (%): 338 (100) $[M]^+$.

4.3.4. Compound 10b. From 0.370 g of zirconacycle **8b** (0.540 mmol) was isolated 0.150 g (0.320 mmol, 59%) of **10b** as a yellow oil.

^1H NMR (200 MHz, C_6D_6) δ=8.24–8.10 (m, 5H, CH_{arom}), 7.47–6.22 (m, 20H, CH_{arom}), 6.21 (s, 1H, =C*H*); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ=158.4 (s, C_{quat}), 151.8 (s, =*C*H), 144.1, 142.6, 141.6, 141.4, 138.0 and 131.1 (s, C_{quat}), 129.3, 129.1, 128.8, 128.7, 128.65, 128.6, 128.5, 128.4, 128.3, 127.7, 127.5 and 125.7 (s, *C*H$_{arom}$); MS (70 eV): *m*/*z* (%): 462 (2) $[M]^+$.

4.4. Preparation of heterocycles 11–15

A solution of ECl_2 (E=Et_2Ge, Me_2Sn, PhP) in THF was added dropwise to a suspension of complex **5** or **8** and CuCl (10 mol%) in THF at room temperature. The reaction mixture was stirred for 4 h (**13**, **14**) or 20 h (**11**, **12**, **15**). After removal of the solvent in vacuo, the residue was extracted with ether (**11**, **12**, **14**, **15**) or pentane (**13**) and purified by column chromatography (SiO_2, ether) to afford the expected derivative.

4.4.1. Compound 11. Et_2GeCl_2 (0.10 mL, 0.600 mmol) and CuCl (0.006 g, 0.060 mmol) in THF (5 mL) and a solution of **5b** (0.379 g, 0.600 mmol) in THF (15 mL) gave **11** as a yellow powder.

$^{31}P\{^1H\}$ (81 MHz, C_6D_6): δ=43.4 (s); ^1H NMR (200 MHz, C_6D_6): δ=7.60–7.11 (m, CH_{arom}), 1.57 and 1.31 (q, 2H, GeCH_2CH$_3$), 1.28 and 1.21 (t, 3H, GeCH$_2$CH_3); MS (70 eV): *m*/*z* (%): 519 (2) $[M]^+$.

4.4.2. Compound 12. Et_2GeCl_2 (0.05 mL, 0.370 mmol) and CuCl (0.004 g, 0.037 mmol) in THF (5 mL) and a solution of **8a** (0.210 g, 0.370 mmol) in THF (15 mL) gave **12** as a yellow powder.

^1H NMR (200 MHz, C_6D_6): δ=7.74–7.10 (m, CH_{arom}), 1.64 (q, 4H, GeCH_2CH$_3$), 1.33 (t, 6H, GeCH$_2$CH_3), 0.22 (s, 6H, (CH_3)$_2$Si); MS (70 eV): *m*/*z* (%): 468 (29) $[M]^+$.

4.4.3. Compound 13. Me_2SnCl_2 (0.210 g, 0.950 mmol) and CuCl (0.010 g, 0.095 mmol) in THF (7 mL) and a solution of **5b** (0.582 g, 0.950 mmol) in THF (20 mL) gave **13** as a yellow powder.

$^{31}P\{^1H\}$ (81 MHz, C_6D_6): δ=47.8 (s); ^1H NMR (200 MHz, C_6D_6): δ=7.78–6.86 (m, CH_{arom}), 0.47 and 0.29 (s, 3H, (CH_3)$_2$Sn); MS (70 eV): *m*/*z* (%): 536 (45) $[M]^+$.

4.4.4. Compound 14. Me_2SnCl_2 (0.079 g, 0.360 mmol) and CuCl (g, 0.036 mmol) in THF (3 mL) and a solution of **8a** (0.200 g, 0.360 mmol) in THF (10 mL) gave **14** as a yellow powder.

^1H NMR (200 MHz, C_6D_6): δ=7.74–7.10 (m, CH_{arom}), 0.65 and 0.33 (s, 6H, (CH_3)$_2$Sn); MS (70 eV): *m*/*z* (%): 486 (85) $[M]^+$.

4.4.5. Compound 15. $PhPCl_2$ (4.08 mL, 0.600 mmol) and CuCl (0.006 g, 0.060 mmol) in THF (10 mL) and a solution of **8a** (0.336 g, 0.600 mmol) in THF (15 mL) gave **15** as a yellow powder.

$^{31}P\{^1H\}$ (81 MHz, C_6D_6): δ=49.8 (s); ^1H NMR (200 MHz, C_6D_6): δ=8.36–8.32 (m, CH_{arom}), 8.06–8.02 (m, CH_{arom}), 7.82–7.78 (m, CH_{arom}), 7.40–7.14 (m, CH_{arom}), 6.99–6.84 (m, CH$_{arom}$), 0.28 and 0.15 (s, 3H, (CH_3)$_2$Si); MS (70 eV): *m*/*z* (%): 444 (100) $[M]^+$.

4.5. Preparation of heterocycles 16–18

A solution of ECl_2 (E=PhAs, PhSb) in toluene was added dropwise to a solution of complex **5** or **8** in toluene cooled to −30 °C. The reaction mixture was left to warm slowly to room temperature and stirred for 20 h. After removal of the solvent in vacuo, the residue was extracted with pentane and purified by column chromatography (SiO_2, pentane) to afford the expected compound.

4.5.1. Compound 16a. $PhAsCl_2$ (0.110 g, 0.520 mmol) in toluene (5 mL) and a solution of **8a** (0.290 g, 0.520 mmol)

in toluene (7 mL) gave **16a** as a yellow powder. Yield: 71% (0.180 g, 0.360 mmol).

^{1}H NMR (200 MHz, C_6D_6): δ=7.70–6.84 (m, CH_{arom}), 0.27 and 0.22 (s, 3H, (CH_3)$_2$Si); ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ=168.0, 157.5, 145.2, 143.0, 142.1, 138.3 and 137.5 (s, C_{quat}), 136.3 (s, CH$_{arom}$), 136.2 and 136.0 (s, C_{quat}), 132.8, 129.7, 129.3, 129.2, 129.1, 129.0, 128.6, 128.4, 128.3, 127.2 and 126.8 (s, CH$_{arom}$), −0.3 and −1.2 (s, (CH$_3$)$_2$Si); MS (70 eV): *m*/*z* (%): 488 (100) [M]$^+$. Anal. calcd for $C_{30}H_{25}AsSi$ (488.5): C 73.76, H 5.16; found C 73.66, H 5.12.

4.5.2. Compound 16b. $PhAsCl_2$ (0.220 g, 0.990 mmol) in toluene (10 mL) and a solution of **8b** (0.670 g, 0.990 mmol) in toluene (17 mL) gave **16b** as a yellow powder. Yield: 76% (0.463 g, 0.760 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ=7.67–7.53 (m, CH_{arom}), 7.46–7.14 (m, CH_{arom}); ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ= 165.2, 162.0, 143.2, 142.2, 141.5, 138.0, 137.5 and 138.2 (s, C_{quat}), 136.0, 135.6, 135.5, 135.4, 135.3, 135.0, 134.8 and 134.5 (s, CH$_{arom}$), 133.6, 133.1 and 133.0 (s, C_{quat}), 132.4, 130.8, 130.3, 130.2, 129.8, 129.4, 129.3, 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0 and 127.7 (s, CH$_{arom}$); MS (70 eV): *m*/*z* (%): 612 (100) [M]$^+$. Anal. calcd for $C_{40}H_{29}AsSi$ (612.7): C 78.42, H 4.77; found C 78.23, H 4.89.

4.5.3. Compound 17a. $PhSbCl_2$ (0.303 g, 1.112 mmol) in toluene (10 mL) and a solution of **5a** (0.660 g, 1.124 mmol) in toluene (15 mL) gave **17a** as a yellow powder. Yield: 28% (0.175 g, 0.309 mmol).

^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ=73.7 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.83–7.78 (m, 2H, CH_{arom}), 7.59–7.06 (m, CH_{arom}), 0.66 (d, J(H,P)=12.0 Hz, 9H, (CH_3)$_3$CP); ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ=163.3 (d, J(C,P)=5.8 Hz, C_{quat}), 146.9 (d, J(C,P)=6.9 Hz, C_{quat}), 140.7 (s, C_{quat}), 140.2 (d, J(C,P)=3.5 Hz, C_{quat}), 140.1 (s, CH$_{arom}$), 137.5–137.3 (2d overlapped, C_{quat}), 137.1 (d, J(C,P)=8.1 Hz, C_{quat}), 136.7 (s, CH$_{arom}$), 135.1 (d, J(C,P)=2.3 Hz, C_{quat}), 133.9 (s, C_{quat}), 131.3, 129.6, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 127.8, 127.2, 127.1 and 127.0 (s, CH$_{arom}$), 33.4 (d, J(C,P)=27.0 Hz, (CH$_3$)$_3$$C$P), 27.6 (d, J(C,P)=12.3 Hz, (CH$_3$)$_3$CP); MS (DCI/CH_4): *m*/*z* (%): 565 (100) [M+1]$^+$, 564 (49) [M]$^+$. Anal. calcd for $C_{32}H_{28}PSb$ (565.3): C 67.99, H 4.99; found C 67.52, H 5.27.

4.5.4. Compound 17b. $PhSbCl_2$ (0.183 g, 6.780 mmol) in toluene (10 mL) and a solution of **5b** (0.412 g, 0.670 mmol) in toluene (20 mL) gave **17b** as a yellow powder. Yield: 67% (0.260 g, 0.450 mmol). Recrystallization from pentane/ether (1/1) afforded **17b** as yellow crystals (0.100 g, 0.170 mmol, 25%).

^{31}P{^{1}H} (81 MHz, $CDCl_3$): δ=42.2 (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.75–7.73 (m, 2H, CH_{arom}), 7.60–7.58 (m, 2H, CH_{arom}), 7.39–7.11 (m, CH_{arom}); ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ=161.9 (s, C_{quat}), 148.4 (d, J(C,P)= 7.6 Hz, C_{quat}), 140.1 (d, J(C,P)=2.3 Hz, C_{quat}), 139.4 (s, CH$_{arom}$), 138.9 (d, J(C,P)=4.5 Hz, C_{quat}), 137.7 (d, J(C,P)= 6.1 Hz, C_{quat}), 136.8 (d, J(C,P)=6.1 Hz, C_{quat}), 136.6 (d, J(C,P)=4.5 Hz, C_{quat}), 136.4 (s, CH$_{arom}$), 135.8, 135.7 and 134.4 (s, C_{quat}), 133.0, 132.8, 130.5, 129.9, 129.6 and 129.5 (s, CH$_{arom}$), 129.4 (d, J(C,P)=1.4 Hz, CH$_{arom}$), 129.2 (s, CH$_{arom}$), 129.1 (d, J(C,P)=1.5 Hz, CH$_{arom}$), 128.6, 128.5, 128.3, 127.4, 127.3, 126.7 and 126.6 (s, CH$_{arom}$); MS (70 eV): *m*/*z* (%): 584 (100) [M]$^+$. Anal. calcd for $C_{34}H_{24}PSb$ (585.3): C 69.77, H 4.13; found C 69.69, H 4.06.

4.5.5. Compound 18a. $PhSbCl_2$ (0.125 g, 0.460 mmol) in toluene (5 mL) and a solution of **8a** (0.256 g, 0.460 mmol) in toluene (10 mL) gave **18a** as yellow powder. Yield: 97% (0.240 g, 0.448 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ=7.78–7.68 (m, CH_{arom}), 7.59–7.15 (m, CH_{arom}), 0.47 and 0.37 (s, 3H, (CH_3)$_2$Si); ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ=172.5, 157.5, 146.0, 144.0 and 139.7 (s, C_{quat}), 139.4 (s, CH$_{arom}$), 139.0 and 137.4 (s, C_{quat}), 135.7 (s, CH$_{arom}$), 135.1 and 133.4 (s, C_{quat}), 130.4, 129.6, 129.1, 129.0, 128.8, 128.4, 128.3, 128.0 and 126.8 (s, CH$_{arom}$), −0.4 and −1.0 (s, (CH$_3$)$_2$Si); MS (70 eV): *m*/*z* (%): 534 (62) [M]$^+$. Anal. calcd for $C_{30}H_{25}SbSi$ (535.4): C 67.30, H 4.71; found C 67.19, H 4.58.

4.5.6. Compound 18b. $PhSbCl_2$ (0.139 g, 0.510 mmol) in toluene (10 mL) and a solution of **8b** (0.352 g, 0.51 mmol) in toluene (15 mL) gave **18b** as yellow crystals. Yield: 72% (0.242 g, 0.367 mmol).

^{1}H NMR (200 MHz, C_6D_6): δ=8.25–8.08 (m, CH_{arom}), 7.81–7.65 (m, CH_{arom}), 7.56–7.34 (m, CH_{arom}), 7.27–6.75 (m, CH_{arom}); ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ=169.0, 146.4, 144.2, 143.8, 143.4, 140.8 and 138.2 (s, C_{quat}), 136.0, 135.6, 135.5, 135.4, 135.3, 135.0, 134.8 and 134.5 (s, CH$_{arom}$), 133.6, 133.1 and 133.0 (s, C_{quat}), 132.4, 130.8, 130.3, 130.2, 129.8, 129.4, 129.3, 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0 and 127.7 (s, CH$_{arom}$); MS (70 eV): *m*/*z* (%): 658 (5) [M]$^+$. Anal. calcd for $C_{40}H_{29}SbSi$ (659.5): C 72.85, H 4.43; found C 72.79, H 4.28.

4.5.7. Synthesis of phosphane 21a. A solution of (*t*BuCp)$_2$ $ZrPh_2$ **1′** (0.442 g, 0.910 mmol) in benzene (10 mL) was refluxed during 6 h. The reaction mixture was left to warm slowly to room temperature and *t*BuP(C≡CPh)$_2$ **4a** (0.264 g, 0.910 mmol) in benzene (10 mL) was added dropwise. Then after 15 h of stirring at room temperature, the reaction mixture was cooled to −30 °C and a solution of HCl in toluene (C=0.3 mol L^{-1}, 6.05 mL, 1.810 mmol) was added dropwise and the reaction mixture was stirred for 2 h at room temperature. After removal of the solvent in vacuo the residue was extracted by pentane and purified by column chromatography (SiO_2, pentane) to afford **21a** as a yellow oil. Yield: 70% (0.140 g, 0.380 mmol).

^{31}P{^{1}H} (81 MHz, $CDCl_3$): δ=−34.8 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.59–7.55 (m, CH_{arom}), 7.48–7.42 (m, CH_{arom}), 6.87 (d, J(H,P)=3.9 Hz, 1H, CH=), 1.35 (d, J(H,P)=13.4 Hz, 9H, (CH_3)$_3$CP); ^{13}C{^{1}H} (125 MHz, $CDCl_3$): δ=157.7 (d, J(C,P)=26.6 Hz, =CPh$_2$), 142.9 (d, J(C,P)=7.9 Hz, C_{quat}), 140.4 (d, J(C,P)=5.9 Hz, C_{quat}), 132.2 and 131.9 (s, CH_{arom}), 130.8 (d, J(C,P)=3.9 Hz, CH_{arom}), 128.6, 128.5, 128.1, 127.4 and 123.8 (s, CH_{arom}), 123.6 (d, J(C,P)=3.9 Hz, CH=), 104.3 (d, J(C,P)=2.0 Hz, ≡C–Ph), 88.7 (d, J(C,P)=20.7 Hz, P–C≡), 32.1 (d,

J(C,P)=5.9 Hz, $(CH_3)_3CP$), 27.8 (d, J(C,P)=14.7 Hz, $(CH_3)_3CP$); IR (KBr): ν=2163 cm^{-1} (C≡C); MS (70 eV): m/z (%): 368 (91) $[M]^+$.

4.5.8. Synthesis of heterocycle 24b. A solution of Cp_2ZrPh_2 **1** (0.260 g, 0.700 mmol) and $PhP(C{\equiv}CPh)_2$ **4b** (0.220 g, 0.700 mmol) in toluene (20 mL) was heated to 80 °C for 20 h. Then the reaction mixture was cooled to −35 °C and a solution of $PhSbCl_2$ (0.190 g, 0.700 mmol) in THF (10 mL) was added dropwise and the reaction mixture was stirred for 20 h at room temperature. After removal of the solvent in vacuo, the residue was extracted by pentane and purified by column chromatography (SiO_2, pentane). Fractional recrystallization from ether/pentane (1/1) afforded **24b** as orange crystals. Yield: 11% (0.050 g, 0.08 mmol).

$^{31}P\{^1H\}$ (81 MHz, C_6D_6): δ=−57.4 (s); ^1H NMR (200 MHz, C_6D_6): δ=8.48–8.44 (m, CH_{arom}), 7.85–7.78 (m, CH_{arom}), 7.39–7.27 (m, CH_{arom}), 7.10–6.88 (m, CH_{arom}); MS (70 eV): m/z (%): 584 (5) $[M]^+$; IR (KBr): ν=2150 cm^{-1} (C≡C). Anal. calcd for $C_{34}H_{24}PSb$ (585.3): C 69.77, H 4.13; found C 69.48, H 4.35.

5. X-Ray analyses

5.1. Crystal data for 8a

$C_{34}H_{30}SiZr$, M=557.89, triclinic, space group P-1, a=8.0851(9) Å, b=11.098(2) Å, c=15.466(2) Å, α=92.92(2)°, β=91.43(2)°, γ=105.41(2)°, Z=2, V=1335.1(3) Å^3, D_c=1.388 mg m^{-3}, Mo Kα radiation (λ=0.71073 Å), μ=0.478 mm^{-1}, crystal dimensions 0.40×0.12×0.08 mm^3, F(000)=576, T=180(2) K. From 7893 reflections, 3929 were unique (R_{int}=0.0344). 3929 with $I>2\sigma(I)$ were used in refinement. Data/parameters ratio 3929/327, R=0.0252, $R\omega$=0.0604.

5.2. Crystal data for 17b

$C_{34}H_{24}PSb$, M=585.25, triclinic, space group P-1, a=11.191(2) Å, b=11.218(2) Å, c=12.535(3) Å, α=99.18(2)°, β=114.43(2)°, γ=107.95(2)°, Z=2, V=1286.2(4) Å^3, D_c=1.511 mg m^{-3}, Mo Kα radiation (λ=0.71073 Å), μ=1.156 mm^{-1}, crystal dimensions 0.25×0.20×0.07 mm^3, F(000)=588, T=160(2) K. From 9429 reflections, 3486 were unique (R_{int}=0.0427). 3486 with $I>2\sigma(I)$ were used in refinement. Data/parameters ratio 3486/325, R=0.0314, $R\omega$=0.0673.

5.3. Crystal data for 24b

$C_{34}H_{24}PSb$, M=585.25, triclinic, space group P-1, a=9.9506(13) Å, b=11.8836(17) Å, c=12.4912(16) Å, α=81.650(16)°, β=69.084(15)°, γ=73.579(16)°, Z=2, V=1321.8(3) Å^3, D_c=1.470 mg m^{-3}, Mo Kα radiation (λ=0.71073 Å), μ=1.125 mm^{-1}, crystal dimensions 0.20×0.15×0.12 mm^3, F(000)=588, T=160(2) K. From 12843 reflections, 4739 were unique (R_{int}=0.0276). 4739 with $I>2\sigma(I)$ were used in refinement. Data/parameters ratio 4739/325, R=0.0207, $R\omega$=0.0540.

For the three compounds, the data were collected on a IPDS STOE diffractometer. The structures were solved by direct methods with the program SIR92[24] and refined by least squares procedures on F with the CRYSTAL package.[25] The molecules were plotted with CAMERON.[26] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-192764 (**8a**), CCDC-192765 (**17b**), CCDC-192766 (**24b**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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