Unexpected Formal [1+3] Cycloadditions between Azides and α-Zirconated Phosphanes: A Route to Unprecedented Phosphazide and Iminophosphorane Complexes

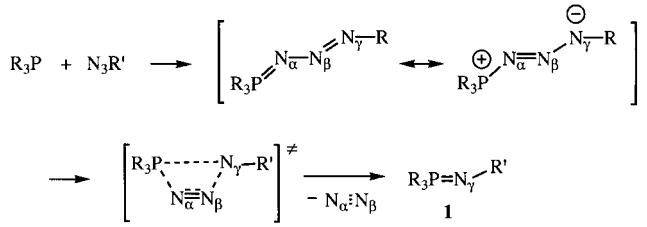
Victorio Cadierno,[a] Maria Zablocka,[b] Bruno Donnadieu,[a] Alain Igau,[a] Jean-Pierre Majoral,*[a] and Aleksandra Skowronska*[b]

Abstract: Polycyclic zwitterionic complexes that incorporate one or two phosphonium unit(s) as cationic center(s) and zirconocene-ate moiety(ies) as the anionic counterpart(s) can be easily prepared by either [1+3] or [1+3] and [2+3] cycloadditions which involve bi- or tricyclic α-zirconated phosphanes **3** or **4** and various azides. Some of these species exhibit unprecedented phosphazide chelation with bonding between the zirconium and a nitrogen atom in the α position relative to phosphorus. When heated, the phosphazide complexes lose dinitrogen to form stable polycyclic zwitterionic phosphonium mono- or dinuclear complexes. The solid-state structure of the two zwitterionic complexes **5** and **8** was determined by X-ray crystallography.

Keywords: azides · cycloadditions · phosphorus · zirconium · zwitterionic states

Introduction

The chemistry of iminophosphorane compounds of general structure $R_3P{=}N{-}R'$, which incorporate a four-coordinate phosphorus and a formal double bond between the phosphorus and the nitrogen, is very well documented. Iminophosphoranes are employed in a number of useful reactions in organic chemistry, such as Aza–Wittig reactions[1] or as neutral, very strong bases.[2] The Staudinger reaction of azides with tertiary phosphanes is one of the two major routes in the preparation of iminophosphoranes.[3] Such a reaction proceeds by nucleophilic attack of the phosphane on the terminal α-nitrogen atom of the azide to afford a linear phosphazide, rarely stable,[4] which then dissociates to the iminophosphorane with elimination of dinitrogen (Scheme 1). Iminophosphoranes form complexes with a variety of metals by *N*-imino complexation (covalent or dative bonds).[1] In marked contrast, only a few phosphazide complexes have been prepared.[5] The unique seven-coordinate complex $[WBr_2(CO)_3(Ar{-}N{=}N{-}N{=}PPh_3)]$ (**1a**) was characterized by X-ray diffraction studies: the phosphazide ligand is bound to the tungsten metal fragment in a bidentate fashion through the α- and γ-nitrogen atoms.[5b] More recently, the cyclic (Z)-phosphazide **2** was found to act as a monodentate two-electron donor through the less sterically hindered β-nitrogen atom.[5c]



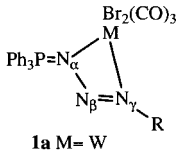
Scheme 1. Mechanism of the Staudinger reaction between phosphanes and azides.

We recently discovered that α-zirconated phosphanes, such as **3** or **4**, can act as donor–acceptor (phosphane part–zirconium moiety) species to allow the synthesis of new zwitterionic zirconocene-ate complexes when reacted with unsaturated organic molecules such as alkynes, heterocumulenes or aldehydes[6] (Scheme 2). Formal [3+2] cycloadditions take place in all cases. Nucleophilic attack of the phosphane moiety may be envisaged in order to rationalize the formation of the zwitterionic final products. Therefore, it was tempting to extend such a synthetic methodology that uses zirconate

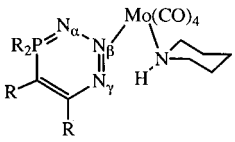
[a] J.-P. Majoral, V. Cadierno, B. Donnadieu, A. Igau
Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne, F-31077 Toulouse cedex 04 (France)
Fax: (+33) 561-55-30-03
E-mail: majoral@lcc-toulouse.fr

[b] A. Skowronska, M. Zablocka
Polish Academy of Sciences
Centre of Molecular and Macromolecular Studies
Sienkiewicza 112, 90-363 Lodz (Poland)
Fax: (+48) 42684126
E-mail: askow@bilbo.cbmm.lodz.pl

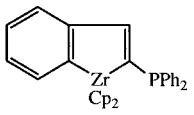
  0947-6539/00/0602-0345 $ 17.50+.50/0



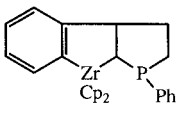
1a M= W
1b M= Mo



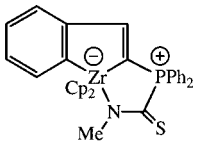
2



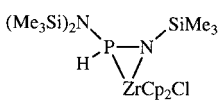
3



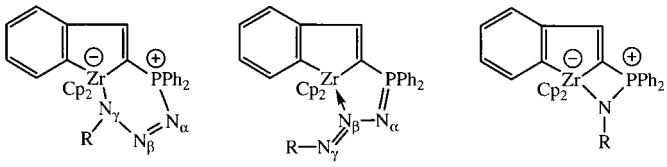
4



6

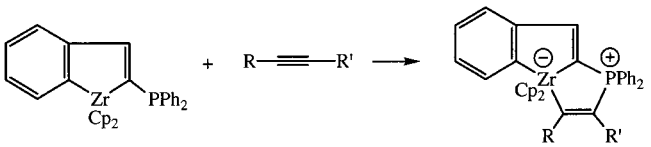


7



A **B** **C**

anions to the addition of various azides to compounds **3** and **4**. One can expect that a Staudinger reaction will take place with the formation of a transient phosphazide or the formation of



3

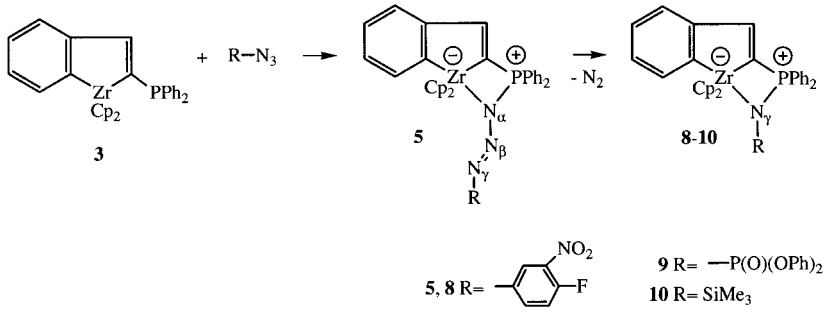
Scheme 2. An example of a [2+3] cycloaddition between an alkyne and **3** in the synthesis of zirconocene-ate complexes.

the more stable iminophosphorane. The trapping of phosphazide through complexation of the γ-nitrogen atom to the zirconium center may be anticipated because of the well established zwitterionic character of the PN_3R fragment ($P^+-N_\alpha=N_\beta-N_\gamma^-R$),[4] with formation of the zirconate species **A**. Complexation of phosphazide through the less-hindered nitrogen atom N_β which would lead to complexes of type **B** can be also envisaged. Otherwise, the chelation of the iminophosphorane would lead to complexes of type **C**, whereby the zirconium counterpart plays the role of a Lewis acid in each case. Lastly, insertion of the azide into a Zr–C bond cannot be totally ruled out.[7]

Herein, we report an unprecedented chelation of phosphazides which involves formal [1+3] cycloadditions that occur exclusively with the α-nitrogen atom of phosphazide moieties to afford a variety of new, stable, polycyclic, zwitterionic complexes. Decomposition of these complexes occurs with loss of nitrogen to lead to other new polycyclic zwitterionic species. Concomitant [1+3] and [2+3] cycloadditions with bifunctional molecules, such as 4-azidophenyl isothiocyanate and 4-azidotetrafluorobenzaldehyde, afford bis(zwitterionic) zirconate complexes. X-ray crystallography studies of two of these unusual systems confirm the proposed structures.

Results and Discussion

We first treated the α-phosphino zirconaindene **3** with 4-fluoro-3-nitrophenyl azide at room temperature in toluene for 30 min (Scheme 3). The reaction was monitored by ^{31}P NMR spectroscopy: the singlet from the isolated product **5** ($\delta = 37.7$) is 30.8 ppm downfield relative to the resonance of the phosphane counterpart of **3** ($\delta = 6.9$). No evolution of dinitrogen was observed. Characteristic ^{13}C NMR chemical shifts at $\delta = 152.4$ (d, $J(C,P) = 51.9$ Hz, ZrCP) and 192.2 (d, $J(C,P) = 8.7$ Hz, ZrC) are detected for sp^2 carbon atoms directly linked to the anionic zirconium center.[6] Mass spectrometry of **5** (electrospray, m/z 689 [M^+]) proved that the N_3 fragment is retained and that a phosphazide is formed. In order to gain more insight into the structure, X-ray crystallography was undertaken on the stable yellow crystals of **5** (Table 1). A view of the molecule is shown in Figure 1 and reveals an unexpected N_α–Zr interaction. The N_α–Zr bond length (2.401(3) Å) is in good agreement with those found in other zwitterionic and neutral compounds (for example, $d(Zr-N) = 2.405(2)$ Å in **6**,[6b] $d(Zr-N) = 2.267(3)$ Å in **7**[8]). It is remarkable that not only the P-N1-N2-N3-C31 linkage is planar (maximum deviation 0.097 Å), but also the fused tricyclic system comprising the C2-C3-C4-C5-C6-C1 aromatic ring, the C6-C1-Zr-C8-C7 five-membered ring, and the Zr-C8-P-N1 four-membered ring. The PN_3 fragment has an E configuration with respect to the central N–N bond. The X-ray crystal structures of some phosphazides have already been determined.[4] Most of these derivatives contain an E-configured phosphazide moiety; a few examples of Z configuration have also been found.[4a, 5c] There is extensive electronic delocalization in the P-N-N-N linkage of **5** and the bond lengths compare fairly well with the average values found for



3 **5** **8-10**

5, 8 R=

9 R= —P(O)(OPh)$_2$
10 R= $SiMe_3$

Scheme 3. Synthesis of zwitterionic complexes **5**, **8**–**10** by a [1+3] cycloaddition.

0947-6539/00/0602-0346 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 2

Table 1. Crystallographic data for **5** and **8**.

	5	**8**
molecular formula	$C_{36}H_{28}N_4O_2FPZr$	$C_{36}H_{28}N_2O_2FPZr$
molecular weight	689.72	661.82
ρ_{calcd} [g cm^{-3}]	1.53	1.53
μ [cm^{-1}]	4.58	4.72
$F(000)$	1396.39	1340.64
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a [Å]	7.969(1)	10.892(2)
b [Å]	19.021(2)	33.424(4)
c [Å]	20.065(3)	7.993(2)
β [°]	100.198(2)	98.797(2)
V (Å^3]	2993(1)	2875(1)
Z	4	4
crystal size	$0.6 \times 0.3 \times 0.1$	$0.7 \times 0.3 \times 0.2$
crystal habit	plate	parallelepiped
crystal color	light yellow	yellow
no. of measured reflections	23079	22179
no. of independent reflections	4681	4419
merging R value	0.03	0.04
refinement on	F_{obs}	F_{obs}
R[a]	0.025	0.028
Rw[b]	0.026	0.029
max./min. residual electron density [e Å^3]	0.57/ – 0.43	0.63/ – 1.36
GOF (S)[c]	0.9	0.64
weighting scheme[d]	Chebyshev	Chebyshev
abs corr.[e]	numerical	numerical
T_{min}—T_{max}	0.707 – 0.791	0.818 – 0.936
no of reflections used [$I > 2\sigma(I)$]	3862	3677
no. of parameters used	429	393

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $Rw = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$. [c] Goodness-of-Fit $= [\Sigma(|F_o - F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$. [d] $w =$ [weight] $\times [1 - \Delta F/6\sigma F)^2]^2$ where weights are calculated from the following expression: weight $= 1/\Sigma\ (r = 1,n) Ar\mathrm{Tr}(X)$, where Ar are the coefficients for the Chebyshev polynomial $\mathrm{Tr}(X)$ with $X = F_c/F_c(\max)$.[10] [e] X-SHAPE Crystal optimization for numerical absorption correction. Revision 1.01 July **1996** Copyright STOE & Cie GmbH, **1996**.

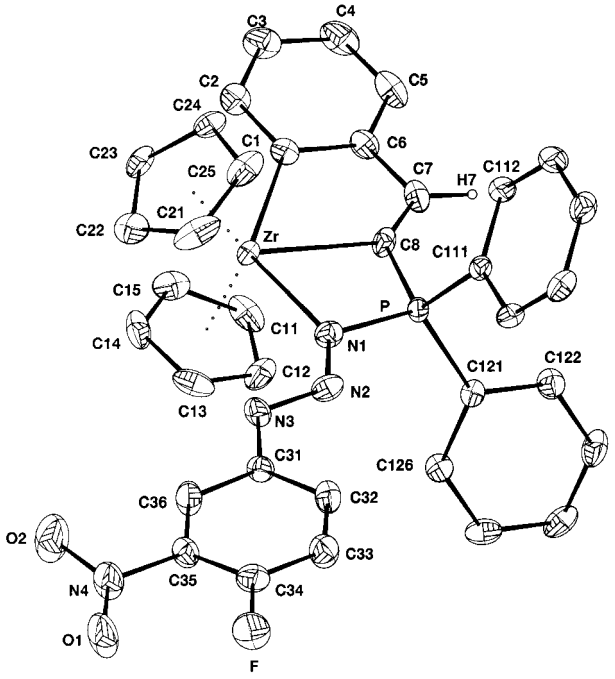
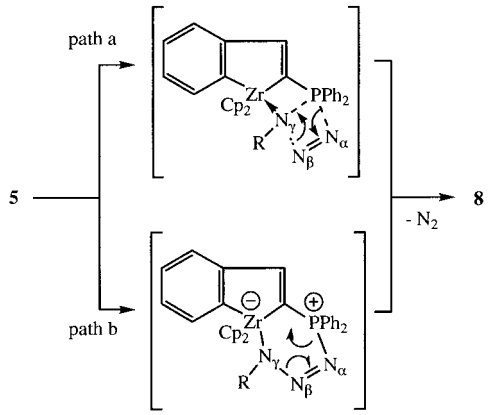


Figure 1. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: N1–Zr 2.399(18), N1–P 1.6532(19), N1–N2 1.338(3), P–C8 1.731(2), Zr–C8 2.351(2), N2–N3 1.294(3), N3–C31 1.416(3); C8-Zr-N1 61.72(7), Zr-N1-P 103.37(8), N1-P-C8 92.1(1), Zr-C8-P 102.81(11).

the other phosphazides: d(P1–N1) = 1.6532(19) Å (av 1.630(1)), d(N1–N2) = 1.337(4) Å (av 1.341(1)), and d(N2–N3) = 1.294(3) Å (av 1.273(11)). The environment around phosphorus is typical for a phosphonium center.

Therefore, in marked contrast to the situation encountered for compounds **1** and **2**, intramolecular donor–acceptor interactions only occur with the α-nitrogen atom which suggests that this nitrogen atom is a better donor than N_γ and that the polarization of the phosphazide moiety is more correctly represented as -P$^+$–N$^-$–N=N–R rather than -P$^+$–N=N–N$^-$–R, at least for the structure reported above.

The zwitterionic zirconocene-ate complex **5** is stable at room temperature and dinitrogen is only liberated on heating under reflux in toluene for 2 h, to give rise to a new complex **8**, isolated in 85 % yield (Scheme 3). This evolution of molecular nitrogen may imply a dissociation of the Zr–N_α bond. Two possible pathways to rationalize the formation of **8** may be proposed (Scheme 4). The first path involves the mechanism



Scheme 4. Proposed mechanism for the formation of complex **8**.

demonstrated for the Staudinger reaction with transient formation of a four-centered transition state, coordination of the γ-nitrogen atom to phosphorus, and elimination of the α- and β-nitrogen atoms (path a) to give compound **8**. However, the transient formation of a six-membered ring (path b) cannot be totally ruled out. The X-ray structure analysis of **8** (Figure 2, Table 1) shows that the nitrogen atom is connected to zirconium (d(Zr–N) = 2.426(2) Å) and the phosphorus–nitrogen bond length (1.620(2) Å) is in the normal range for such a bond. No structural change is observed for this derivative in comparison with **5**; the fused tricyclic system is still planar (maximum deviation 0.062 Å).

Interestingly, the reaction of **3** with the azide $N_3P(O)(OPh)_2$ in toluene at room temperature for 1 h gave the zwitterionic derivative **9** directly (Scheme 3); the transient formation of a phosphazide complex was not detected in this case. Indeed, ^{31}P NMR spectra show the disappearance of the singlet at $\delta =$ 6.9 from **3** and the appearance of a doublet of doublets at $\delta =$ – 2.9 (P(OPh)$_2$) and 32.9 (PPh$_2$) (^2J(P,P) = 20.2 Hz) which is strongly indicative of the direct formation of a P-N-P unit. Mass spectrometry (electrospray) ($m/z = 754$ [M^+]) corroborates such an assumption. A similar result was observed when a toluene solution of **3** was treated for 1 h with trimethylsi-

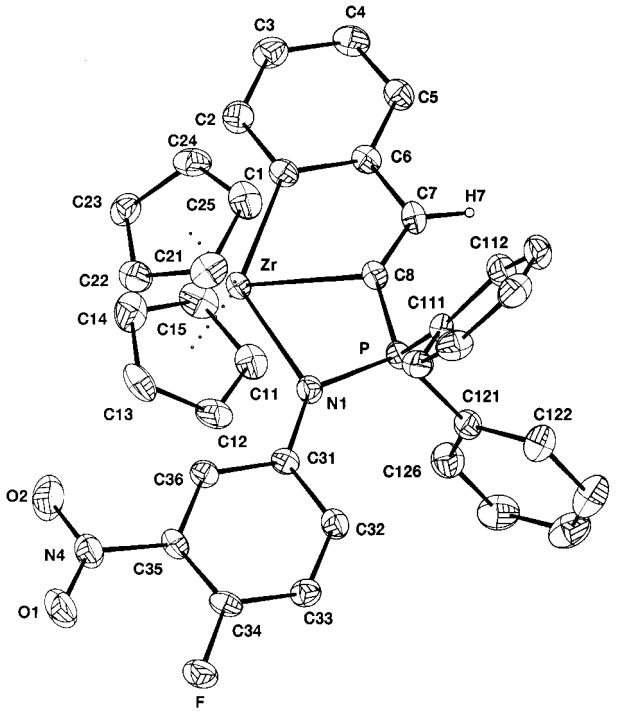
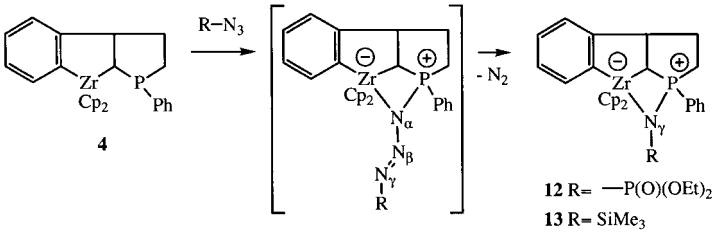


Figure 2. Molecular structure of **8**. Selected bond lengths [Å] and angles [°]: N1–Zr 2.426(2), N1–P 1.620(2), N1–C31) 1.396(3), P–C8 1.723(3), Zr–C8 2.322(3); C8-Zr-N1 62.79(8), Zr-N1-P 100.2(1), N1-P-C8 95.47(12), Zr-C8-P 101.11(12).

lylazide: the complex **10** was the only product formed and was isolated in 61% yield (Scheme 3). However, this reaction did not proceed at room temperature; it was necessary to reflux for 1 h in order for the reaction to go to completion.

Such a formal [1+3] cycloaddition which involves azides and α-zirconated phosphanes can be extended to tricyclic systems, such as **4** (Scheme 5). Indeed, when a solution of **4** and $N_3P(O)(OPh)_2$ in toluene was stirred at room temperature for 1 h, in contrast to the reaction which led to **9**, the



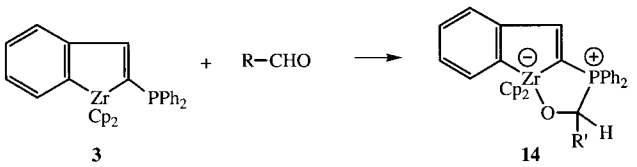
Scheme 5. Synthesis of zwitterionic zircona-phosphazide complexes **11**–**13**.

formation of a transient phosphazide complex **11** was detected by ^{31}P NMR spectroscopy: two broad singlets at $\delta = 61.0$ (PPh) and -4.46 ($P(OPh)_2$), which correspond to the P=N–N=N–P(O)$(OPh)_2$ linkage appeared and then disappeared in favor of two doublets of doublets at $\delta = 59.5$ (PPh) and -2.3 ($P(OPh)_2$) ($^2J(P,P) = 17.2$ Hz) attributed to the P-N-P fragment of the final product **12**, which was isolated in 90% yield.

Lastly, as in the reaction of trimethylsilylazide with **3**, the iminophosphorane complex **13** was directly formed when the tricyclic system **4** was treated with trimethylsilylazide at room temperature. Remarkably, only one isomer of each complex **12** and **13** was formed, as indicated by NMR spectroscopy.

Therefore, it appears that the lifetime of transient phosphazide complexes is greatly dependent on the nature of both the starting α-zirconated phosphanes and the azide used. As previously shown,[1] phosphazides are thermodynamically stabilized by the presence of electron-withdrawing groups on nitrogen and of electron-donating groups on phosphorus. This is also demonstrated in this work. Indeed, the phosphazide **5**, with the 4-fluoro-3-nitrophenyl group linked to nitrogen, is the only stable phosphazide detected and isolated from the reaction of azides with **3**. Moreover, transient formation of a phosphazide is observed when $N_3P(O)(OPh)_2$ is treated with **4**; such an intermediate is not detected in the reaction of the same azide with **3**, because the vinylphosphane is a weaker electron-donating group than the phospholane unit.

In a previous paper we have shown that the α-zirconated phosphane **3** reacts readily with aldehydes to give the zwitterionic zirconocene-ate complexes **14** in a [2+3] cycloaddition (Scheme 6).[6c] Reactions are generally conducted in toluene for 1 h at either $-78\,^\circ C$ or room temperature, depending on the aldehyde. Taking these observations into

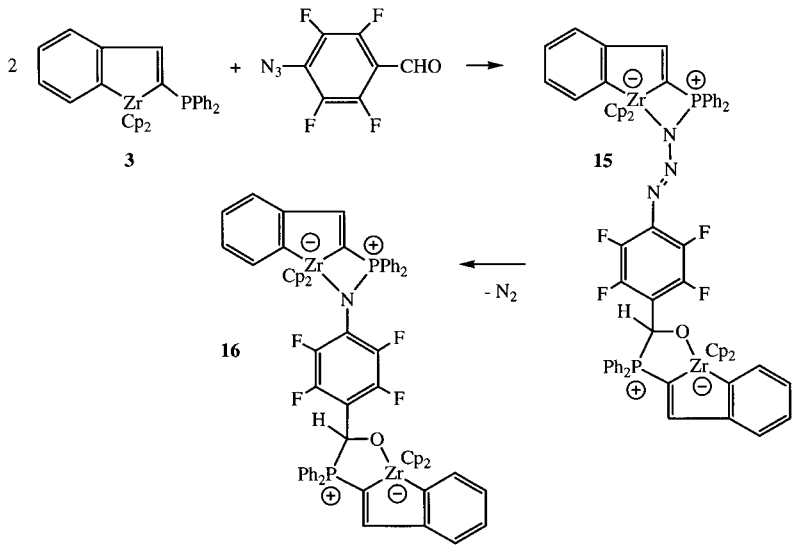


Scheme 6. The [2+3] cycloadditions between aldehydes and **3**.

account and the results reported above, it was tempting to extend such investigations to the study of the reactivity of compounds **3** and **4** towards *difunctional* species which incorporate both azide and aldehyde functionalities or an azide and another functional group that is able to react with derivatives **3** and **4**. Several questions arise: are the reactions selective? Is it possible to obtain products from both [1+3] and [2+3] cycloadditions? Is it possible to trap phosphazide intermediates, if any, by the same unusual coordination mode?

The first step was the treatment of **3** (2 equiv) with 4-azido tetrafluorobenzaldehyde in toluene at room temperature for 30 min. This reaction led directly to the bis(zwitterionic) species **15** in 75% yield (Scheme 7). The consumption of **3** (disappearance of the signal at $\delta = 6.9$) and the formation of the two phosphonium centers of **15** ($\delta = 28.7$ (s, Ph_2PC), 36.6 (s, Ph_2PN)) was detected by ^{31}P NMR spectroscopy. The ^{13}C NMR data fit perfectly well with the proposed structure, particularly if the chemical shifts and coupling constants of the carbon atoms directly linked to the zirconium centers are considered. Mass spectrometry data (FAB; m/z 1232 [M^++1]) unambiguously corroborates the structure and shows that the PN_3 unit is retained. Remarkably, no difference in the reactivity between the azido and the aldehyde groups is detected, and the expected [1+3] and [2+3] cycloadditions occurred concomitantly, even when stoichiometric conditions

0947-6539/00/0602-0348 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 2



Scheme 7. The [1+3] and [2+3] cycloadditions between 4-azido-tetrafluorobenzaldehyde and **3**.

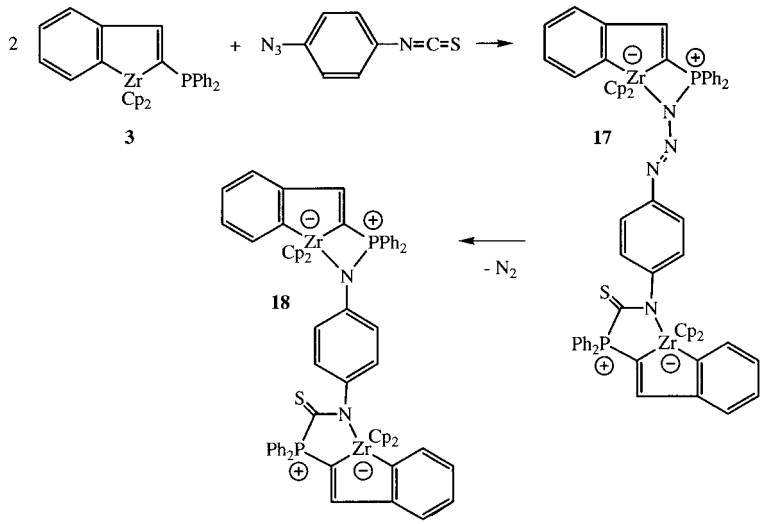
are used. When **15** was heated in refluxing toluene, dinitrogen was liberated and adduct **16** was formed, which was fully characterized by the usual spectroscopic methods; mass spectrometry (FAB; *m*/*z* 1204 [M^++1]) confirmed that dinitrogen was evolved.

A similar reactivity was observed when compound **3** was treated with 4-azidophenyl isothiocyanate in toluene at room temperature for 30 min. A clean reaction occurred to give, after workup, the stable polycyclic bis(zwitterionic) adduct **17** (yield: 80%) which contains four- and five-membered rings with Zr-C-P-N and Zr-N-C-P-C backbones, respectively (Scheme 8). The NMR data, especially ^{13}C NMR data, indicate that the cycloaddition involving the isothiocyanate moiety occurred on the carbon–nitrogen double bond [δ(C=S) = 172.8 (d, J(C,P) = 124.7 Hz)]. Moreover, the presence of a P–N_3 fragment is revealed by mass spectrometry. Monitoring the reaction by ^{31}P NMR spectroscopy did not allow us to detect a difference in the reactivity between the two cycloadditions involved in this process. As for all the reactions reported here, the phosphazide complex can be easily transformed into a iminophosphorane-like complex by heating **17** in refluxing toluene. This reaction afforded the new bis(zwitterionic) zirconocene-ate complex **18**.

Analogous reactions conducted with **4** instead of **3** and with 4-azidotetrafluorobenzaldehyde or with 4-azidophenyl isocyanate allowed us to isolate the bis(zwitterionic complexes) **19** and **20** in good yields (81 and 89%, respectively). These complexes both contain two sets of fused tetracyclic systems which arise from concomitant [1+3] and [2+3] cycloadditions (Scheme 9). Mass spectrometry (FAB; **19**: *m*/*z* 1138 [M^++1]; **20**: *m*/*z* = 1095 [M^++1]) shows that the PN_3 unit is still present in the backbone, as in **15** and **17**. Because of the presence of several chiral centers, one can expect the formation of several diastereoisomers for both **19** and **20**. However, such isomers are not detected by NMR spectroscopy, except in part for compound **20** which exhibits two doublets at δ = 170.5 (J(C,P) = 121.4 Hz) and 170.4 (J(C,P) = 121.05 Hz) for the C=S group. All the other ^{13}C NMR data are fully consistent with those obtained for compound **14**, which incorporates the same [2+3] cycloadduct moiety, and are also consistent with those obtained for compound **21**, which contains an analogous [2+3] cycloadduct unit.[6b]

It is reasonable to postulate an *E* configuration for all the phosphazide linkages in view of the X-ray data collected for **5**. Moreover, the *Z* configuration is very rare[4a] and no particular steric or electronic effects can be evoked in favor of the *Z* configuration.

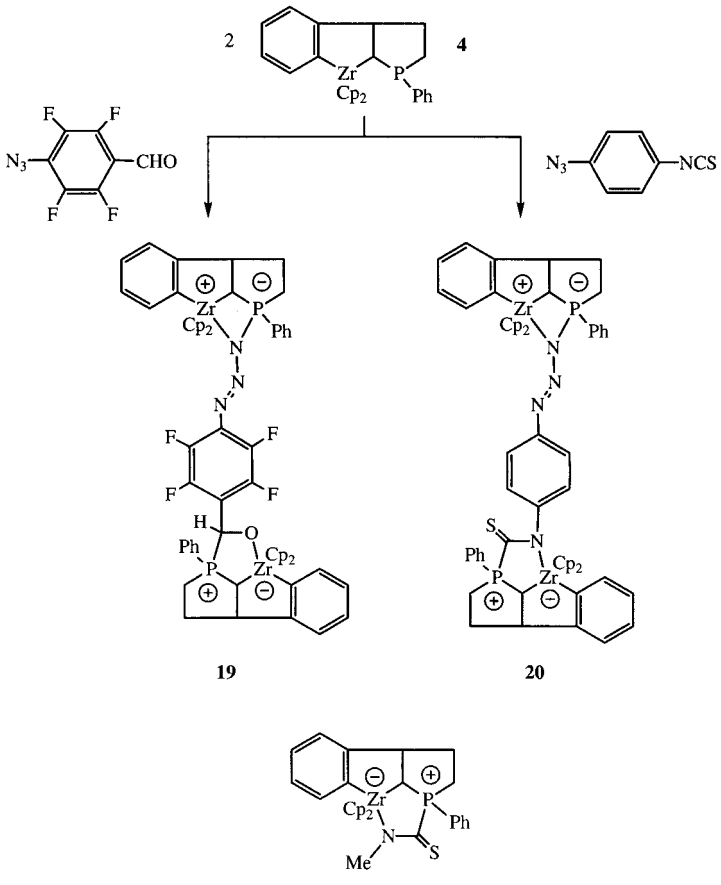
Contrary to what was observed with the other phosphazide complexes reported above, **19** and **20** do not lose dinitrogen cleanly when refluxed in toluene: decomposition of these complexes occurs with formation of numerous unidentified derivatives.



Scheme 8. The [1+3] and [2+3] cycloadditions between 4-azidophenyl isothiocyanate and **3**.

Conclusions

The reactions of azides with α-zirconated phosphanes allow the synthesis of a number of original zwitterionic (phosphonium) zirconocene-ate complexes as a result of unexpected [1+3] cycloadditions. The use of bifunctional reagents that contain an azido group and either an aldehyde group or an isothiocyanate group, permits a facile access to various unusual



Scheme 9. The [1+3] and [2+3] cycloadditions between **4** and 4-azidotetrafluorobenzaldehyde or 4-azidophenyl isothiocyanate.

bis(zwitterionic) species through [1+3] and [2+3] cycloadditions. Unprecedented phosphazide chelation and stabilization were well established. Mechanistic studies and investigations concerning the chemistry and the potential use of these new zwitterionic systems are underway.

Experimental Section

Complex 5: To a solution of complex **3** (0.476 g, 0.937 mmol) in toluene (10 mL) was added 4-fluoro-3-nitrophenyl azide (0.170 g, 0.937 mmol) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The solid residue was extracted with THF/pentane (10 mL/40 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **5** as a yellow powder. Yield: 65 % (0.420 g); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.7$ (s); ^1H NMR ($CDCl_3$): $\delta = 5.90$ (s, 10H, CH_{Cp}), 7.98 – 7.02 (m, 2H, CH_{arom}), 7.23 – 7.77 (m, 14H, CH_{arom}), 8.11 (dd, 1H, J(H,H) = 6.9 Hz, J(H,F) = 2.5 Hz, CH_{arom}), 8.29 (d, 1H, J(H,P) = 24.9 Hz, PCCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 107.9$ (s, CH_{Cp}), 117.6 (s, CH_{arom}), 118.4 (d, J(C, F) = 31.8 Hz, CH_{arom}), 122.8, 125.2 and 125.6 (s, CH_{arom}), 127.4 (d, J(C, F) = 7.8 Hz, CH_{arom}), 129.0 (d, J(C,P) = 11.2 Hz, *o*-PPh_2), 130.2 (d, J(C,P) = 66.6 Hz, *i*-PPh_2), 131.4 (d, J(C,P) = 10.2 Hz, *m*-PPh_2), 132.3 (s, *p*-PPh_2), 137.5 (d, J(C, F) = 8.7 Hz, C_{arom}), 140.8 (s, CH_{arom}), 148.0 (s, C_{arom}), 152.4 (d, J(C,P) = 51.9 Hz, ZrCP), 152.9 (d, J(C, F) = 203.2 Hz, C_{arom}), 155.8 (d, J(C,P) = 27.9 Hz, ZrC*C*), 164.8 (s, ZrC*C*H), 192.2 (d, J(C,P) = 8.7 Hz, ZrC); anal. calcd for $C_{36}H_{28}N_4O_2PFZr$ (689.8): C 62.68, H 4.09, N 8.12; found: C 62.45, H 3.97, N 8.22; MS (electrospray): m/z: 689.1 [M^++1], 661.2 [$M^+ - N_2$+1].

Complex 8: A solution of complex **5** (0.150 g, 0.217 mmol) in toluene (5 mL) was heated under reflux for 2 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/25 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **8** as a yellow powder. Yield: 85 % (0.122 g); m.p. 197 – 198 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 24.6$ (s); ^1H NMR ($CDCl_3$): $\delta = 5.94$ (s, 10H, CH_{Cp}), 6.91 – 7.70 (m, 17H, CH_{arom}), 7.96 (d, 1H, J(H,P) = 24.3 Hz, PCCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 108.3$ (s, CH_{Cp}), 116.6 (d, J(C,P) = 18.7 Hz, CH_{arom}), 118.0 (d, J(C, F) = 21.6 Hz, CH_{arom}), 122.8, 125.0 and 125.4 (s, CH_{arom}), 126.7 (dd, J(C, F) = 14.2 Hz, J(C,P) = 6.5 Hz, CH_{arom}), 129.2 (d, J(C,P) = 10.8 Hz, *o*-PPh_2), 131.3 (d, J(C,P) = 10.3 Hz, *m*-PPh_2), 132.2 (s, *p*-PPh_2), 136.7 (d, J(C, F) = 6.8 Hz, C_{arom}), 140.9 (s, CH_{arom}), 146.6 (s, C_{arom}), 148.9 (d, J(C, F) = 219.2 Hz, C_{arom}), 154.2 (d, J(C,P) = 32.5 Hz, ZrC*C*), 155.3 (d, J(C,P) = 64.8 Hz, ZrCP), 161.3 (d, J(C,P) = 4.6 Hz, ZrC*C*H), 191.4 (d, J(C,P) = 7.1 Hz, ZrC); *i*-PPh_2 not observed; anal. calcd for $C_{36}H_{28}N_2O_2PFZr$ (661.8): C 65.33, H 4.26, N 4.23; found: C 65.40, H 4.19, N 4.18; MS (DCI/NH_3): m/z: 661 [M^++1].

Complex 9: To a solution of complex **3** (0.331 g, 0.652 mmol) in toluene (8 mL) was added diphenylphosphoryl azide (0.140 mL, 0.652 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/40 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **9** as a brown powder. Yield: 73 % (0.359 g); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -2.9$ (d, J(P,P) = 20.2 Hz, $P(OPh)_2$), 32.9 (d, J(P,P) = 20.2 Hz, PPh_2); ^1H NMR (C_6D_6): $\delta = 5.91$ (s, 10H, CH_{Cp}), 6.84 – 7.70 (m, 24H, CH_{arom}), 7.85 (d, 1H, J(H,P) = 35.4 Hz, PCCH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 111.2$ (s, CH_{Cp}), 121.4 (d, J(C,P) = 4.6 Hz, *o*-$P(OPh)_2$), 123.6 (s, CH_{arom}), 125.1 (s, *p*-$P(OPh)_2$), 126.6 and 127.4 (s, CH_{arom}), 128.8 (d, J(C,P) = 10.6 Hz, *o*-PPh_2), 130.3 (s, *m*-$P(OPh)_2$), 131.6 (s, *p*-PPh_2), 132.9 (d, J(C,P) = 9.5 Hz, *m*-PPh_2), 140.3 (s, CH_{arom}), 152.1 (d, J(C,P) = 62.6 Hz, ZrCP), 152.6 (d, J(C,P) = 33.7 Hz, ZrC*C*), 163.5 (d, J(C,P) = 6.0 Hz, *i*-$P(OPh)_2$), 168.1 (s, ZrC*C*H), 195.8 (d, J(C,P) = 5.3 Hz, ZrC); *i*-PPh_2 not observed; anal. calcd for $C_{42}H_{35}O_3P_2NZr$ (754.9): C 66.82, H 4.67, N 1.85; found: C 66.74, H 4.62, N 1.90; MS (electrospray): m/z: 754.3 [M^++1].

Complex 10: To a solution of complex **3** (0.518 g, 1.020 mmol) in toluene (15 mL) was added trimethylsilyl azide (0.135 mL, 1.020 mmol) at room temperature. The mixture was heated under reflux for 1 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (10 mL/40 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **10** as a brown powder. Yield: 61 % (0.368 g); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 19.4$ (s); ^1H NMR (C_6D_6): $\delta = 0.07$ (s, 9H, $SiMe_3$), 5.90 (s, 10H, CH_{Cp}), 7.03 – 7.36 (m, 10H, CH_{arom}), 7.54 – 7.65 (m, 4H, CH_{arom}), 7.88 (d, 1H, J(H,P) = 23.4 Hz, PCCH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 5.0$ (d, J(C,P) = 2.7 Hz, $SiMe_3$), 109.3 (s, CH_{Cp}), 123.5, 125.9 and 126.2 (s, CH_{arom}), 129.0 (d, J(C,P) = 10.5 Hz, *o*-PPh_2), 131.6 (s, *p*-PPh_2), 132.0 (d, J(C,P) = 10.4 Hz, *m*-PPh_2), 136.6 (d, J(C,P) = 71.8 Hz, *i*-PPh_2), 141.3 (s, CH_{arom}), 154.6 (d, J(C,P) = 32.7 Hz, ZrC*C*), 159.2 (s, ZrC*C*H), 162.0 (d, J(C,P) = 63.8 Hz, ZrCP), 193.6 (d, J(C,P) = 7.4 Hz, ZrC); anal. calcd for $C_{33}H_{34}PNSiZr$ (594.9): C 66.62, H 5.76, N 2.35; found: C 66.35, H 5.66, N 2.41; MS (electrospray): m/z: 594.2 [M^++1].

Complex 12: To a solution of complex **4** (0.230 g, 0.500 mmol) in toluene (5 mL) was added diphenylphosphoryl azide (0.107 mL, 0.500 mmol) at room temperature. The mixture was stirred at room temperature for 2 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/20 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **12** as a brown powder. Yield: 90 % (0.317 g); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -2.3$ (d, J(P,P) = 17.2 Hz, $P(OPh)_2$), 59.5 (d, J(P,P) = 17.2 Hz, PPh_2); ^1H NMR (C_6D_6): $\delta = 1.62 - 2.10$ (m, 4H, CH_2), 2.78 (t, 1H, J(H,H) = 6.8 Hz, C*H*CH_2), 3.94 (m, 1H, ZrCH), 5.78 (s, 5H, CH_{Cp}), 6.03 (s, 5H, CH_{Cp}), 6.70 – 7.20 (m, 14H, CH_{arom}), 7.50 (d, J(H,H) = 6.8 Hz, CH_{arom}), 7.52 – 7.80 (m, 4H, CH_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 31.9$ (dd, J(C,P) = 74.2 Hz, J(C,P) = 2.6 Hz, PCH_2), 33.7 (d, J(C,P) = 9.5 Hz, *C*H_2CH), 35.0 (dd, J(C,P) = 41.6 Hz, J(C,P) = 4.5 Hz, *C*HCH$_2$), 59.4 (d, J(C,P) = 16.5 Hz, ZrCH), 111.7 (s, CH_{Cp}), 112.1 (s, CH_{Cp}), 121.1 (d, J(C,P) = 11.1 Hz, 2*o*-$P(OPh)_2$), 121.8, 123.7, 124.3, 124.7, 125.1, 125.2, 129.4 and 131.1 (s, 4CH_{arom}, 2*m*-$P(OPh)_2$, 2*p*-$P(OPh)_2$ and *p*-PPh), 130.2 (d, J(C,P) = 10.7 Hz, *o*-PPh or *m*-PPh), 130.7 (d, J(C,P) = 9.9 Hz, *o*-PPh or *m*-PPh), 139.2 (dd, J(C,P) = 85.1 Hz, J(C,P) = 2.6 Hz, *i*-PPh), 140.7 (s, CH_{arom}), 152.6 (d, J(C,P) = 23.1 Hz, *i*-$P(OPh)_2$), 152.7 (d, J(C,P) = 23.4 Hz, *i*-$P(OPh)_2$), 156.5 (d, J(C,P) = 21.0 Hz, ZrC*C*), 185.6 (s, ZrC); anal. calcd for $C_{38}H_{35}O_3P_2NZr$

0947-6539/00/0602-0350 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 2

(706.8): C 64.57, H 4.99, N 1.98; found: C 64.25, H 4.82, N 1.89; MS (FAB): m/z: 706 [M^++1].

Complex 13: To a solution of complex **4** (0.183 g, 0.400 mmol) in toluene (5 mL) was added trimethylsilyl azide (0.053 mL, 0.400 mmol) at room temperature. The mixture was stirred at room temperature for 2 h and then evaporated to dryness to give **13** as a yellow powder. Yield: 92 % (0.211 g); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 43.4$ (s); ^1H NMR (C_6D_6): $\delta = -0.16$ (s, 9H, $SiMe_3$), 1.62–1.91 (m, 2H, CH_2), 2.22–2.41 (m, 2H, CH_2), 2.64 (t, 1H, J(H,H) = 6.1 Hz, C*H*CH_2), 3.44 (m, 1H, ZrCH), 5.78 (s, 5H, CH_{Cp}), 5.82 (s, 5H, CH_{Cp}), 6.99–7.35 (m, 9H, CH_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 4.2$ (d, J(C,P) = 3.5 Hz, $SiMe_3$), 27.0 (d, J(C,P) = 76.7 Hz, *C*HCH_2), 30.8 (d, J(C,P) = 57.1 Hz, PCH_2), 33.5 (d, J(C,P) = 6.3 Hz, *C*H_2CH), 53.3 (d, J(C,P) = 15.6 Hz, ZrCH), 110.1 (s, CH_{Cp}), 111.4 (s, CH_{Cp}), 123.6, 124.6 and 124.7 (s, 3CH_{arom} and *p*-PPh), 129.1 (d, J(C,P) = 9.8 Hz, *o*-PPh or *m*-PPh), 130.0 (d, J(C,P) = 9.6 Hz, *o*-PPh or *m*-PPh), 130.8 (s, CH_{arom}), 140.6 (d, J(C,P) = 57.4 Hz, *i*-PPh), 160.5 (d, J(C,P) = 19.4 Hz, ZrC*C*), 185.0 (d, J(C,P) = 9.9 Hz, ZrC); anal. calcd for $C_{29}H_{34}PNSiZr$ (546.9): C 63.69, H 6.26, N 2.56; found: C 63.52, H 6.30, N 2.61.

Complex 15: To a solution of complex **3** (0.328 g, 0.647 mmol) in toluene (8 mL) was added 4-azidotetrafluorobenzaldehyde (0.070 g, 0.323 mmol) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The solid residue was extracted with THF/pentane (20 mL/20 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with diethyl ether (5 mL) to give **15** as a green powder. Yield: 75 % (0.301 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-O moiety: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 28.7$ (s, P_B), 36.6 (s, P_A); ^1H NMR ($CDCl_3$): $\delta = 5.90$ (s, 5H, CH_{Cp}), 5.91 (s, 5H, CH_{Cp}), 5.96 (s, 5H, CH_{Cp}), 5.99 (s, 5H, CH_{Cp}), 6.66 (s, 1H, PCH), 6.98–7.77 (m, 28H, CH_{arom}), 7.95 (d, 1H, J(H,P) = 26.6 Hz, P_BCCH), 8.35 (d, 1H, J(H,P) = 24.6 Hz, P_ACCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 79.6$ (d, J(C,P) = 66.0 Hz, PCH), 107.9 (s, CH_{Cp}), 108.1 (br s, CH_{Cp}), 109.8 (s, CH_{Cp}), 122.3 and 122.9 (s, CH_{arom}), 122.7 (d, J(C,P) = 65.6 Hz, *i*-P_BPh_2), 125.4 (s, 2CH_{arom}), 126.0 and 129.1 (br s, *o*-P_APh_2, *o*-P_BPh_2, *i*-P_APh_2 and *i*-P_BPh_2), 132.4 (m, *m*-P_APh_2, *m*-P_BPh_2, *p*-P_APh_2 and *p*-P_BPh_2), 140.0 and 141.0 (s, CH_{arom}), 143.6 and 146.8 (m, 6C_{arom}), 152.5 (d, J(C,P) = 48.5 Hz, $ZrCP_A$), 155.3 (d, J(C,P) = 32.1 Hz, Zr_ACC and Zr_BCC), 160.3 (d, J(C,P) = 5.0 Hz, $ZrCP_B$), 165.2 (s, Zr_ACCH), 172.0 (s, Zr_BCCH), 192.5 (d, J(C,P) = 7.9 Hz, Zr_AC), 195.7 (s, Zr_BC); anal. calcd for $C_{67}H_{51}F_4N_3P_2Zr_2O$ (1234.5): C 65.18, H 4.16, N 3.40; found: C 64.93, H 4.07, N 3.51; MS (FAB): m/z: 1232 [M^++1].

Complex 16: A solution of complex **15** (0.180 g, 0.146 mmol) in toluene (5 mL) was heated under reflux for 1 h and then evaporated to dryness. The solid residue was extracted with diethyl ether (30 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (2 × 5 mL) to give **16** as a green powder. Yield: 56 % (0.098 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-O moiety: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 28.0$ (s, P_A), 29.0 (s, P_B); ^1H NMR (C_6D_6): $\delta = 5.85$ (s, 5H, CH_{Cp}), 5.88 (s, 5H, CH_{Cp}), 5.94 (s, 5H, CH_{Cp}), 5.98 (s, 5H, CH_{Cp}), 6.68 (s, 1H, PCH), 6.94–7.66 (m, 28H, CH_{arom}), 7.92 (d, 1H, J(H,P) = 26.6 Hz, P_BCCH), 7.98 (d, 1H, J(H,P) = 23.4 Hz, P_ACCH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 81.3$ (d, J(C,P) = 64.7 Hz, PCH), 108.6 (s, CH_{Cp}), 109.8 (s, CH_{Cp}), 109.9 (s, CH_{Cp}), 110.7 (s, CH_{Cp}), 123.1, 123.2, 123.8, 126.3, 126.4 and 126.7 (s, CH_{arom}), 128.0 (br s, *o*-P_APh_2 and *o*-P_BPh_2), 132.5 (m, *m*-P_APh_2, *m*-P_BPh_2, *p*-P_APh_2 and *p*-P_BPh_2), 140.8 and 141.2 (s, CH_{arom}), 143.8 and 148.0 (m, 6C_{arom}), 154.7 (d, J(C,P) = 32.0 Hz, Zr_ACC or Zr_BCC), 156.5 (d, J(C,P) = 33.0 Hz, Zr_ACC or Zr_BCC), 159.2 (d, J(C,P) = 66.1 Hz, $ZrCP_A$), 161.1 (d, J(C,P) = 6.7 Hz, $ZrCP_B$), 161.8 (d, J(C,P) = 3.0 Hz, Zr_ACCH), 171.0 (s, Zr_BCCH), 193.0 (d, J(C,P) = 4.0 Hz, Zr_AC), 196.7 (s, Zr_BC); *i*-P_APh_2 and *i*-P_BPh_2 not observed; anal. calcd for $C_{67}H_{51}F_4P_2Zr_2NO$ (1206.5): C 66.70, H 4.26, N 1.16; found: C 66.52, H 4.18, N 1.20; MS (FAB): m/z: 1204 [M^++1].

Complex 17: To a solution of complex **3** (0.335 g, 0.660 mmol) in toluene (8 mL) was added 4-azidophenyl isothiocyanate (0.058 g, 0.330 mmol) at room temperature. The mixture was stirred at room temperature for 30 min and then evaporated to dryness. The solid residue was extracted with THF/pentane (15 mL/30 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (2 × 5 mL) to give **17** as a yellow powder. Yield: 80 % (0.314 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-N moiety: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 27.9$ (s, P_B), 35.5 (s, P_A); ^1H NMR (C_6D_6): $\delta = 5.83$ (s, 10H, CH_{Cp}), 6.07 (s, 10H, CH_{Cp}), 7.06–8.07 (m, 32H, CH_{arom}), 8.27 (d, 1H, J(H,P) = 21.7 Hz, P_BCCH), 8.39 (d, 1H, J(H,P) = 24.6 Hz, P_ACCH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 108.9$ (s, CH_{Cp}), 109.5 (s, CH_{Cp}), 122.3, 123.6, 123.9, 124.5, 126.3, 126.7, 126.9 and 127.2 (s, CH_{arom}), 127.4 (d, J(C,P) = 51.4 Hz, *i*-P_BPh_2), 129.5 (d, J(C,P) = 8.9 Hz, *o*-P_BPh_2), 129.6 (d, J(C,P) = 8.9 Hz, *o*-P_APh_2), 132.3 (d, J(C,P) = 10.1 Hz, *m*-P_APh_2), 132.4 and 132.7 (s, *p*-P_APh_2 and *p*-P_BPh_2), 133.9 (d, J(C,P) = 8.5 Hz, *m*-P_BPh_2), 141.8 and 142.0 (s, CH_{arom}), 149.6 (s, C_{arom}), 150.7 (d, J(C,P) = 27.8 Hz, $ZrCP_B$), 152.8 (d, J(C,P) = 14.0 Hz, C_{arom}), 154.2 (d, J(C,P) = 32.7 Hz, Zr_BCC), 154.5 (d, J(C,P) = 53.2 Hz, $ZrCP_A$), 156.5 (d, J(C,P) = 31.3 Hz, Zr_ACC), 164.8 (s, Zr_ACCH), 172.0 (s, Zr_BCCH), 172.8 (d, J(C,P) = 124.7 Hz, C=S), 193.6 (d, J(C,P) = 9.9 Hz, Zr_AC), 193.8 (s, Zr_BC); *i*-P_APh_2 not observed; anal. calcd for $C_{67}H_{54}N_4P_2Zr_2S$ (1191.6): C 67.53, H 4.56, N 4.70; found: C 67.58, H 4.60, N 4.62; MS (electrospray): m/z: 1191.3 [M^++1], 1163.4 [$M^+ - N_2$+1].

Complex 18: A solution of **17** (0.140 g, 0.117 mmol) in toluene (5 mL) was heated under reflux for 1.5 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/25 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **18** as a yellow powder. Yield: 93 % (0.127 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-N moiety: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 22.7$ (s, P_A), 28.2 (s, P_B); ^1H NMR ($CDCl_3$): $\delta = 5.81$ (s, 10H, CH_{Cp}), 5.96 (s, 10H, CH_{Cp}), 6.86–7.80 (m, 32H, CH_{arom}), 7.91 (d, 1H, J(H,P) = 28.2 Hz, P_BCCH), 7.97 (d, 1H, J(H,P) = 23.9 Hz, P_ACCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 108.3$ (s, CH_{Cp}), 108.7 (s, CH_{Cp}), 120.7 (d, J(C,P) = 16.0 Hz, CH_{arom}), 122.5, 122.8, 124.3, 124.7, 124.9, 125.7 and 125.9 (s, CH_{arom}), 127.0 (d, J(C,P) = 78.3 Hz, *i*-P_BPh_2), 128.8 (d, J(C,P) = 11.9 Hz, *o*-P_BPh_2), 128.9 (d, J(C,P) = 11.9 Hz, *o*-P_APh_2), 131.5 (d, J(C,P) = 9.6 Hz, *m*-P_APh_2), 131.6 (d, J(C,P) = 1.0 Hz, *p*-P_APh_2), 132.1 (d, J(C,P) = 1.0 Hz, *p*-P_BPh_2), 133.1 (d, J(C,P) = 7.6 Hz, *m*-P_BPh_2), 140.8 and 141.1 (s, CH_{arom}), 140.9 (d, J(C,P) = 71.2 Hz, *i*-P_APh_2), 148.1 (s, C_{arom}), 152.8 (d, J(C,P) = 26.5 Hz, $ZrCP_B$), 153.1 (d, J(C,P) = 42.9 Hz, Zr_BCC), 154.4 (d, J(C,P) = 32.0 Hz, Zr_ACC), 157.3 (d, J(C,P) = 66.5 Hz, $ZrCP_A$), 159.9 (d, J(C,P) = 4.3 Hz, Zr_ACCH), 165.8 (d, J(C,P) = 129.4 Hz, C=S), 170.8 (s, Zr_BCCH), 191.7 (d, J(C,P) = 8.5 Hz, Zr_AC), 192.7 (s, Zr_BC); C_{arom} not observed; anal. calcd for $C_{67}H_{54}N_2P_2Zr_2S$ (1163.6): C 69.15, H 4.68, N 2.41; found: C 68.95, H 4.51, N 2.45; MS (FAB): m/z: 1162 [M^+].

Complex 19: To a solution of complex **4** (0.230 g, 0.500 mmol) in toluene (5 mL) was added 4-azidotetrafluorobenzaldehyde (0.055 g, 0.250 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/20 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **19** as a green powder. Yield: 81 % (0.460 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-O moiety: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 57.9$ (s, P_A), 63.9 (s, P_B); ^1H NMR (C_6D_6): $\delta = 1.53–1.90$ (m, 4H, CH_2), 2.00–2.35 (m, 4H, CH_2), 2.71–2.80 (m, 1H, C*H*CH_2), 3.32–3.41 (m, 1H, C*H*CH_2), 3.46–3.68 (m, 2H, ZrCH), 5.34 (s, 5H, CH_{Cp}), 5.88 (s, 5H, CH_{Cp}), 5.95 (s, 5H, CH_{Cp}), 6.10 (s, 5H, CH_{Cp}), 6.17 (s, 1H, CHO), 7.07–7.57 (m, 18H, CH_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 25.3$ (d, J(C,P) = 44.7 Hz, P_BCH_2), 25.6 (d, J(C,P) = 47.3 Hz, P_ACH_2), 26.1 (d, J(C,P) = 77.6 Hz, C_AHCH_2), 32.2 (s, C_BHCH_2), 33.4 (s, *C*H_2CH), 35.0 (s, *C*H_2CH), 54.1 (d, J(C,P) = 16.0 Hz, Zr_ACH), 55.6 (d, J(C,P) = 13.8 Hz, Zr_BCH), 109.8 (s, CH_{Cp}), 111.1 (s, CH_{Cp}), 111.3 (s, CH_{Cp}), 112.5 (s, CH_{Cp}), 123.5–132.3 (m, CH_{arom}, *o*-PPh, *m*-PPh and *p*-PPh), 139.53 (s, CH_{arom}), 141.1 (d, J(C,P) = 6.0 Hz, CH_{arom}), 143.1–150.0 (m, 6C_{arom} and *i*-PPh), 159.3 (d, J(C,P) = 20.4 Hz, Zr_BCC), 160.8 (d, J(C,P) = 18.4 Hz, Zr_ACC), 182.9 (s, Zr_BC), 183.7 (d, J(C,P) = 10.8 Hz, Zr_AC); anal. calcd for $C_{59}H_{51}F_4N_3P_2Zr_2O$ (1138.4): C 62.24, H 4.51, N 3.69; found: C 61.99, H 4.45, N 3.82; MS (FAB): m/z: 1138 [M^++1].

Complex 20: To a solution of complex **4** (0.230 g, 0.500 mmol) in toluene (5 mL) was added 4-azidophenyl isothiocyanate (0.044 g, 0.250 mmol) at room temperature. The mixture was stirred at room temperature for 1 h and then evaporated to dryness. The solid residue was extracted with THF/pentane (5 mL/20 mL) and filtered. The volatiles were removed from the solution and the resulting solid was washed with pentane (5 mL) to give **20** as a brown powder. Yield: 89 % (0.480 g). NMR resonances noted by "A" correspond to the Zr-C-P-N unit and those noted by "B" to the Zr-C-P-C-N moiety: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 54.6$ (s, P_B), 52.1 (s, P_A); ^1H NMR (C_6D_6): $\delta = 1.63–2.00$ (m, 4H, CH_2), 2.14–2.36 (m, 4H, CH_2), 2.68–2.78 (m, 2H, C*H*CH_2), 3.60–3.95 (m, 2H, ZrCH), 5.49 (s, 5H, CH_{Cp}), 5.66 (s, 5H, CH_{Cp}),

5.95 (s, 5H, CH_{Cp}), 5.92 (s, 5H, CH_{Cp}), 6.99 – 7.22 (m, 16H, CH_{arom}), 6.99 – 7.22 (m, 6H, CH_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 24.9$ (d, $J(C,P) = 45.9$ Hz, P_BCH_2), 26.6 (d, $J(C,P) = 70.7$ Hz, C_BHCH_2), 26.8 (d, $J(C,P) = 70.8$ Hz, C_BHCH_2), 27.3 (d, $J(C,P) = 50.9$ Hz, C_AHCH_2), 29.3 (d, $J(C,P) = 49.7$ Hz, P_ACH_2), 33.4 (s, CH_2CH), 34.6 (s, CH_2CH), 54.2 (d, $J(C,P) = 14.8$ Hz, Zr_ACH), 58.8 (d, $J(C,P) = 15.8$ Hz, Zr_BCH), 109.7 (s, CH_{Cp}), 109.8 (s, CH_{Cp}), 110.1 (s, CH_{Cp}), 111.0 (s, CH_{Cp}), 122.0, 126.1, 127.6, 128.0, 129.7, 131.5, 131.7, 139.4 and 141.8 (s, CH_{arom}), 125.1 – 125.4 (m, *p*-PPh, CH_{arom} and *o*-PPh or *m*-PPh), 129.1 (d, $J(C,P) = 10.8$ Hz, *o*-PPh or *m*-PPh), 129.6 (d, $J(C,P) = 10.1$ Hz, *o*-PPh or *m*-PPh), 131.0 (d, $J(C,P) = 12.0$ Hz, *o*-PPh or *m*-PPh), 149.5 (d, $J(C,P) = 27.9$ Hz, *i*-PPh), 149.6 (d, $J(C,P) = 28.2$ Hz, *i*-PPh), 156.2 (d, $J(C,P) = 21.1$ Hz, Zr_BCC), 161.2 (d, $J(C,P) = 19.0$ Hz, Zr_ACC), 170.3 (d, $J(C,P) = 121.0$ Hz, C=S), 170.5 (d, $J(C,P) = 121.4$ Hz, C=S), 182.0 (s, Zr_BC), 184.2 (d, $J(C,P) = 10.8$ Hz, Zr_AC); C_{arom} not observed; anal. calcd for $C_{59}H_{54}N_4P_2Zr_2S$ (1095.5): C 64.68, H 4.96, N 5.11; found: C 64.52, H 4.92, N 5.20; MS (FAB): *m*/*z*: 1095 [M^++1].

X-ray structure analysis of 5 and 8: Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cooler Device. The structures were solved by direct methods (SIR 92)[9] and refined by least-squares procedures on F_{obs}. All hydrogen atoms were located on difference Fourier maps; however, they were introduced into the calculation in idealized positions (d(C–H) = 0.96 Å). Their atomic coordinates were recalculated after each cycle of refinement, and were given isotropic thermal parameters 20% higher than those of the carbon atoms to which they were attached. The only exception was hydrogen atom H7 (connected to the C7 atom), which was isotropically refined. For both structures, all non-hydrogen atoms were anisotropically refined. A statistic disorder was found for the NO_2 group of **5**; the oxygen atoms were isotropically refined on two sites with a occupancy ratio of 1:1. Least-squares refinement was carried out by minimization of 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 was used in the last refinement cycles, whereby weights were calculated from the following expression: $w = [\text{weight}] \times [1 - (\Delta(F)/6\sigma(F)]^2$[10] and a numerical absorption corrections[11] were applied to the intensity data for **5** and **8**. Models reached convergence with the formulas: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $Rw = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$. The calculations were performed with the CRYSTALS program[12] running on a PC; the molecules were drawn with the program CAMERON.[13] The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120851 (**5**) and CCDC-120852 (**8**). 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).

Acknowledgments

This work was supported by the CNRS (France) and K.B.N. (Poland). V.C. thanks the Spanish Ministerio de Educacion y Cultura for a postdoctoral fellowship.

[1] For a review see: A. W. Johnson in *Ylides and Imines of Phosphorus*, Wiley, New York **1993**. For recent examples see: M. T. Reetz, E. Bohres, R. Goddard, *Chem. Commun.* **1998**, 935; R. W. Reed, B. Santarsiero, R. G. Cavell, *Inorg. Chem.* **1996**, *35*, 4292.

[2] See, for example: a) R. Schwesinger, H. Schlemper, *Angew. Chem.* **1987**, *99*, 1212; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167; b) R. Link, R. Schwesinger, *Angew. Chem.* **1992**, *104*, 864; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 850, and references therein.

[3] The second major route to the iminophosphoranes is the Kirsanov reaction; see ref. [1].

[4] For X-ray structures of phosphazides see: a) M. Alajarin, P. Molina, A. Lopez-Lazaro, C. Foces-Foces, *Angew. Chem.* **1997**, *109*, 147 – 150; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 67; b) P. Molina, C. Lopez-Leonardo, J. Llamas-Botia, C. Foces-Foces, C. Fernandez-Castano, *Tetrahedron* **1996**, *52*, 9629; c) J. R. Goerlich, M. Farkens, A. Fischer, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 707; d) A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, M. P. Ponomarchuk, L. F. Kasukhin, V. P. Kukhar, *Zh. Obshch. Khim.* **1992**, *62*, 2675; e) C. G. Chidester, J. Szmuszkovicz, D. J. Duchamp, L. G. Laurian, J. P. Freeman, *Acta Crystallogr. Sect. C* **1988**, *44*, 1080; f) A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, I. E. Boldeskul, M. P. Ponomarchuk, L. F. Kasukhin, V. P. Kukhar, *Zh. Obshch. Khim.* **1984**, *54*, 1979.

[5] a) G. L. Hilhouse, B. L. Haymore, *J. Organomet. Chem.* **1978**, *162*, C23; b) G. L. Hillhouse, G. V. Goeden, B. L. Haymore, *Inorg. Chem.* **1982**, *21*, 2064; c) K. Bieger, G. Bouhadir, R. Réau, F. Dahan, G. Bertrand, *J. Am. Chem. Soc.* **1996**, *118*, 1038.

[6] a) Y. Miquel, A. Igau, B. Donnadieu, J.-P. Majoral, N. Pirio, P. Meunier, *J. Am. Chem. Soc.* **1998**, *120*, 3504; b) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral, A. Skowronska, *Organometallics* **1999**, *18*, 1882; c) V. Cadierno, A. Igau, B. Donnadieu, A.-M. Caminade, J.-P. Majoral, *Organometallics* **1999**, *18*, 1580.

[7] a) K. W. Chiu, G. Wilkinson, M. Thornton-Pett, M. Hursthouse, *Polyhedron* **1984**, *3*, 79; b) T. Luker, R. J. Whitby, M. Webster, *J. Organomet. Chem.* **1995**, *492*, 53. c) Recently, it was also demonstrated that azides add smoothly and without loss of N_2, to a polarized metal – metal bond in an early/late heterobinuclear complex, with formation of a bridging imido complex: T. A. Hanna, A. M. Baranger, R. G. Bergman, *Angew. Chem.* **1996**, *108*, 693 – 696; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 653.

[8] N. Dufour, J.-P. Majoral, A.-M. Caminade, R. Choukroun, Y. Dromzee, *Organometallics* **1991**, *10*, 45.

[9] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guargliardi, M. C. Burla, G. Polidori, M. Camalli, "SIR 92 a Program for Automatic Solution of Crystal Structures by Direct Methods", *J. Appl. Crystallogr.* **1994**, *27*, 435.

[10] J. R. Carruthers, D. J. Watkin *Acta Crystallogr. Sect. A* **1979**, *35*, 698 – 699.

[11] D. J. Watkin, J. R. Carruthers, P. W. Betteridge, CRYSTALS, Issue 10 Chemical Crystallography Laboratory, University of Oxford, Oxford, **1996**.

[12] D. J. Watkin, C. K. Prout, L. J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, Oxford, **1996**.

[13] *International Tables for X-Ray Crystallography*, *vol. IV*, **1974**, Kynoch press, Birmingham, England.

Received: May 31, 1999
Revised version: September 1, 1999 [F 1824]

  0947-6539/00/0602-0352 $ 17.50+.50/0