X–H (X = C, N, O, P, S) Bond Activations Induced by β-Heterosubstituted Zirconaindenes

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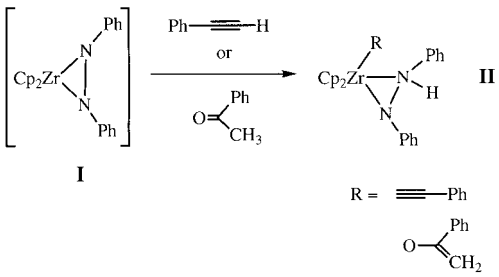
Abstract: The azazirconacyclopentene-substituted phosphines **3** and **4** have been found to activate the C–H bonds of acetylenic systems, such as methylpropiolate, diphenylphosphinoacetylene and phenylacetylene, or of methylene compounds, such as malonitrile and diethylmalonate, to give complexes **5a–c, 6a** and **6b**. C–H bond activation also takes place with vinylacetate. Similar reactions with amines, alcohols, enolisable ketones, phenols, phosphonates, thiols and a second-generation SH-terminated dendrimer lead through X–H bond activation (X = N, O, P, S) to new complexes **8a–c**, **9**, **12a,b**, **13**, **14a–c**, **15, 16a** and **16b**. The azazirconacyclopentene-substituted amine **20** reacts to form analogous complexes. Zr–X bonds of these complexes (X = C, N, O, S) can be cleaved with diphenylchlorophosphine to give P–X phosphorus derivatives in high yield.

Keywords: C–H activation · dendrimers · phosphorus · zirconium

Introduction

The activation of C–H bonds is currently one of the most fascinating challenges encountered in the construction of organic molecules. Two recent reviews have pointed out how important this process is from an economical point of view.[1, 2] In particular, C–H bond activation initiated by transition metal complexes has been the subject of a number of reports in organometallic chemistry. Indeed a lot of electronically unsaturated metal complexes have been found to activate C–H bonds and different strategies have been proposed. One can cite 1,2-additions at M=X units (X = O,[3] NR,[4, 5] CRR′[6]), oxidative addition of a late transition metal,[7] σ-bond metathesis,[8] homolytic cleavage by UV–excited mercury atoms,[9] activation at porphyrin–Rh^{II} complexes[10] and heterolytic activation by late transition metals in polar media.[11] C–H bond activation at d^0 metal centres is found to be effective, since these complexes remove hydrocarbons reversibly;[5] in this case concerted processes are generally assumed to take place.

In a previous work, it was shown that a non-isolated complex, that is, the (η^2-1,2-diphenylhydrazido(2–))zirconocene complex $Cp_2Zr(N_2Ph_2)$ **I** reacts with phenylacetylene or acetophenone to give the corresponding complexes **II** resulting from C–H and O–H bond insertion on a zirconium–nitrogen bond of the coordinatively unsaturated intermediate **I**[12] (Scheme 1).



Scheme 1. Reactivity of (η^2-1,2-diphenylhydrazido(2)) zirconocene complex **I** with phenylacetylene and acetophenone.

Our research, which is concerned with the studies of interactions between Group 4 elements and main group elements, has shown that the presence of phosphino groups in α- or β-position relative to a zirconium centre can often induce unusual reactions in comparison to those observed with more classical organic zirconium species.[13] Therefore, we reasoned that *stable* azazirconacyclopentene-substituted phosphines such as **3** and **4** (16-electron zirconium–nitrogen bond species, see Scheme 2 below) might allow similar or new activation processes in milder experimental conditions than those already reported.[12] We describe here the unique properties of the phosphines **3** and **4** and their corresponding amines that allow sp and sp^3 C–H as well as X–H bond

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activations (X = O, N, P, S) in the formation of new 18-electron zirconium complexes; these last complexes can be used as efficient reagents for the formation of phosphorus species bearing P–C, P–O, P–N or P–S bonds.

Results and Discussion

We have already reported that thermolysis of diphenylzirconocene Cp_2ZrPh_2 in the presence of bis(diisopropylamino)- or bis(dicyclohexylamino)cyanophosphine (**1** or **2**) generates azazirconacyclopentenes **3** or **4**, respectively, in high yield.[14] This reaction takes place in mild conditions, that is, heating under reflux in toluene for 45 min, in contrast to the reaction of Cp_2ZrPh_2 with organic nitriles, which requires 17 h of heating at 110 °C to go to completion.[15]

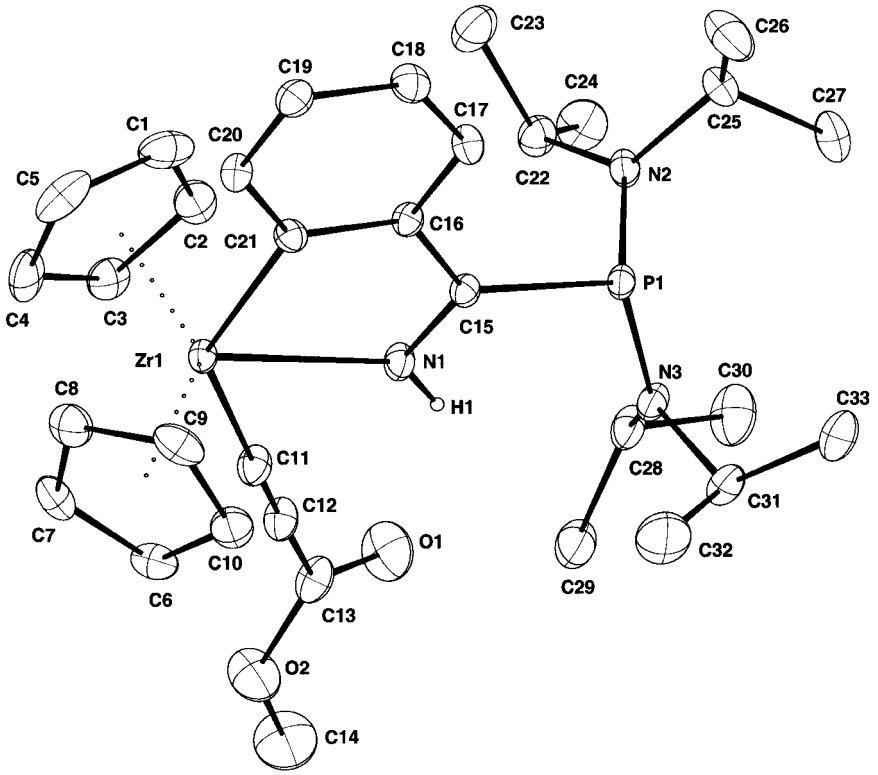
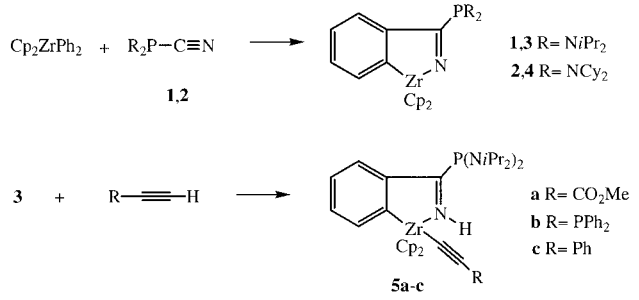


Figure 1. Molecular structure of **5a** with crystallographic numbering scheme. Selected bond lengths (Å) and bond angles (°): Zr–C21 2.3571(19); Zr–N1 2.3269(17); Zr–C11 2.328(2); C11–C12 1.211(3); C21-Zr-N1 67.61(6); N1-Zr-C11 71.19(7).

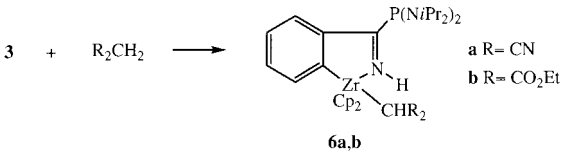
C–H bond activation: Treatment of **3** with methylpropiolate in toluene at room temperature resulted in the formation of the 18-electron zirconium complex **5a** in 93% isolated yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **5a** exhibits a single signal at $\delta = 60.8$ (**3**: $\delta = 45$). Besides the signals from the methylpropiolate fragments at $\delta = 110.6$ (C≡) and 154.7 (C=O), a deshielded peak is detected at $\delta = 142.6$ in the ^{13}C NMR spectrum, which is characteristic of an sp carbon atom from the acetylenic moiety directly bound to the zirconium atom. IR spectroscopy confirms the presence of a carbon–carbon triple bond ($\nu(C{\equiv}C) = 2039\ cm^{-1}$) and that of a NH group ($\nu(N{-}H) = 3355\ cm^{-1}$). The NH group is also detected in the ^1H NMR spectrum; a doublet is observed at $\delta = 10.01$ ($J_{HP} = 5.6$ Hz). These data are in agreement with the proposed structure for **5a**. The solid-state structure of **5a** has been corroborated by a single-crystal X-ray diffraction study. An ORTEP diagram of **5a** is shown in Figure 1 with selected bond lengths and angles. The most striking features of the molecular structure will be discussed later.

This preliminary experiment shows that the azazirconacyclopentene **3** can activate a sp C–H bond. This result encouraged us to investigate the reaction of **3** with other acetylenic systems. Indeed, Scheme 2 shows that a similar activation proceeds with other alkynes, such as diphenylphosphinoacetylene or phenylacetylene, and leads to the formation of complexes **5b** and **5c** respectively.

This C–H bond activation is not limited to sp C–H bond, since activation of a sp^3 C–H bond also occured when **3** was treated with malonitrile or with diethylmalonate (Scheme 3).



Scheme 2. Reactivity of azazirconacyclopentene **3** with acetylenic derivatives.



Scheme 3. Reactivity of azazirconacyclopentene **3** with malonitrile and diethylmalonate.

The resulting complexes **6a** and **6b** were obtained as pure products in high yield. The formation of a NH bond was confirmed by ^1H NMR (**6a** $\delta_{NH} = 9.38$, $J_{HP} = 5.1$ Hz; **6b** $\delta_{NH} = 10.1$, $J_{PH} = 4.7$ Hz) and by IR (**6a**: $\nu(NH) = 3286\ cm^{-1}$; **6b**: $\nu(NH) = 3290\ cm^{-1}$).

Remarkably, sp^3 C–H bond activation of vinyl acetate takes place when this reagent is treated with **3** in the same experimental conditions as those reported above. Complex **7**

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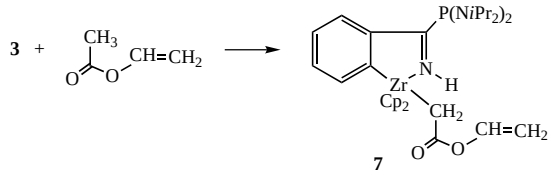
was isolated and fully characterized (Scheme 4). The NMR data are in accord with the proposed structure. In particular, a characteristic deshielding signal at $\delta = 58.1$ in the ^{13}C NMR spectrum is observed for the methylene unit directly bonded to the zirconium atom.

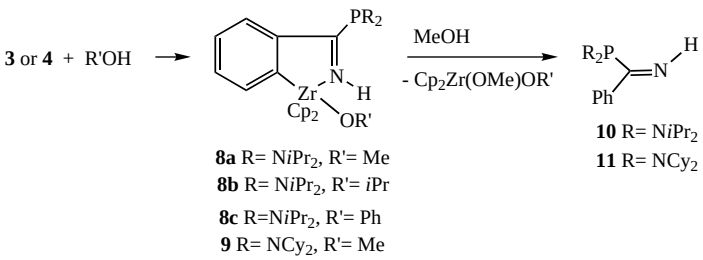


Scheme 4. Reactivity of azazirconacyclopentene **3** with vinylacetate.

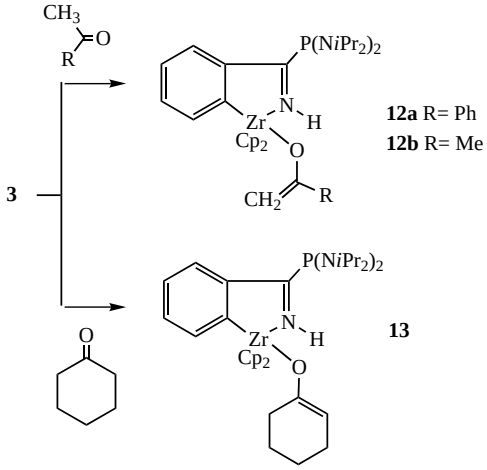
The imino carbon chemical shift in the ^{13}C NMR spectrum constitutes an excellent probe with which to follow C–H bond activation and 18-electron zirconium complex formation of the experiments that have been described up to this point. The $\delta_{C=N}$ signal moves downfield from $\delta = 191.3$ (**3**) to 201.6–205.3 (**5a–c**, **6a**,**b**, **7**), while the carbon phosphorus coupling constant increases from 19 Hz (**3**) to 39.2–41 Hz (**5a–c**, **6a**,**b**, **7**).

X–H (X = O, N, P, S) bond activation: In order to investigate the generality of the reaction, the reaction of **3** and **4** with alcohols was studied. Addition of one equivalent of methanol to a solution of **3** or **4** in toluene at room temperature affords the new 18-electron complexes **8a** or **9**, which arise from the formal 1,2-addition of methanol on the zirconium–nitrogen bond of **3** and **4** (Scheme 5). These compounds are stable species that are easily isolated and characterized. The addition of a second equivalent of methanol to **8a** or **9** or treatment of **3** or **4** directly with two equivalents of methanol afford the *N*-unsubstituted imines **10** or **11**, which result from methanolysis of the zirconium sp^2 carbon bond in **3** and **4** or **8a** and **9** with the release of $[Cp_2Zr(OMe)_2]$ (Scheme 5). Alcohols such as isopropyl alcohol and phenol react in a similar manner to give rise to the complexes **8b** and **8c**, respectively (Scheme 5).

Interestingly, enol forms of ketones undergo similar reactions. Acetophenone, acetone and cyclohexanone are converted into zirconium derivatives **12a**, **12b** and **13** respectively in the presence of complex **3** (Scheme 6). Compound **12a** was isolated in crystal form and a single-crystal X-ray analysis was performed to confirm its structure (Figure 2).



Scheme 5. Reactivity of azazirconacyclopentenes **3** and **4** with alcohols and phenols.



Scheme 6. Reactivity of azazirconacyclopentene **3** with ketones.

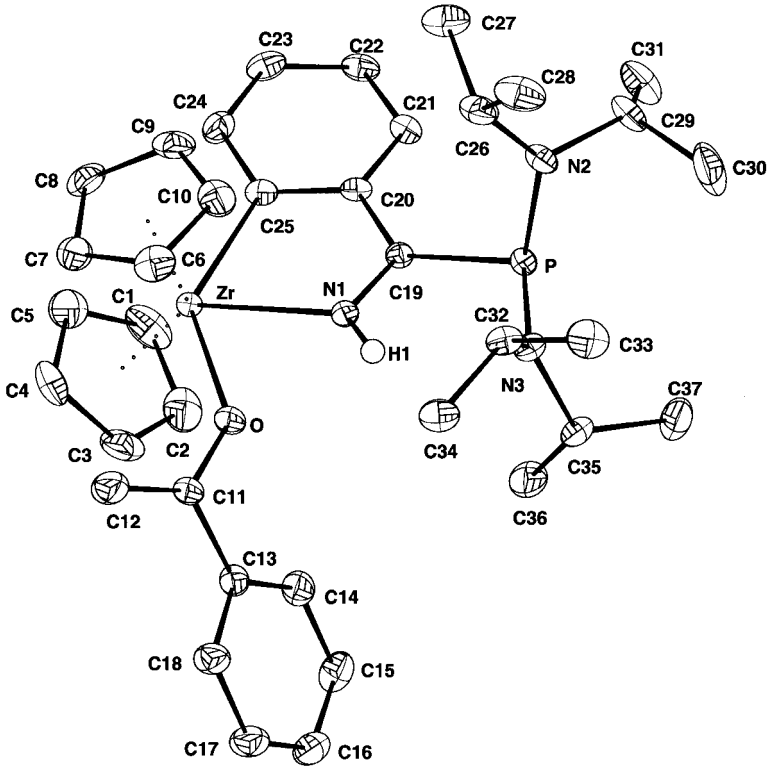
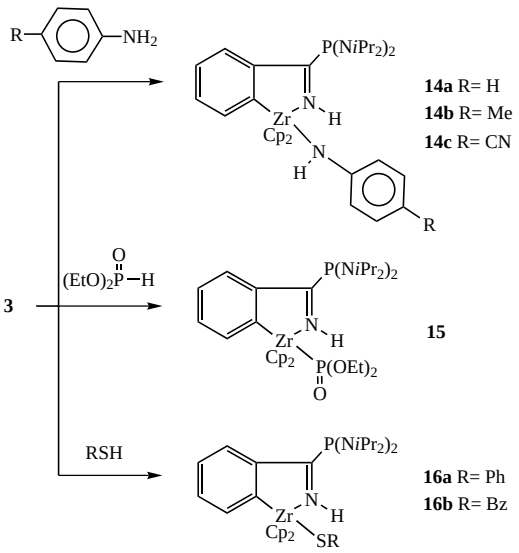


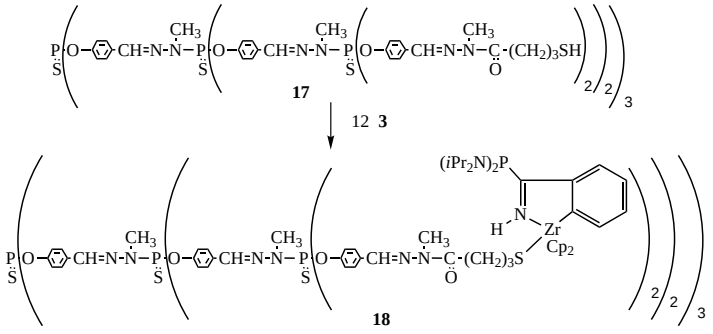
Figure 2. Molecular structure of **12a** with crystallographic numbering scheme. Selected bond lengths (Å) and bond angles (°): Zr–O 2.1497(13); O–C11 1.333(2); C11–C12 1.336(3), Zr–N1 2.2957(15); Zr–C25 2.3836(17); C25-Zr-N1 67.19(1); N1-Zr-O 70.14(1).

The azazirconacyclopentene **3** can be converted to the corresponding 18-electron zirconium complexes **14a–c**, **15**, **16a** and **16b** through reaction with aromatic amines (aniline, *p*-toluidene, 4-amino benzonitrile), phosphonates (such as $(EtO)_2P(O)H$) or thiols (thiophenol, benzylmercaptan) (Scheme 7). These one-pot reactions yield Zr–N, Zr–P and



Scheme 7. Reactivity of azazirconacyclopentene **3** with amines, phosphonate and thiols.

Zr–S species as single products. Polyfunctionalized macromolecules as SH-terminated dendrimers[16] also react easily to afford the first example of a neutral zirconadendrimer. The reaction of a second-generation dendrimer, **17** (1 equiv), which incorporates twelve terminal SH groups on the surface, and **3** (12.2 equiv) gives **18** in 72% yield after work-up (Scheme 8). The reaction can be followed by ^{31}P NMR spectroscopy in which the signal of **3** disappears with the concomitant increase of a new signal at $\delta = 58.2$. The ^{1}H and ^{13}C NMR spectra of **18** have signals at $\delta_{NH} = 9.87$ ($J_{HP} = 5.4$ Hz) and $\delta_{PC=N} = 204.4$ ($J_{CP} = 40.6$ Hz), respectively.

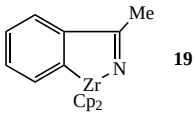


Scheme 8. Reactivity of azazirconacyclopentene **3** with a second-generation SH-terminated dendrimer.

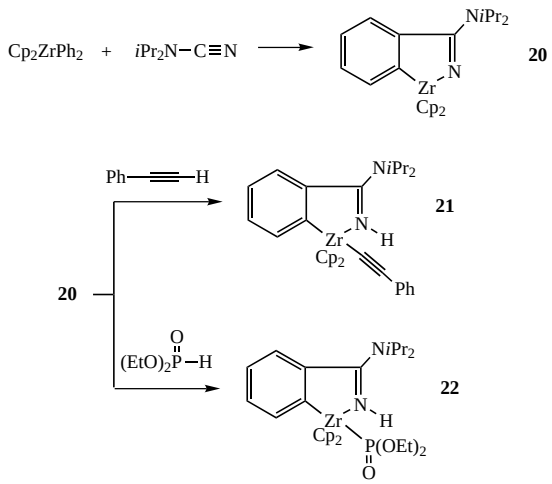
Scope and limitations: No intermediate species were observed by ^{1}H and ^{31}P NMR spectroscopy during the reaction. This X–H bond activation can be viewed as a formal 1,2-addition to a single 16-electron zirconium–nitrogen covalent bond, which affords a 18-electron zirconium–nitrogen dative bond species. Although a concerted four-centre mechanism cannot be ruled out, it is reasonable to postulate that the first step is the protonation of the cyclic imino nitrogen atom followed by the attack of the activated nucleophile X^- on zirconium with formation of a Zr–X covalent bond. The basicity of the cyclic imino nitrogen atom plays a key role in this process. Aliphatic amines do not react with **3**, while aromatic amines, which are less basic than aliphatic amines, react cleanly.

A question remains: does the presence of a phosphino group present in **3** and **4**, or the presence of any exocyclic group bearing a donor heteroatom, increase the basic character of the cyclic imino nitrogen atom and facilitate X–H bond activation? To answer this question, two types of experiments were performed.

The first experiment consists of the treatment of the metallacycle **19**,[15] which bears a methyl group on the sp^2 imino carbon atom, with diphenylphosphino acetylene $Ph_2P–C\equiv C–H$. No reaction takes place; this suggests that the role of the phosphorus lone pair in **3** or **4** renders the cyclic imino nitrogen atom more basic through delocalisation along the P–C=N linkage.



A new azazirconacyclopentene **20** was prepared to confirm this assumption; its reactivity with diphenylphosphinoacetylene and phosphonate $(EtO)_2P(O)H$ was investigated. The preparation of the complex **20** involves the heating of $[Cp_2ZrPh_2]$ under reflux with diisopropylamino cyanamide in toluene for 1 h (Scheme 9). Reactions of **20** with diphenylphosphinoacetylene and phosphonate proceed at room temperature in toluene for 30 min. The products are, as expected, the 18-electron zirconium metallacycles **21** and **22**, which are formed through C–H and P–H bond activation (Scheme 9). It is clear that the nitrogen lone pair of the exocyclic amino



Scheme 9. Reactivity of azazirconacyclopentene **20** with diphenylphosphinoacetylene and phosphonate.

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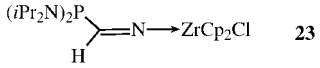
group in **20** plays the same role as the phosphorus lone pair in **3** and **4**.

In order to gain more insight in the scope and limitations of these X–H bond activation processes, we investigated the reactivity of the acyclic complex **23**, which was prepared



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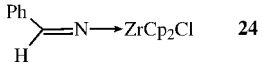

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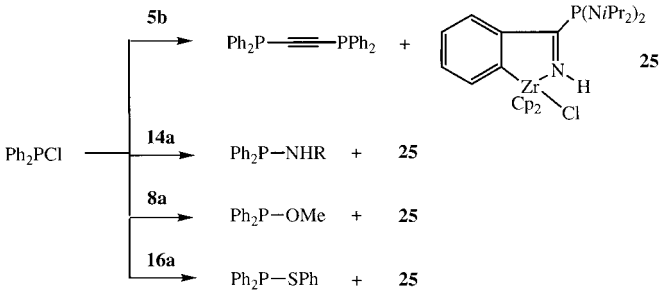
through addition of the Schwartz reagent [Cp_2ZrHCl] to bis(diisopropylamino)cyanophosphine.[17] We anticipated that **23** would not react as the cyclic systems **3** and **4** did, because complex **23** can be considered as an organometallic compound with heteroallene structure and an sp-hybridized nitrogen atom. A similar heteroallene structure was found for (benzylideneamino)zirconocene chloride **24**.[18] The X-ray structure of **24** revealed the presence of an almost linear Zr-N-C moiety (170.5(5)°) with a C=N bond length of 1.259(7) Å, which is somewhat shorter than that of a normal sp^2 C=N double-bond system. These data are in marked contrast with those observed both for the cyclic azazirconacyclopentene **19** (Zr-N-C 119.0(2)°, C=N 1.290(4) Å),[15] **5a** (Zr-N-C 123.54(14)°, C=N 1.294(3) Å), and **12a** (Zr-N-C 125.22(3)°, C=N 1.283(2) Å). As expected, no reaction was detected when the acyclic metallocomplex **23** was treated either with diphenylphosphinoacetylene or with the bisphosphonate derivative $H_2C[P(O)(OEt)_2]_2$. Retrocoordination of the nitrogen lone pair to the zirconium moiety is likely to account for the lack of reactivity of **23**.

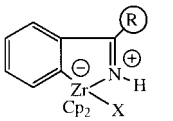
All the new 18-electron azazirconacyclopentenes with Zr–X bonds (X = C, N, O, P, S) are potentially starting reagents for the formation of a variety of derivatives by means of Zr–X bond cleavage. Preliminary experiments show that, for example, addition of an electrophile such as diphenylchlorophosphine to these complexes allows the quantitative formation of phosphorus species with P–C, P–N, P–O and P–S bonds (Scheme 10). Reactions take place at room temperature over a few hours. In addition to the formation of these compounds, the 18-electron azazirconacyclopentene **25** is isolated in high yield.



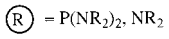
Scheme 10. Reactivity of diphenylchlorophosphine with azazirconacyclopentenes **5b**, **14a**, **8a** and **16a**.

Conclusion

The azazirconacyclopentene-substituted phosphines **3**, **4** and amine **20** are useful new reagents for X–H (X = C, N, O, P, S) bond activation. This remarkable behaviour results from the combination of two facts: i) the presence of the phosphorus lone pair in **3** and **4** (or the nitrogen lone pair in **20**) renders the cyclic imino nitrogen atom more basic through delocalisation along the P–C=N unit and ii) the presence of a 16-electron zirconium–nitrogen covalent bond in **3**, **4** (or **20**) allows a 18-electron zirconium–nitrogen dative bond to be incorporated in a stable heterosubstituted-cyclopentene bicyclic structure. One can describe the later compounds as betaines **III** with the imino nitrogen bearing the positive



III



charge and Zr bearing the negative charge. The resulting Zr–X bonds can be readily cleaved, as shown when an electrophile like diphenylchlorophosphine is added to some of these systems. This work is being extended to the study of other bond activation processes and to the investigation of Zr–X bond cleavages as a method of preparation of a variety of organic and organometallic species.

Experimental Section

General Remarks: Experiments were conducted under a dry argon atmosphere with standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under argon before use. Nuclear magnetic resonance (NMR) spectra were recorded on Brucker AC200, AM250 or MSL400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H; ^{13}C) or H_3PO_4 (^{31}P). IR spectra were recorded on a Perkin Elmer FT 1725x spectrometer. Mass spectra and elemental analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS.

Complexes 5a–c: Methyl propiolate (0.061 mL, 0.692 mmol) was added to a solution of **3** (0.384 g, 0.692 mmol) in toluene (8 mL) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give the yellow solid **5a** (0.411 g, 93% yield). The same procedure was used to prepare **5b** (0.478 g, 87% yield) from **3** (0.398 g, 0.718 mmol) and diphenylphosphinoacetylene (0.150 g, 0.718 mmol) and to prepare **5c** (0.322 g, 90% yield) from **3** (0.302 g, 0.545 mmol) and phenylacetylene (0.059 mL, 0.545 mmol).

Compound ***5a***: IR (KBr): $\tilde{\nu}$ = 1586 (C=N), 1710 (C=O), 2039 (C≡C), 3355 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 60.8 (s); ^1H NMR (C_6D_6): δ = 1.11 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.23 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 3.27 (m, 4H; NCH), 3.54 (s, 3H; OCH_3), 5.73 (s, 10H; CH_{Cp}), 6.97–7.21 (m, 2H; CH_{arom}), 7.48 (d, J_{HH} = 7.1 Hz, 1H; CH_{arom}), 8.25 (d, J_{HH} = 7.9 Hz, 1H; CH_{arom}), 10.01 ppm (d, 1H; J_{HP} = 5.6 Hz, NH); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.4 (d, J_{CP} = 6.0 Hz; CH_3), 25.1 (d, J_{CP} = 5.0 Hz; CH_3), 49.6 (d, J_{CP} = 10.9 Hz; NCH), 51.5 (s; OCH_3), 108.4 (s; CH_{Cp}), 110.6 (s; ≡C), 122.9, 129.5, 141.7 (s; CH_{arom}), 129.7 (d, J_{CP} = 23.2 Hz; CH_{arom}), 142.6 (s; ≡CZr), 145.8 (d, J_{CP} = 23.9 Hz; ZrC*C*), 154.7 (s; C=O), 197.3 (d, J_{CP} = 5.6 Hz; ZrC),

204.7 (d, $J_{CP}=40.7$ Hz; PC=N); elemental analysis calcd (%) for $C_{33}H_{46}N_3O_2PZr$ (638.94): C 62.03, H 7.25, N 6.57; found: C 62.09, H 7.23, N 6.61.

Compound ***5b***: IR (KBr): $\tilde{\nu}=1572$ (C=N), 2020 (C≡C), 3293 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=-30.4$ (s, PPh_2), 60.0 (s, $(iPr_2N)_2P$); ^1H NMR (C_6D_6): $\delta=1.07$ (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 1.17 (d, $J_{HH}=6.5$ Hz, 12H; CH_3), 3.20 (m, 4H; NCH), 5.84 (s, 10H; CH_{Cp}), 6.99–8.06 (m, 13H; CH_{arom}), 8.25 (d, $J_{HH}=8.1$ Hz, 1H; CH_{arom}), 10.13 (d, $J_{HP}=5.7$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.5$ (d, $J_{CP}=6.1$ Hz; CH_3), 25.2 (d, $J_{CP}=4.9$ Hz; CH_3), 49.6 (d, $J_{CP}=10.3$ Hz; NCH), 108.5 (s; CH_{Cp}), 110.3 (d, $J_{CP}=3.2$ Hz; ≡CP), 122.8, 128.9, 130.1 and 141.7 (s; CH_{arom}), 128.8 (d, $J_{CP}=17.7$ Hz; CH_{arom}), 129.9 (d, $J_{CP}=17.9$ Hz; CH_{arom}), 133.2 (d, $J_{CP}=20.0$ Hz; CH_{arom}), 141.5 (d, $J_{CP}=9.7$ Hz; *i*PPh_2), 145.9 (d, $J_{CP}=23.7$ Hz; ZrC*C*), 166.3 (d, $J_{CP}=8.1$ Hz; ≡CZr), 197.8 (d, $J_{CP}=5.9$ Hz; Zr*C*), 204.2 (d, $J_{CP}=41.1$ Hz; PC=N); elemental analysis calcd (%) for $C_{43}H_{53}N_3P_2Zr$ (765.07): C 67.50, H 6.98, N 5.49; found: C 67.52, H 6.95, N 5.53; MS (FAB/MNBA): *m*/*z*: 764 $[M+H]^+$.

Compound ***5c***: IR (KBr): $\tilde{\nu}=1576$ (C=N), 2089 (C≡C), 3335 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=60.2$ (s); ^1H NMR (C_6D_6): δ 1.07 (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 1.18 (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 3.20 (m, 4H; NCH), 5.87 (s, 10H; CH_{Cp}), 7.01–7.26 (m, 5H; CH_{arom}), 7.56–7.63 (m, 3H; CH_{arom}), 8.25 (d, $J_{HH}=7.8$ Hz, 1H; CH_{arom}), 10.20 (d, $J_{HP}=5.8$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.4$ (d, $J_{CP}=6.5$ Hz; CH_3), 25.1 (d, $J_{CP}=4.9$ Hz; CH_3), 49.5 (d, $J_{CP}=10.9$ Hz; NCH), 108.4 (s; CH_{Cp}), 118.9 (s; ≡C), 122.7, 125.9, 128.7, 129.4, 131.8 and 141.8 (s; CH_{arom}), 129.8 (d, $J_{CP}=13.0$ Hz; CH_{arom}), 139.7 (s; ≡CZr), 146.0 (d, $J_{CP}=23.7$ Hz; ZrC*C*), 198.0 (d, $J_{CP}=5.6$ Hz; Zr*C*), 203.4 (d, $J_{CP}=40.3$ Hz; PC=N), *i*Ph not observed; elemental analysis calcd (%) for $C_{37}H_{48}N_3PZr$ (657.01): C 67.64, H 7.36, N 6.39; found: C 67.59, H 7.40, N 6.34.

Complex 6a: Malononitrile (0.022 g, 0.330 mmol) was added to a solution of **3** (0.183 g, 0.330 mmol) in toluene (5 mL) at room temperature. The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (10 mL) and filtered. The volatiles were removed from the solution to give **6a** as a yellow solid(0.170 g, 83% yield). IR (KBr): $\tilde{\nu}=1561$ (C=N), 2080 (C≡N), 3286 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=61.4$ (s); ^1H NMR (C_6D_6): $\delta=1.11$ (d, $J_{HH}=5.8$ Hz, 12H; CH_3), 1.14 (d, $J_{HH}=5.9$ Hz, 12H; CH_3), 3.19 (m, 4H; NCH), 5.69 (s, 10H; CH_{Cp}), 5.96 (s, CH), 6.92–7.35 (m, 3H; CH_{arom}), 8.16 (d, $J_{HH}=7.8$ Hz, 1H; CH_{arom}), 9.38 (d, $J_{HP}=5.1$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.4$ (d, $J_{CP}=6.6$ Hz; CH_3), 24.9 (d, $J_{CP}=4.4$ Hz; CH_3), 49.7 (d, $J_{CP}=10.7$ Hz; NCH), 110.8 (s; CH_{Cp}), 112.8 (s; ZrCH), 123.1, 130.2, 141.1 (s; CH_{arom}), 130.5 (d, $J_{CP}=12.8$ Hz; CH_{arom}), 145.2 (d, $J_{CP}=21.9$ Hz; ZrC*C*), 150.6 (s; C≡N), 197.3 (d, $J_{CP}=5.0$ Hz; Zr*C*), 205.3 (d, $J_{CP}=41.2$ Hz; PC=N); elemental analysis calcd (%) for $C_{32}H_{44}N_5PZr$ (620.92): C 61.90, H 7.14, N 11.27; found: C 61.85, H 7.17, N 11.32.

Complex 6b: Diethylmalonate (87.6 μL, 0.577 mmol) was added to a solution of **3** (0.320 g, 0.577 mmol) in toluene (6 mL) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give **6b** as a yellow solid (0.338 g, 82% yield). IR (KBr): $\tilde{\nu}=3920$ cm^{-1} (N–H); $^{31}P\{^1H\}$NMR (C_6D_6): $\delta=46.8$; ^1H NMR (C_6D_6): $\delta=1.14$ (t, $J_{HH}=6.7$ Hz, 6H; CH_2CH_3), 1.16 (d, $J_{HH}=6.6$ Hz, 12H; $CHCH_3$), 1.28 (d, $J_{HH}=6.7$ Hz, 12H; $CHCH_3$), 3.69 (m, 4H; CH), 4.16 (q, 4H; $J_{HH}=6.8$ Hz, CH_2), 6.03 (s, 10H; CH_{Cp}), 7.21 (m, 3H; CH_{arom}), 8.4(m, 1H; CH_{arom}), 10.1 (d, $J_{HP}=4.7$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR(C_6D_6): $\delta=15.2$ (s; CH_2CH_3), 15.4 (s; CH_2CH_3), 24.5 (d, $J_{CP}=6.7$ Hz; $CHCH_3$), 24.8 (d, $J_{CP}=6.0$ Hz; $CHCH_3$), 49.1 (d, $J_{CP}=11.7$ Hz; ZrCH), 57.7 (s; CH_2), 62.8 (s; CH_2), 66.37 (s; CHZr), 111.5 (s; CH_{Cp}), 123.2 (s; CH_{arom}), 129.5 (s; CH_{arom}), 129.9 (d, $J_{CP}=19.7$ Hz; CH_{arom}), 141.3 (s; CH_{arom}), 148.0 (d, $J_{CP}=29.2$ Hz; ZrC*C*), 169.8 (s; C=O), 174.8 (s; C=O), 196.8 (d, $J_{CP}=5$ Hz; Zr*C*), 201.6 (d, $J_{CP}=40.9$ Hz; C=N); elemental analysis calcd (%) for $C_{36}H_{54}O_4N_3PZr$ (715.03): C 60.47, H 7.61, N 5.88; found C 60.41, H 7.58, N 5.85.

Complex 7: Complex **3** (0.295 g, 0.532 mmol) was treated with vinyl acetate (0.049 mL, 0.532 mmol) in the same manner as **6a** and **6b**. Compound **7** was isolated as a yellow solid (0.269 g, 79% yield). IR (KBr): 1591 (C≡N), 1630 (C=O), 3315 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=55.9$ (s); ^1H NMR (C_6D_6): $\delta=1.12$ (d, $J_{HH}=6.8$ Hz, 12H; CH_3), 1.15 (d, $J_{HH}=6.8$ Hz, 12H; CH_3), 2.98 (s, 1H; CH_2), 3.30 (m, 4H; NCH), 3.41 (s, 1H; CH_2), 4.21 (d, $J_{HH}=6.2$ Hz, 1H; =CH), 4.75 (d, $J_{HH}=14.0$ Hz, 1H; =CH), 5.94 (s, 10H; CH_{Cp}), 6.98 (dd, $J_{HH}=14.0$, 6.2 Hz, 1H; =CH), 7.01–7.32 (m, 3H; CH_{arom}), 8.22 (m, 1H; CH_{arom}), 9.62 (d, $J_{HP}=5.5$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.5$ (d, $J_{CP}=6.4$ Hz; CH_3), 24.8 (d, $J_{CP}=4.5$ Hz; CH_3), 49.6 (d, $J_{CP}=11.1$ Hz; NCH), 58.1 (s; CH_2), 91.6 (s; $=CH_2$), 111.1 (s; CH_{Cp}), 122.7, 129.5, 141.2 (s; CH_{arom}), 130.0 (d, $J_{CP}=15.0$ Hz; CH_{arom}), 146.9 (d, $J_{CP}=24.2$ Hz; ZrC*C*), 148.2 (s; =CH), 168.2 (s; C=O), 198.7 (d, $J_{CP}=6.1$ Hz; ZrC), 202.1 (d, $J_{CP}=39.2$ Hz; PC=N); elemental analysis calcd (%) for $C_{33}H_{48}N_3O_2PZr$ (640.92): C 61.84, H 7.54, N 6.55; found: C 61.81, H 7.57, N 6.60.

Complexes 8a–c and 9: Methanol (0.020 mL, 0.505 mmol) was added to a solution of **3** (0.280 g, 0.505 mmol) in toluene (5 mL) at room temperature. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give the yellow solid **8a** (0.245 g, 83% yield). The same experimental procedure was used for the preparation of **8b** [from **3** (0.233 g, 0.420 mmol) and isopropanol (0.032 mL, 0.420 mmol)], **8c** [from **3** (0.222 g, 0.401 mmol) and phenol (0.037 g, 0.401 mmol)] and **9** [from **4** (0.289 g, 0.404 mmol) and methanol (0.016 mL, 0.404 mmol)].Complexes **8b**,**c** and **9** were obtained as yellow solids in 81, 87 and 71% yield, respectively.

Complex ***8a***: IR (Kbr): $\tilde{\nu}=1576$ (C=N), 3335 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=56.9$ (s); ^1H NMR (C_6D_6): $\delta=1.13$ (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 1.18 (d, $J_{HH}=6.5$ Hz, 12H; CH_3), 3.24 (m, 4H; NCH), 3.86 (s, 3H; OCH_3), 5.90 (s, 10H; CH_{Cp}), 7.03–7.25 (m, 2H; CH_{arom}), 7.52 (d, $J_{HH}=7.3$ Hz, 1H; CH_{arom}), 8.19 (m, 1H; CH_{arom}), 9.80 (d, $J_{HP}=5.9$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.6$ (d, $J_{CP}=6.0$ Hz; CH_3), 49.5 (d, $J_{CP}=10.9$ Hz; NCH), 59.6 (s; OCH_3), 110.0 (s; CH_{Cp}), 122.4, 129.0, 141.8 (s; CH_{arom}), 129.5 (d, $J_{CP}=11.7$ Hz; CH_{arom}), 148.3 (d, $J_{CP}=23.1$ Hz; ZrC*C*), 198.8 (d, $J_{CP}=36.5$ Hz; PC=N), 199.2 (d, $J_{CP}=7.8$ Hz; ZrC); elemental analysis calcd (%) for $C_{30}H_{46}N_3POZr$ (586.89): C 61.39, H 7.89, N 7.16; found: C 61.41, H 7.92, N 7.13.

Complex ***8b***: IR (KBr): $\tilde{\nu}=1566$ (C=N), 3236 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=58.1$ (s); ^1H NMR (C_6D_6): $\delta=1.13$ (d, $J_{HH}=6.3$ Hz, 12H; CH_3), 1.17 (d, $J_{HH}=6.7$ Hz, 12H; CH_3), 1.27 (d, $J_{HH}=5.7$ Hz, 6H; $OCHCH_3$), 3.26 (m, 4H; NCH), 3.98 (sept, $J_{HH}=5.7$ Hz, 1H; OCH), 5.87 (s, 10H; CH_{Cp}), 7.02–7.30 (m, 2H; CH_{arom}), 7.52 (m, 1H; CH_{arom}), 8.21 (d, $J_{HH}=7.8$ Hz, 1H; CH_{arom}), 9.69 (d, $J_{HP}=6.2$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.4$ (d, $J_{CP}=6.5$ Hz; CH_3), 25.1 (d, $J_{CP}=5.3$ Hz; CH_3), 27.9 (s; $OCHCH_3$), 49.4 (d, $J_{CP}=10.9$ Hz; NCH), 70.7 (s; OCH), 110.0 (s; CH_{Cp}), 122.2, 129.2, 141.6 (s; CH_{arom}), 129.5 (d, $J_{CP}=13.2$ Hz; CH_{arom}), 147.9 (d, $J_{CP}=23.5$ Hz; ZrC*C*), 198.2 (d, $J_{CP}=38.7$ Hz; PC=N), 199.7 (d, $J_{CP}=5.2$ Hz; ZrC); elemental analysis calcd (%) for $C_{32}H_{50}N_3POZr$ (614.96): C 62.50, H 8.19, N 6.83; found: C 62.42, H 8.22, N 6.91.

Complex ***8c***: IR (KBr): $\tilde{\nu}=1568$ (C=N), 3410 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=56.7$ (s); ^1H NMR (C_6D_6): $\delta=1.09$ (d, $J_{HH}=6.5$ Hz, 12H; CH_3), 1.10 (d, $J_{HH}=6.5$ Hz, 12H; CH_3), 3.24 (m, 4H; NCH), 5.92 (s, 10H; CH_{Cp}), 6.80–7.45 (m, 8H; CH_{arom}), 8.25 (m, 1H; CH_{arom}), 9.71 (d, $J_{HP}=5.7$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.4$ (d, $J_{CP}=7.0$ Hz; CH_3), 24.7 (d, $J_{CP}=5.4$ Hz; CH_3), 49.5 (d, $J_{CP}=10.6$ Hz; NCH), 110.9 (s; CH_{Cp}), 120.2, 122.6, 129.6, 129.7, 129.9, 130.1, 141.2 (s; CH_{arom}), 147.1 (d, $J_{CP}=23.6$ Hz; ZrC*C*), 168.9 (s; *i*OPh), 199.1 (d, $J_{CP}=5.1$ Hz; ZrC), 201.2 (d, $J_{CP}=38.7$ Hz; PC=N); elemental analysis calcd (%) for $C_{35}H_{48}N_3POZr$ (648.97): C 64.77, H 7.45, N 6.47; found: C 64.69, H 7.49, N 6.51.

Complex ***9***: IR (KBr): $\tilde{\nu}=1591$ (C=N), 3325 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=62.9$ (s); ^1H NMR (C_6D_6): $\delta=0.83-2.14$ (m, 40H; CH_2), 2.90 (m, 4H; NCH), 3.84 (s, 3H; OCH_3), 5.95 (s, 10H; CH_{Cp}), 7.07–7.26 (m, 2H; CH_{arom}), 7.53 (d, $J_{HH}=7.2$ Hz, 1H; CH_{arom}), 8.33 (m, 1H; CH_{arom}), 9.94 (d, $J_{HP}=6.1$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=26.3$, 27.5 (s; CH_2), 35.6 (d, $J_{CP}=5.7$ Hz; CH_2), 59.6 (br; NCH, OCH_3), 110.0 (s; CH_{Cp}), 122.3, 128.9, 141.6 (s; CH_{arom}), 129.7 (d, $J_{CP}=10.5$ Hz; CH_{arom}), 148.2 (d, $J_{CP}=24.2$ Hz; ZrC*C*), 198.6 (d, $J_{CP}=38.2$ Hz; PC=N), 199.5 (d, $J_{CP}=5.8$ Hz; ZrC); elemental analysis calcd (%) for $C_{45}H_{62}N_3POZr$ (747.17): C 72.33, H 8.36, N 5.62; found: C 72.28, H 8.30, N 5.70.

Iminophosphines 10, 11: For the first step, methanol (0.029 mL, 0.734 mmol or 0.028 mL, 0.702 mmol) was added to a solution of **3** (0.203 g, 0.367 mmol) or **4** (0.251 g, 0.351 mmol) in toluene (5 mL) at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give **10** (0.107 g, 87% yield) and **11**

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(0.145 g, 90% yield) as yellow powders. In the second step the same procedure was followed, however, **8a** replaced **3** and **9** replaced **4**.

*Compound **10***: IR (KBr): $\tilde{\nu}$ = 1583 (C=N), 3219 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 64.9 (s); ^{1}H NMR (C_6D_6): δ = 0.96 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.11 (d, J_{HH} = 6.7 Hz, 12H; CH_3), 3.06 (m, 4H; NCH), 7.15 (m, 3H; CH_{arom}), 8.10 (m, 2H; CH_{arom}), 11.14 (d, J_{HP} = 12.5 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.7 (d, J_{CP} = 5.4 Hz; CH_3), 49.4 (br; NCH), 128.5, 128.7, 130.0 (s; CH_{arom}), 142.1 (d, J_{CP} = 29.1 Hz; *i*Ph), 188.2 (d, J_{CP} = 30.7 Hz; PC=N); elemental analysis calcd (%) for $C_{19}H_{34}N_3P$ (335.47): C 68.02, H 10.21, N 12.52; found: C 68.10, H 10.15, N 12.63; MS (DCI/CH_4): *m*/*z*: 336 [*M*+H]$^+$.

*Complex **11***: IR (KBr): 1567 (C=N), 3222 cm^{-1} $\tilde{\nu}$(N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 70.8 (s); ^{1}H NMR (C_6D_6): δ = 0.83–2.11 (m, 40H; CH_2), 2.80 (m, 4H; NCH), 7.15 (m, 3H; CH_{arom}), 8.12 (m, 2H; CH_{arom}), 11.27 (d, J_{HP} = 12.2 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 26.4, 27.5 (s; CH_2), 35.8 (d, J_{CP} = 2.6 Hz; CH_2), 59.7 (br; NCH), 128.4, 128.5, 129.9 (s; CH_{arom}), 142.6 (d, J_{CP} = 28.8 Hz; *i*Ph), 188.7 (d, J_{CP} = 32.3 Hz; PC=N); elemental analysis calcd (%) for $C_{31}H_{50}N_3P$ (495.73): C 75.10, H 10.16, N 8.47; found: C 74.98, H 10.12, N 8.70; MS (DCI/CH_4): *m*/*z*: 496 [*M*+H]$^+$.

Complexes 12a,b and 13: Acetophenone (0.083 mL, 0.718 mmol) was added to a solution of **3** (0.398 g, 0.718 mmol) in toluene (8 mL) at room temperature. The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (15 mL) and filtered. The volatiles were removed from the solution to give the yellow solid **12a** (0.426 g, 88% yield). The same procedure with **3** (0.261 g, 0.471 mmol) and acetone (0.035 mL, 0.471 g) or **3** (0.287 g, 0.519 mmol) and cyclohexanone (0.053 mL, 0.519 mmol) to prepare complexes **12a** (0.265 g, 92% yield) and **13** (0.264 g, 78% yield), respectively.

*Complex **12a***: IR (KBr): $\tilde{\nu}$ = 1566 (C=N), 3345 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 54.1 (s); ^{1}H NMR (CD_2Cl_2): δ = 1.11 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.32 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 3.46 (m, 4H; NCH), 3.82 (s, 1H; =CH), 4.46 (s, 1H; =CH), 6.09 (s, 10H; CH_{Cp}), 7.02–7.69 (m, 8H; CH_{arom}), 8.12 (m, 1H; CH_{arom}), 9.51 (d, J_{HP} = 5.3 Hz, 1H; NH); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 24.0 (d, J_{CP} = 7.3 Hz; CH_3), 24.1 (d, J_{CP} = 6.9 Hz; CH_3), 49.2 (d, J_{CP} = 11.2 Hz; NCH), 82.1 (s; =CH_2), 110.1 (s; CH_{Cp}), 122.1, 125.8, 126.9, 127.7, 128.7, 140.6 (s; CH_{arom}), 129.1 (d, J_{CP} = 16.8 Hz; CH_{arom}), 143.6 (s; *i*Ph), 146.6 (d, J_{CP} = 24.6 Hz; ZrC*C*), 166.7 (s; =C), 197.3 (d, J_{CP} = 5.6 Hz; ZrC), 201.3 (d, J_{CP} = 37.7 Hz; PC=N); elemental analysis calcd (%) for $C_{37}H_{50}N_3POZr$ (675.01): C 65.80; H 7.46, N 6.22; found: C 65.77, H 7.52, N 6.18.

*Complex **12b***: IR (KBr): $\tilde{\nu}$ = 1521 (C=N), 3335 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 56.8 (s); ^{1}H NMR (C_6D_6): δ = 1.11 (d, J_{HH} = 6.6 Hz, 6H; CH_3), 1.13 (d, J_{HH} = 6.6 Hz, 18H; CH_3), 1.94 (s, 3H; $OCCH_3$), 3.30 (m, 4H; NCH), 3.67 (d, J_{HH} = 1.1 Hz, 1H; =CH), 4.00 (d, J_{HH} = 1.1 Hz, 1H; =CH), 5.96 (s, 10H; CH_{Cp}), 6.99–7.43 (m, 3H; CH_{arom}), 8.22 (m, 1H; CH_{arom}), 9.60 (d, J_{HP} = 5.8 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.5 (d, J_{CP} = 6.5 Hz; CH_3), 24.9 (d, J_{CP} = 5.5 Hz; CH_3), 26.3 (s; OC*C*H_3), 49.5 (d, J_{CP} = 11.1 Hz; NCH), 82.4 (s; =CH_2), 110.7 (s; CH_{Cp}), 122.5, 129.5, 141.2 (s; CH_{arom}), 129.7 (d, J_{CP} = 14.9 Hz; CH_{arom}), 146.9 (d, J_{CP} = 24.2 Hz; ZrC*C*), 167.5 (s; =C), 199.1 (d, J_{CP} = 5.6 Hz; ZrC), 201.2 (d, J_{CP} = 38.8 Hz; PC=N); elemental analysis calcd (%) for $C_{32}H_{48}N_3POZr$ (612.94): C 62.70, H 7.89, N 6.85; found: C 62.65, H 7.93, N 6.78.

*Complex **13***: IR (KBr): $\tilde{\nu}$ = 1576 (C=N), 3305 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 56.5 (s); ^{1}H NMR (C_6D_6): δ = 1.13 (d, J_{HH} = 6.4 Hz, 12H; CH_3), 1.14 (d, J_{HH} = 6.4 Hz, 12H; CH_3), 1.45 (m, 2H; CH_2), 1.75 (m, 4H; CH_2), 2.36 (m, 2H; CH_2), 3.28 (m, 4H; NCH), 4.35 (t, J_{HH} = 3.6 Hz, 1H; =CH), 5.87 (s, 10H; CH_{Cp}), 7.03–7.20 (m, 2H; CH_{arom}), 7.44 (d, J_{HH} = 7.2 Hz, 1H; CH_{arom}), 8.20 (m, 1H; CH_{arom}), 9.60 (d, J_{HP} = 5.9 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 23.2, 25.1, 26.0, 33.4 (s; CH_2), 24.5 (d, J_{CP} = 6.5 Hz; CH_3), 24.7 (d, J_{CP} = 6.4 Hz; CH_3), 49.6 (d, J_{CP} = 10.8 Hz; NCH), 94.4 (s; =CH), 110.7 (s; CH_{Cp}), 122.4, 129.5, 141.1 (s; CH_{arom}), 129.6 (d, J_{CP} = 14.6 Hz; CH_{arom}), 146.8 (d, J_{CP} = 24.0 Hz; ZrC*C*), 161.8 (s; =C), 199.4 (d, J_{CP} = 5.3 Hz; ZrC), 200.9 (d, J_{CP} = 38.2 Hz; PC=N); elemental analysis calcd (%) for $C_{35}H_{52}N_3POZr$ (653.01): C 64.37, H 8.02, N 6.43; found: C 64.28, H 7.98, N 6.51.

Complexes 14a–c: The same procedure as above for complexes **12** and **13** was used here to react **3** (0.205 g, 0.370 mmol) with aniline (0.033 mL, 0.370 mmol) or **3** (0.233 g, 0.420 mmol) with benzylamine (0.046 mL, 0.420 mmol) or **3** (0.280 g, 0.505 mmol) with 4-aminobenzonitrile (0.060 g, 0.505 mmol) to give the yellow powders **14a** (0.187 g, 78% yield), **14b** (0.247 g, 89% yield) and **14c** (0.291 g, 87% yield), respectively.

*Complex **14a***: IR (KBr): $\tilde{\nu}$ = 1561 (C=N), 3226 (N–H), 3325 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 56.8 (s); ^{1}H NMR (CD_2Cl_2): δ = 1.11 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.31 (d, J_{HH} = 6.7 Hz, 12H; CH_3), 3.42 (m, 4H; NCH), 3.64 (s, 1H; NH), 5.96 (s, 10H; CH_{Cp}), 6.33 (m, 3H; CH_{arom}), 6.96–7.27 (m, 4H; CH_{arom}), 7.63 (d, J_{HH} = 7.4 Hz, 1H; CH_{arom}), 8.10 (m, 1H; CH_{arom}), 9.16 (d, J_{HP} = 5.5 Hz, 1H; =NH); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 24.0 (d, J_{CP} = 6.8 Hz; CH_3), 24.1 (d, J_{CP} = 6.8 Hz; CH_3), 49.2 (d, J_{CP} = 11.0 Hz; NCH), 109.5 (s; CH_{Cp}), 116.0, 122.0, 128.7, 141.1 (s; CH_{arom}), 129.1 (d, J_{CP} = 15.1 Hz; CH_{arom}), 146.2 (d, J_{CP} = 25.5 Hz; ZrC*C*), 159.4 (s; *i*Ph), 196.8 (d, J_{CP} = 5.6 Hz; ZrC), 203.9 (d, J_{CP} = 39.1 Hz; PC=N); elemental analysis calcd (%) for (647.99): C 64.87, H 7.62, N 8.64; found: C 64.79, H 7.64, N 8.70.

*Complex **14b***: IR (KBr): $\tilde{\nu}$ = 1564 (C=N), 3315 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 54.5; ^{1}H NMR (C_6D_6): δ = 1.04 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.12 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 2.11 (s, 3H; CH_3), 3.29 (m, 4H; CH), 3.75 (s, 1H; N–H), 5.80 (s, 10H; CH_{Cp}), 7.22 (m, 8H; CH_{arom}), 8.15 (m, 1H; CH_{arom}), 8.32 (m, 1H; CH_{arom}), 9.36 (d, J_{HP} = 5.5 Hz, 1H; =NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 21.2 (s; CH_3), 24.4 (s; CH_3), 24.5 (s; CH_3), 49.7 (d, J_{CP} = 10.7 Hz; CH), 110.0 (s; CH_{Cp}), 112.5 (s; CH_{arom}), 124.5 (s; C_{arom}), 125.4 (s; CH_{arom}), 126.0 (s; CH_{arom}), 127.6 (s; CH_{arom}), 130.2 (s; CH_{arom}), 141.8 (s; CH_{arom}), 145.5 (d, J_{CP} = 24.2 Hz; ZrC*C*), 157.6 (s; *i*Ph), 196.0 (d, J_{CP} = 5.1 Hz; ZrC), 204.5 (d, J_{CP} = 38.6 Hz; PC=N); elemental analysis calcd (%) for $C_{36}H_{51}N_4PZr$ (662.02): C 65.31, H 7.76, N 8.46; found: C 65.27, H 7.72, N 8.41.

*Complex **14c***: ^{31}P{^{1}H} NMR (C_6D_6): δ = 56.6; ^{1}H NMR(C_6D_6): δ = 0.93 (d, J_{HH} = 5.7 Hz, 12H; CH_3), 1.07 (d, J_{HH} = 6.8 Hz, 12H; CH_3), 3.15 (m, 4H; N–H), 4.06 (s, 1H; N–H), 5.68 (s, 10H; CH_{Cp}), 7.3 (m, 5H; CH_{arom}), 8.1 (m, 1H; CH_{arom}), 8.23 (m, 1H; CH_{arom}), 8.0 (d, J_{HH} = 5.2 Hz, 1H; CH_{arom}), 11.1 (d, J_{HP} = 12.2 Hz, 1H; =NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.5 (d, J_{CP} = 5.3 Hz; CH_3), 49.7 (d, J_{CP} = 11 Hz; N–CH), 92.6 (s; CN), 110.3 (s; CH_{Cp}), 112.5 (s; CH_{arom}), 122.8 (s; C–CN_{arom}), 123.6 (s; CH_{arom}), 141.8 (s; CH_{arom}), 146.7 (d, J_{CP} = 24.7 Hz; C_{arom}), 163.1 (s; *i*Ph), 197,0 (d, J_{CP} = 5.9 Hz; ZrC), 205.4 (d, J_{CP} = 39.1 Hz; PC=N); elemental analysis calcd (%) for $C_{36}H_{48}N_5PZr$ (673.01): C 64.25, H 7.19, N 10.41; found: C 64.21, H 7.21, N 10.36.

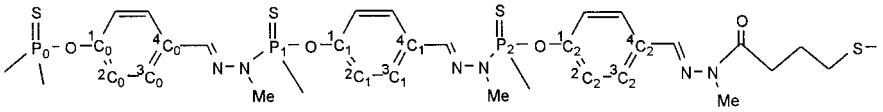
Complex 15: Again, the same procedure that was used from the preparation of complexes **12** and **13** was followed with **3** (0.324 g, 0.585 mmol) in toluene (8 mL) and diethylphosphite (0.075 mL, 0.585 mmol). Complex **15** was obtained as an orange solid (0.377 g, 93% yield). IR (Kbr): $\tilde{\nu}$ = 1576 (C=N), 3305 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 57.6 (s; (iPr$_2$N)$_2$P), 143.8 (s; (EtO)$_2$P=O); ^{1}H NMR (C_6D_6): δ = 1.12 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.18 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.33 (t, J_{HH} = 7.1 Hz, 6H; OCH_2CH_3), 3.27 (m, 4H; NCH), 3.97 (dt, J_{HH} = 7.1 Hz, J_{HP} = 4.2 Hz, 4H; OCH), 6.05 (s, 10H; CH_{Cp}), 6.99–7.22 (m, 2H; CH_{arom}), 7.39 (d, J_{HH} = 7.2 Hz, 1H; CH_{arom}), 8.27 (m, 1H; CH_{arom}), 9.61 (d, J_{HP} = 5.7 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 18.3 (d, J_{CP} = 4.3 Hz; OCH_2CH_3), 24.4 (d, J_{CP} = 6.5 Hz; CH_3), 25.1 (d, J_{CP} = 5.2 Hz; CH_3), 49.5 (d, J_{CP} = 10.4 Hz; NCH), 55.9 (d, J_{CP} = 13.8 Hz; OCH_2), 111.0 (s; CH_{Cp}), 122.5, 129.6, 141.2 (s; CH_{arom}), 129.9 (d, J_{CP} = 16.0 Hz; CH_{arom}), 146.8 (d, J_{CP} = 23.6 Hz; ZrC*C*), 199.7 (d, J_{CP} = 4.8 Hz; ZrC), 201.6 (d, J_{CP} = 39.9 Hz; PC=N); elemental analysis calcd (%) for $C_{33}H_{53}N_3O_3P_2Zr$ (692.96): C 57.19, H 7.70, N 6.06; found: C 57.12, H 7.73, N 6.13.

Complexes 16a,b: The same procedure that was used from the preparation of complexes **12** and **13** was followed with **3** (0.257 g, 0.463 mmol) in toluene (5 mL) and thiophenol (0.047 mL, 0.463 mmol) or with **3** (0.201 g, 0.362 mmol) in toluene (5 mL) and benzylmercaptan (0.042 mL, 0.362 mmol) to give the yellow powders, **16a** (0.274 g, 89% yield) or **16b** (0.199 g, 81% yield).

*Complex **16a***: IR (KBr): $\tilde{\nu}$ = 1591 (C=N), 3296 cm^{-1} (N–H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 57.3 (s); ^{1}H NMR (C_6D_6): δ = 1.12 (d, J_{HH} = 6.6 Hz, 12H; CH_3), 1.17 (d, J_{HH} = 6.7 Hz, 12H; CH_3), 3.30 (m, 4H; NCH), 5.82 (s, 10H; CH_{Cp}), 6.98–7.70 (m, 8H; CH_{arom}), 8.34 (m, 1H; CH_{arom}), 9.87 (d, J_{HP} = 5.4 Hz, 1H; NH); ^{13}C{^{1}H} NMR (C_6D_6): δ = 24.5 (d, J_{CP} = 6.8 Hz; CH_3), 25.1 (d, J_{CP} = 5.3 Hz; CH_3), 49.7 (d, J_{CP} = 11.6 Hz; NCH), 110.2 (s; CH_{Cp}), 122.8, 122.9, 128.0, 128.5, 128.9, 129.7, 133.5, 141.9 (s; CH_{arom}), 129.9 (d, J_{CP} = 17.6 Hz; CH_{arom}), 146.3 (d, J_{CP} = 25.2 Hz; ZrC*C*), 151.2 (s; *i*Ph), 197.4 (d, J_{CP} = 6.1 Hz; ZrC), 204.4 (d, J_{CP} = 40.6 Hz; PC=N); elemental analysis calcd (%) for $C_{35}H_{48}N_3PSZr$ (665.04): C 63.21, H 7.27, N 6.31; found: C 63.27, H 7.19 N 6.40.

Compound ***16b***: IR (KBr): $\tilde{\nu}=1571$ (C=N), 3276 cm^{-1} (N–H); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=57.7$ (s); ^1H NMR (C_6D_6): $\delta=1.10$ (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 1.17 (d, $J_{HH}=6.6$ Hz, 12H; CH_3), 3.28 (m, 4H; NCH), 3.94 (s, CH_2), 5.80 (s, 10H; CH_{Cp}), 6.99–7.79 (m, 8H; CH_{arom}), 8.31 (m, 1H; CH_{arom}), 9.63 (d, $J_{HP}=5.4$ Hz, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=24.5$ (d, $J_{CP}=6.7$ Hz; CH_3), 25.1 (d, $J_{CP}=5.0$ Hz; CH_3), 38.1 (s; CH_2), 49.6 (d, $J_{CP}=11.2$ Hz; NCH), 109.6 (s; CH_{Cp}), 122.8, 126.4, 128.8, 129.6, 141.9 (s; CH_{arom}), 129.8 (d, $J_{CP}=17.3$ Hz; CH_{arom}), 146.3 (s; *i*Ph), 146.6 (d, $J_{CP}=24.4$ Hz; ZrC*C*), 197.6 (d, $J_{CP}=6.1$ Hz; ZrC), 204.1 (d, $J_{CP}=40.8$ Hz; PC=N); elemental analysis calcd (%) for $C_{36}H_{50}N_3PSZr$ (679.07): C 63.67, H 7.42, N 6.18; found: C 63.61, H 7.38, N 6.24.

Dendritic complex 18: The dendrimer $G_2(SH)_{12}$ **17** (0.378 g, 0.076 mmol) in THF (15 mL) was added to a solution of **3** (0.505 g, 0.912 mmol) in toluene(5 mL) at room temperature. The mixture was stirred at room temperature for 1 hour and then evaporated to dryness. The resulting solid residue was washed with diethyl ether (5 mL). The product **18** was obtained as a yellow solid (0.320 g, 72 % yield). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=51.6$ (s; P_o), 58.2 (s; PC=N), 61.7 (s; P_1, P_2); ^1H NMR ($[D]_8THF$): $\delta=1.12$ (d,



$J_{HH}=6.6$ Hz, 144H; CH_3), 1.17 (d, $J_{HH}=6.6$ Hz, 144H; CH_3), 1.96 (t, $J_{HH}=6.9$ Hz, 24H; CH_2CH_2), 2.52 (t, $J_{HH}=7$ Hz, 24H; CH_2-S-Zr), 2.94 (t, $J_{HH}=7.2$ Hz, 24H; CH_2–CO), 3.35 (m, 111H; C*H*CH_3 and N–CH_3), 5.82 (s, 120H; CH_{Cp}), 7.45 (m, 129H; CH_{arom} and CH=N), 8.34 (m, 12H; CH_{arom}), 9.87 (d, $J_{HH}=5.4$ Hz, 12H; NH); $^{13}C\{^1H\}$ NMR ($[D]_8THF$) $\delta=24.3$ (s; CH_2), 24.6 (d, $J_{CP}=6.8$ Hz; CH_3), 25.1 (d, $J_{CP}=6.8$ Hz; CH_3), 27.8 (s; CH_2), 29.3 (s; CH_2), 32.0 (s; N–CH_3), 33.1 (d, $J_{CP}=12.9$ Hz; PNCH_3), 49.7 (d, $J_{CP}=11.9$ Hz, CH; *i*Pr), 110.2 (s; CH_{Cp}), 121.8 (br d, $J_{CP0,1}=3$ Hz; $^2C_{0,1}$), 123.2 (br s; CH_{arom}), 128.3 (s; $^3C_{0,1}$), 129.5, 129.9 (br s; CH_{arom}), 132.2 (s; $^4C_{0,1}$), 137.6 (s; CH=N), 138.9 (d, $J_{CP1}=12.9$ Hz; CH=N), 146.3 (d, $J_{CP}=25.2$ Hz; ZrC*C*), 151.4 (d, $J_{CP}=7.8$ Hz; $^1C_0$), 151.5 (d, $J_{CP1}=6$ Hz; $^1C_1$), 147.2 (s; C=O), 197.4 (d, $J_{CP}=6.1$ Hz; Zr–C), 204.4 (d, $J_{CP}=40.6$ Hz; PC=N); elemental analysis calcd (%) for $C_{564}H_{756}N_{78}O_{33}P_{22}S_{22}Zr_{12}$ (10634.72): C 63.70, H 7.16, N 10.27; found: C 62.94, H 6.98, N 10.06.

Azazirconacyclopentene 20: Diisopropylaminocyanamide (0.063 mL, 0.420 mmol) was added to a solution of diphenylzirconocene (0.157 g, 0.420 mmol) in toluene (5 mL). The mixture was heated at 90 °C for 1 h, then evaporated to dryness. The resulting solid was extracted with pentane (20 mL) to give the yellow solid **20** (0.163 g, 92 %). IR (KBr): $\tilde{\nu}=1576$ cm^{-1} (C=N); ^1H NMR (C_6D_6): $\delta=1.26$ (d, $J_{HH}=6.8$ Hz, 12H; CH_3), 3.80 (sept, $J_{HH}=6.8$ Hz, 2H; CH), 5.94 (s, 10H; CH_{Cp}), 7.12 (m, 4H; CH_{arom}); $^{13}C\{^1H\}$ NMR(C_6D_6): $\delta=22.6$ (s; CH_3), 48.9 (s; NCH), 111.1 (s; CH_{Cp}), 141.6 (CH_{arom}), 160.8 (s; C=N), 162.6 (s; CH_{arom}), 189.0 (s; CH_{arom}); elemental analysis calcd (%) for $C_{23}H_{28}N_2Zr$ (423.71): C 65.20, H 6.66, N 6.61; found: C 65.08, H 6.61, N 6.57.

Complex 21: Diphenylphosphinoacetylene was added (0.109 g, 0.52 mmol) to a solution of **20** (0.220 g, 0.52 mmol) in toluene (5 mL) at room temperature. The mixture was stirred for 30 min, then evaporated to dryness. The resulting solid was extracted with pentane (20 mL) to give **21** as a yellow powder (0.237 g, 72 %). IR (KBr): $\tilde{\nu}=1573$ (C=N), 2015 (C=C), 3418 cm^{-1} (N–H); ^1H NMR (C_6D_6): $\delta=0.94$ (d, $J_{HH}=6.8$ Hz, 12H; CH_3), 3.73 (sept, $J_{HH}=6.8$ Hz, 2H; NCH), 5.87 (s, 10H; CH_{Cp}), 7.12 (m, 12H; CH_{arom}), 8.05 (m.2H; CH_{arom}); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta=21.7$ (s; CH_3), 49.4 (s; NCH), 108.4 (s; CH_{Cp}), 122.7 (s; CH_{arom}), 126.4 (s; CH_{arom}), 128.6 (s; CH_{arom}), 128.8 (s; CH_{arom}), 129.0 (s; CH_{arom}), 133.0 (s; CH_{arom}), 133.4 (s; CH_{arom}), 141.7 (s; C≡*C*–Ph), 142.2 (s; CH_{arom}), 169.0 (d, $J_{CP}=8.4$ Hz; C≡*C*–Zr), 174.0 (s; CH_{arom}), 194.1 (s; CH_{arom}), C=N not detected; elemental analysis calcd (%) for $C_{37}H_{39}N_2PZr$ (633.92): C 70.10, H 6.2, N 4.42; found: C 70.04, H 6.12, N 4.34.

Complex 22: The same procedure that was used to prepare complex **21** was also used to prepare **22**. The starting reageants were **20** (0.247 g, 0.585 mmol) in toluene (5 mL) and diethylphosphite (0.075 mL, 0.585 mmol). Complex **22** was obtained as a yellow solid (0.296 g, 91 % yield). IR (KBr): $\tilde{\nu}=1572$ (C=N), 3413 cm^{-1} (N–H); ^1H NMR (C_6D_6): $\delta=$ 1.03 (d, $J_{HH}=6.8$ Hz, 12H; CH_3), 1.31 (q, $J_{HH}=7.0$ Hz, 6H; CH_3CH_2), 3.41 (sept, $J_{HH}=6.8$ Hz, 2H; NCh), 3.88 (m, 4H; CH_2), 6.03 (s, 10H; CH_{Cp}), 7.11 (m, 2H; CH_{arom}), 7.32 (d, $J_{HH}=7.8$ Hz, 1H; CH_{arom}), 7.48 (d, $J_{HH}=7.8$ Hz, 1H; CH_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=21.3$ (s; CH_2CH_3), 21.7 (s; $CHCH_3$), 49.6 (s; $CHCH_3$), 55.5 (d, $J_{CP}=11.1$ Hz; CH_2), 111.2 (s; CH_{Cp}), 122.4 (s; CH_{arom}), 126,4 (s; CH_{arom}), 127.9 (s; CH_{arom}), 141.3 (CH_{arom}), 173.1 (s; CH_{arom}) 196.3 (s; CH_{arom}) 198.3 (s; C=N); elemental analysis calcd (%) for $C_{27}H_{39}N_2O_3PZr$ (561.81): C 57.72, H 6.99, N 4.98; found: C 57.68, H 6.94, N 4.93.

Zr–M cleavage with Ph_2PCl: Ph_2PCl was added to a solution of **5b** (0.420 g, 0.550 mmol), **14a** (0.420 g, 0.650 mmol), **8a** (0.246 g, 0.420 mmol), or **16a** (0.279 g, 0.420 mmol) in toluene (6 mL) in stoichiometric amount. The mixture was stirred for 2 h (monitored by ^{31}P NMR) then evaporated to dryness. The resulting phosphorus species Ph_2P–C≡C–PPh_2,[19] Ph_2P–NHPh,[20] Ph_2POMe[21] or Ph_2PSH[22] were extracted with pentane and characterized by comparison of their NMR data with that reported in the literature.

X-ray structure analysis of 5a and 12a: Crystallographioc data are summarised in Table 1. Data were collected at low temperature (160 K) on a STOE imaging plate diffraction system (IPDS) equipped with an Oxford Cryosystems cooler device. The structures were solved by Direct Methods (SIR92)[23] and refined by least-squares procedures on F_o. All hydrogen atoms were located on a difference Fourier maps, but they were introduced in calculation in idealized positions (d(C–H) = 0.96 Å) with an isotropic thermal parameters fixed at 20 % higher than those of the carbon atoms to which they were connected; their atomic coordinates were recalculated after each cycle of refinement. The exception was the hydrogen atom H1 (connected to the N1 atom), which was isotropically refined. For both structures non-hydrogen atoms were anisotropically refined. The procedures of least-squares refinement were carried out by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, respectively. A weighting scheme[24] was used in the last refinement cycles. Models reached convergence with the formulas: $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $Rw=[\Sigma w(||F_o|-|F_c||)^2/\Sigma(|F_o|)^2]^{1/2}$. The calculations were performed with

Table 1. Crystallographic data, summary of data collection and refinement of **5a** and **12a**.

	5a	**12a**
formula	$C_{33}H_{46}N_3O_2PZr \cdot 0.5$ toluene	$C_{37}H_{50}N_3OPZr$
M_w	677.99	675.02
ρ_{calcd} [g cm^{-3}]	1.32	1.33
μ [cm^{-1}]	3.96	3.97
$F(000)$	708.29	1412.55
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a [Å]	11.950(2)	12.131(2)
b [Å]	12.424(2)	12.298(2)
c [Å]	13.167(3)	19.535(3)
α [°]	68.69(2)	90.0
β [°]	80.05(2)	92.34(2)
γ [°]	69.69(2)°	90.0
V [Å^3]	1705.6(3)	3385.7(4)
Z	2	4
crystal size [mm]	0.30 × 0.30 × 0.20	0.35 × 0.30 × 0.20
crystal shape	parallelepiped	parallelepiped
color	light yellow	light yellow
measured reflections	16689	26516
independent reflections	6193	6444
merging R value	0.0277	0.0397
R	0.0279	0.0288
Rw	0.0311	0.0337
$\Delta\rho_{max/min}$ [e Å^3]	0.698/ – 0.620	0.674/ – 0.550
$G.O.F$ (S)	0.7	1.04
weighting scheme	Chebyshev	Chebyshev
reflections used [$I > 2\sigma(I)$]	5380	5063
parameters	393	393

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a CRYSTALS programs,[25] and the drawing of the molecules was realized with the aid of CAMERON.[26] The atomic scattering factors were taken from International Tables for X-ray Crystallography.[27] Crystallographic data (excluding structures factors) for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-145620 (**5a**) and CCDC-145621 (**12a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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