A Straightforward Synthesis of *N*-Functionalized β-Diimines

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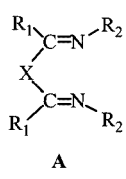
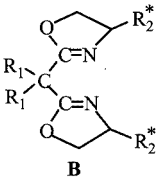
Reaction of Schwartz's reagent $[Cp_2ZrHCl]_n$ (**1**) (one or two equivalents) with *gem*-dinitrile compounds of the type $X(CN)_2$ [X = CMe_2, $CBenz_2$, $P(NiPr_2)_2$] gives the corresponding mono- and di-*N*-zirconated imino complexes selectively. Substitution reactions of the zirconocene metal fragment with electrophiles such as, for example, chlorophosphanes of the type R_2PCl, acid chlorides RC(O)Cl or the iminium salt $[CH_2NMe_2]Cl$ allowed the preparation of a large variety of stable *N*-functionalized mono- and β-diimine derivatives. The nature of the X group is of particular importance for the success of the substitution reaction step. The X-ray crystal structures obtained for the *N*-functionalized *gem*-aldiminonitrile compounds **9**, **10b**, the *N*-phosphorylated β-diimine **32**, and the *gem*-formyl nitrile derivative **12b** are presented.

Introduction

Metal complexes with chiral bidentate ligands containing at least one hard donor atom have attracted much attention recently. In the past decade, there has been a surge of interest in nitrogen-donor ligands for use in catalysis. Imine-based C_2-symmetry ligands[1] have been found to be particularly attractive in early and late transition metal systems. β-Diimines **A** such as semicorrins, and particularly bis(oxazoline) derivatives **B**, are the subject of intense studies.[2]

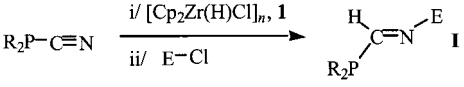


A



B

The neutral β-diketimine ligands **A** offer the potential advantages of being able to modulate the steric and electronic properties by varying the nature of the substituents bonded to the nitrogen atoms. It has been demonstrated that in all the systems of type **A** that are active in catalytic processes, sterically demanding substituents on the nitrogen atoms of the β-diimines are needed.[3] However, the synthetic approach used up to now for the preparation of diketimines **A** allowed only limited tuning of the electronic properties of the substituents linked to the nitrogen atom.[4] In preliminary studies, using the hydrozirconation/substitution reaction sequence, we prepared and structurally characterized a large variety of stable *N*-heterosubstituted imine compounds **I** [Equation (1)].[5]



(1)

Starting from *gem*-dinitrile compounds $X(CN)_2$ we report here the preparation of *N*-functionalized β-diimine systems repeating the same hydrozirconation/substitution reaction sequence on the two nitrile sites. We also report the X-ray crystal structures obtained for the *N*-functionalized aldimino compounds **9**, **10b**, and **32**, and the *gem*-formyl nitrile derivative **12b**.

Results and Discussion

In a first approach, we tested mono-hydrozirconation reactions on *gem*-dinitrile derivatives $X(CN)_2$ as the selective mono-hydrozirconation of polynitrile compounds has not been reported in the literature.[6,7] The substituted malonitrile $Me_2C(CN)_2$ (**2a**) was treated with one equivalent of Schwartz's reagent $[Cp_2Zr(H)Cl]_n$, (**1**) to form the *N*-zirconaimino nitrile derivative **3a** in quantitative yield (Scheme 1). In addition to the signal corresponding to the η^5-cyclopentadienyl ligands, the ^1H NMR spectrum reveals the presence of the proton signal of the aldimine fragment HC=N at δ = 8.23 ppm. The deshielded chemical shift at δ = 167.6 ppm observed in the ^{13}C NMR spectrum is indicative of the imino carbon atom. The signal at δ = 118.0 ppm is in the region expected for aliphatic nitriles. In an identical manner the reaction conducted with **2b** and **1** allowed the formation of **3b** in quantitative yield

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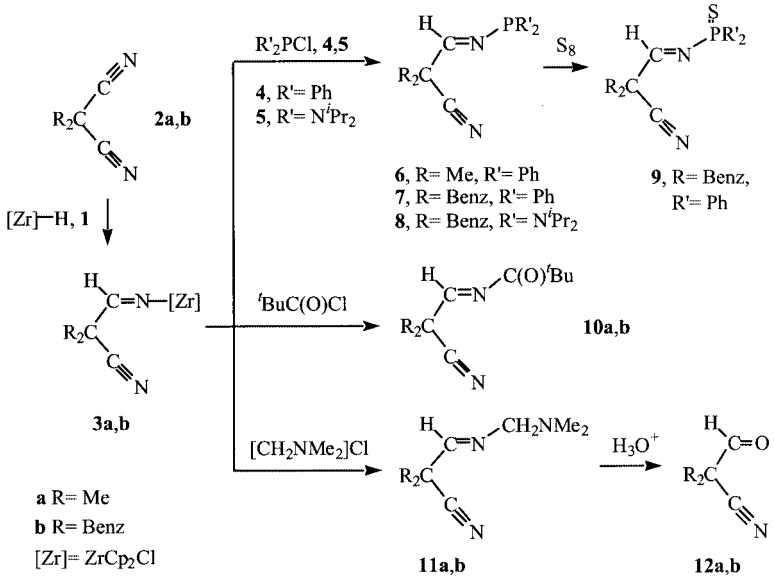


Scheme 1

(Scheme 1). The composition and constitution of **3b** followed from mass analysis and IR, ^{1}H, and ^{13}C NMR spectra. Therefore, selective mono-hydrozirconation occurs with *gem*-dinitrile substrates $R_2C(CN)_2$ to give the corresponding *N*-zirconaimino nitrile complexes $R_2C(C{=}N{-}ZrCp_2Cl)CN$ (**3a**,**b**).

Derivatives **3a**,**b** are potentially useful starting reagents for the synthesis of *N*-functionalized aldimines. Thus, treatment of **3a**,**b** with Ph_2PCl (**4**) gave the exchange reaction products **6** and **7**, respectively, along with the loss of the metal fragment $[Cp_2ZrCl_2]$ (Scheme 1). The ^{31}P NMR chemical shifts in the region of δ = 49 ppm for **6** and **7** are in agreement with tricoordinate Ph_2P-N derivatives. In the ^{13}C NMR spectrum the aldimines **6** and **7** exhibit characteristic signals for the CH=N fragment at $\delta_{C=N}$ = 164 ppm. The *N*-zirconated compound **3b** was also reacted with $(iPr_2N)_2PCl$ (**5**) to give the corresponding *N*-phosphanyl derivative **8** (δ^{31}_P = 85 ppm). The presence of the aldiminato moiety -CH=N- is proven by the significantly deshielded chemical shift in the ^{1}H NMR spectrum at δ_{CH} = 7.89 ($^3J_{H,P}$ = 18.9 Hz) ppm and in the ^{13}C NMR spectrum at $\delta_{C=N}$ = 160.1 ppm ($^2J_{C,P}$ = 31.2 Hz). The nitrile carbon atom appears at $\delta_{C\equiv N}$ = 120.2 ppm. All the spectroscopic analyses are in full agreement with the structure proposed for the *N*-phosphanyl *gem*-imino nitrile compounds **6**–**8**.

The substitution reaction of **3a**,**b** with *t*BuC(O)Cl gave the expected acylimido compounds **10a**,**b** in 92 and 67% yield, respectively (Scheme 1). The aldiminato proton -CH=N- in **10a**,**b** is observed at δ = 7.67 and 7.65 ppm. In the ^{13}C NMR spectrum, besides the signals attributed to the imine, nitrile and *tert*-butyl fragments, the deshielded chemical shifts at δ = 193 ppm in **10a**,**b** are typical for a carbonyl >C=O group.

To expand the scope of the formation of *N*-functionalized imino-nitrile compounds we investigated the addition of the iminium salt $[CH_2NMe_2]Cl$ to **3a**,**b**. After three hours, compounds **11a**,**b** were isolated in excellent yield and were subsequently fully characterized (Scheme 1). The structures of these imino-nitrile derivatives were confirmed from their ^{1}H and ^{13}C NMR spectra. Thus, for **11a**,**b** the proton of the aldiminato moiety -CH=N- appears in the expected region at δ = 7.82–7.84 ppm, and the methylene >N–CH_2–N= group is found at δ = 4.56 and 4.35 ppm, respectively. Hydrolysis of **11a**,**b** by flash chromatography on silica gel allowed the preparation of the corresponding *gem*-aldehyde-nitrile compounds **12a**,**b**. In the ^{1}H and ^{13}C NMR spectra, the deshielded chemical shifts for **12a**,**b** at δ = 9.46 and 9.74, and 193 and 195 ppm, respectively, are typical for the formyl -CH(O) group.

To gain more insight into the structure of the *gem*-aldimine nitrile and aldehyde derivatives prepared, X-ray crystallography was performed with single crystals of **9** — prepared after treatment of **7** with sulfur — **10b**, and **12b** (Figure 1–3, respectively).

The X-ray structure analysis shows the presence of the remaining nitrile function, which deviates slightly from linearity (Table 1). The main features of the $Benz_2C$ unit are as expected, with the two benzyl groups in a W conformation. The central C(2) carbon atom in compounds **9**, **10b**, and **12b** is tetrahedrally coordinated with angles near the ideal tetrahedral angle. The average nitrile C(1)–N(1) bond length is 1.14 Å, and the average imine C(3)–N(2) bond is 1.26 Å in **9**, and **10b** (Table 1).

These values are similar to those commonly found for nitrile and imine functions in non-*gem* positions. More interesting is the observation that in the structures of both **9** and **10b** the H(31) proton and the corresponding thiophosphanyl or acyl group are in the *cis*-configuration. Hydrozirconation reactions on C–C double or triple bonds are *cis*-stereoselective. The same reaction recorded on nitrile derivatives leads to the corresponding linear *N*-zirconocene complexes due to back donation of the nitrogen lone pair to the zirconium moiety.[7c,7d] Exchange reactions with electrophiles on the latter complexes result in an overall *cis*-

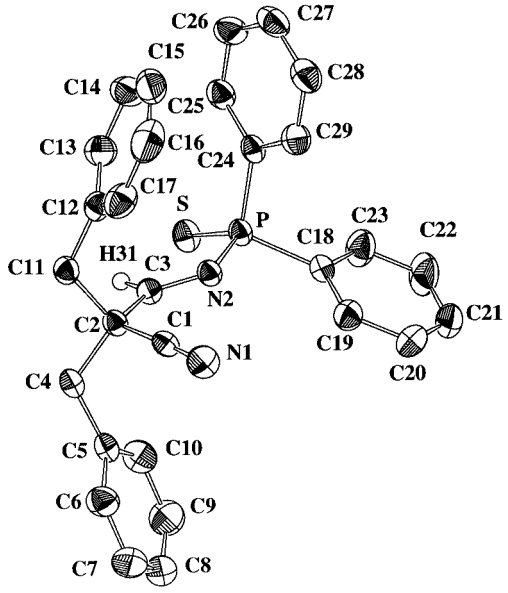


Figure 1. X-ray crystal structure of **9** (CAMERON drawing with thermal ellipsoids at 50% probability)

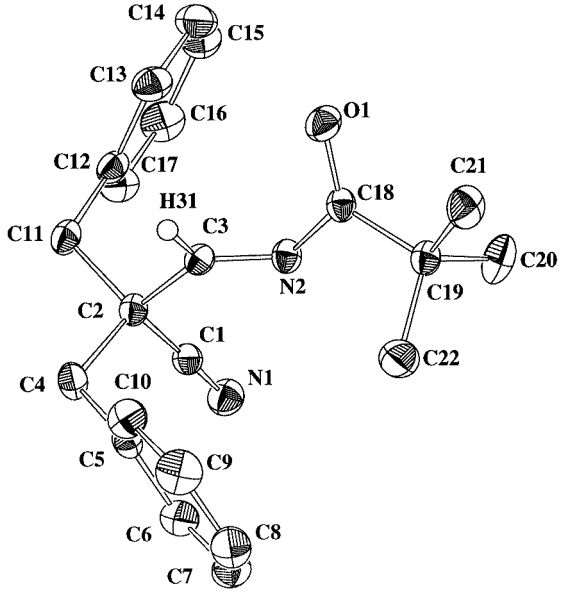
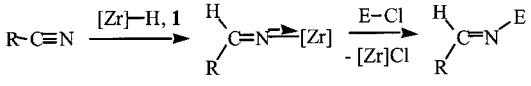


Figure 2. X-ray crystal structure of **10b** (CAMERON drawing with thermal ellipsoids at 50% probability)

configuration between the proton H(31) of the aldimine function and the electrophilic reagent E [Equation (2)].



(2)

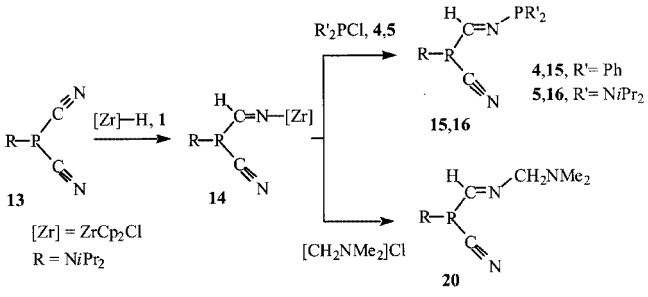
The hydrozirconation reaction with one equivalent of **1** was tested on the dicyanophosphane compound **13** (Scheme 2). Selective formation of the monozirconated product **14**[6b] was observed in quantitative yield as monitored by ^{31}P NMR spectroscopy (δ = 15.2 ppm). The resonances for the Cp groups in **14** appear as a singlet at δ = 6.26 ppm in the ^{1}H NMR spectrum and at δ = 110.7 ppm in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum exhibits (besides the signals corresponding to the protons of the amino substituent bonded to the phosphorus atom) one doublet at δ = 9.34 ($^{2}J_{H,P}$ = 75.4 Hz) ppm assigned to the aldimine proton CH=N; the imino carbon atom is detected in the ^{13}C NMR spectrum at δ = 171.8 ppm ($^{1}J_{C,P}$ =

Figure 3. X-ray crystal structure of **12b** (CAMERON drawing with thermal ellipsoids at 50% probability)

Table 1. Selected bond lengths (Å) and angles (deg) for **9**, **10b**, **12b**

	Lengths		
	9	**10b**	**12b**
C(1)–N(1)	1.139(3)	1.1420(16)	1.134(4)
C(1)–C(2)	1.475(3)	1.4741(17)	1.459(4)
C(2)–C(3)	1.514(3)	1.5068(16)	1.506(3)
C(3)–X	1.263(3)[a]	1.2586(15)[a]	1.141(3)[b]
	Angles		
C(2)–C(3)–N(1)	177.7(2)	177.13(12)	179.0(4)
C(1)–C(2)–C(3)	109.98(18)	110.24(9)	108.7(2)
C(2)–C(3)–X	123.2(2)[a]	122.88(11)[a]	135.0(3)[b]
C(4)–C(2)–C(11)	106.27(18)	107.91(9)	

[a] X = N(2). [b] X = O(1).

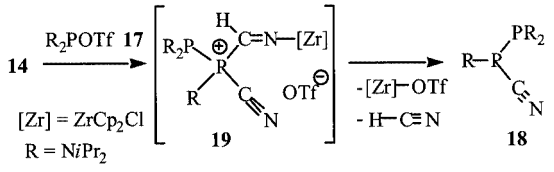


Scheme 2

17.0 Hz). The doublet observed at δ = 120.8 ppm ($^1J_{C,P}$ = 101.2 Hz) ppm is typical for the phosphanyl P−C≡N skeleton.

At −78 °C, **14** was reacted with R′$_2$PCl (R′ = Ph **4**; R′ = N*i*Pr$_2$ **5**) to give the corresponding *N*-phosphanyl compounds **15** and **16**, respectively, in good isolated yield (Scheme 2). The parent [M^+ + 1] ions detected in the mass spectra are in agreement with the general formula *i*Pr$_2$N−P(CN)CH=N−PR$_2$ for **15** and **16**. The ^{31}P NMR spectra display two doublets in the region expected for cyano P−CN [δ^{31}P = 18.7 (**15**), 15.6 (**16**) ppm] and imino = N−PR′$_2$ [δ^{31}P = 58.1 (**15**), 91.2 (**16**) ppm] phosphanes substituted with the corresponding R and R′ groups. The structure of the prepared compounds were unambiguously determined by ^{1}H and ^{13}C NMR spectroscopy. As an example, in the ^{1}H NMR spectra, along with the signals corresponding to the substituents on the phosphorus atoms, each *C*- and *N*-phosphanyl β-imino-nitrile derivative **15** and **16** exhibits a doublet of doublet in the region δ = 8.1−8.7 ppm ($^2J_{H,P}$ = 65−72, $^3J_{H,P}$ = 22 Hz) for the proton of the aldimido -CH=N- fragment. IR data are also instructive as characteristic bands appear at $\tilde{\nu}$ = 1596−1597 cm^{-1} and 2155−2156 cm^{-1} assigned to the C=N and C≡N stretching modes, respectively, of **15** and **16**. Note that no exchange reaction occurs after addition of *t*Bu$_2$PCl to **14**.

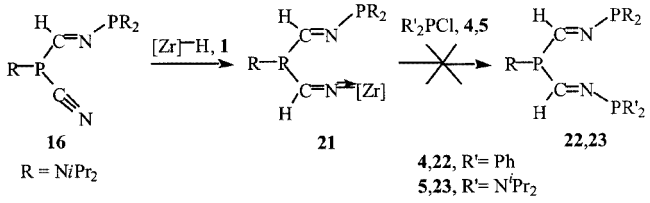
Surprisingly, addition of one equivalent of (*i*Pr$_2$N)$_2$POTf (**17**) to **14** gave, along with the formation of polymeric material, two phosphorus compounds which were identified as the cyanophosphane (*i*Pr$_2$N)$_2$PCN and the diphosphane **18**. Formation of the latter compound may be rationalized by a nucleophilic attack of the phosphenium reagent **17** on the phosphorus atom in **14** to give **19** as a transient species with elimination of HCN and [Cp$_2$Zr(OTf)Cl] (Scheme 3). This behavior has already been observed in the ring-opening reaction of β-zirconocene phospholane with **17**.[8] Moreover, the evolution of HCN during the course of the reaction may also result in the formation of the identified cyanophosphane compound (*i*Pr$_2$N)$_2$PCN.



Scheme 3

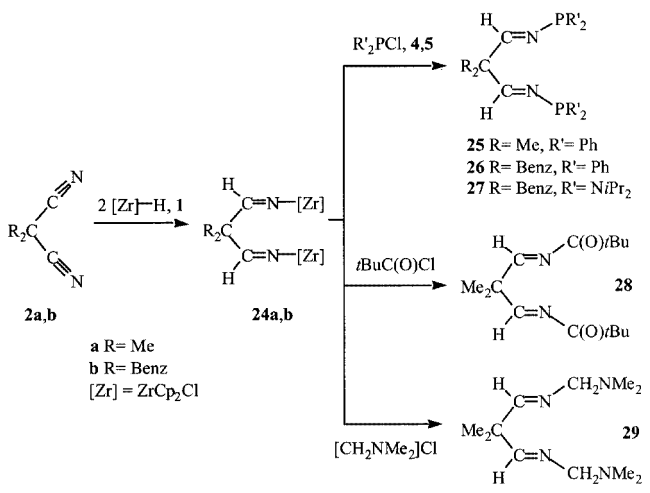
In marked contrast to **3a**,**b**, addition of *t*BuC(O)Cl to **14** gave unidentified polymers. When **14** was treated with one equivalent of the iminium salt [CH$_2$NMe$_2$]Cl the corresponding *N*-alkylamino aldimido compound **20** was formed and isolated in 72% isolated yield (Scheme 2). Compound **20** was fully characterized by NMR spectroscopy (^{31}P, ^{1}H, ^{13}C). Along with the signals corresponding to the phosphaimino nitrile skeleton *i*Pr$_2$N−P(CN)(CH=N−) the chemical shift of the methylene group bonded to both the nitrogen atoms of the imino and amino functions appears in the ^{1}H and ^{13}C NMR spectra at δ = 2.21 and 85.1 ppm respectively.

Starting from the *gem*-imino nitrile compounds **7**, **10b** and **15**, addition of one equivalent of Schwartz's reagent **1** led to a multitude of products which have not been identified. In the case of the hydrozirconation reaction of **16** a single new set of doublet of doublet appeared in the ^{31}P NMR spectrum at δ = 92.8 [NP(N*i*Pr$_2$)$_2$] and 46.9 [CP(N*i*Pr$_2$)] ppm ($^3J_{PP}$ = 23 Hz), which is in agreement with the expected zirconated compound **21**. However exchange reactions performed with **4** and **5** did not give the unsymmetrical diimine compounds **22** and **23** (Scheme 4).

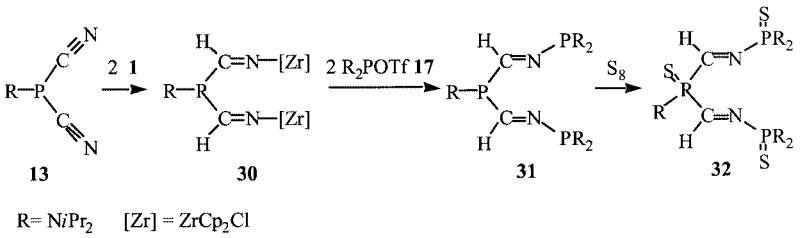


Scheme 4

Dihydrozirconation reactions of *gem*-dinitrile derivatives R$_2$C(CN)$_2$ (**2a**,**b**) with two equivalents of Schwartz's reagent [Cp$_2$Zr(H)Cl]$_n$ (**1**) gave the expected *N*-zirconaimino derivatives **24a**,**b** in quantitative yield (Scheme 5). The Cp groups of the two zirconocene metal fragments in **24a**,**b** are inequivalent. In the ^{13}C NMR spectrum the signals corresponding to the nitrile function of the starting compounds **2a**,**b** disappear completely. The ^{1}H NMR spectra of **24a**,**b** reveal the presence of the proton of the aldimine fragment at δ = 8.49 and 8.70 ppm, respectively. The deshielded chemical shifts at δ = 167.4 and 176.3 ppm observed in the ^{13}C NMR spectrum are indicative of the imino carbon atom of **24a**,**b**.



Scheme 5



Scheme 6

The stable *N*-zirconaimino derivatives **24a**,**b** were also reacted with a large variety of electrophiles, such as chlorophosphanes R_2PCl (**4**,**5**),the acid chloride *t*BuC(O)Cl and the iminium salt $[CH_2NMe_2]Cl$ to give, in excellent isolated yields, the corresponding exchange reaction products **25**−**29** after elimination of $[Cp_2ZrCl_2]$ (Scheme 4). The ^{31}P NMR chemical shifts of compounds **25**−**27** are in agreement with the presence of the R_2P-N fragment. The ^1H and ^{13}C NMR spectra exhibit, beside the chemical shifts corresponding to the protons and carbons of the *N*-substituted phospha- (**25**−**27**), acyl- (**28**) or alkylamino (**29**) groups, signals in the region expected for CH=N aldimine groups (δ^1H = 7.60−8.60 ppm; $\delta^{13}C$ = 164.4−173.2 ppm).

The hydrozirconation reaction of dicyanophosphane $iPr_2N-P(CN)_2$ (**13**) with two equivalents of Schwartz's reagent $[Cp_2Zr(H)Cl]_n$ (**1**) gave the expected bis(*N*-zirconaimino) derivative **30** (Scheme 6) in quantitative yield as monitored by ^{31}P NMR spectroscopy (δ = 15.2 ppm).[6b]

Surprisingly, treatment of the bis(*N*-zirconaimino) complex **30** with chlorophosphanes R_2PCl [R = Ph (**4**), *t*Bu, iPr_2N (**5**)] did not give the corresponding exchange reaction products. The ^{31}P NMR spectrum shows that addition of R_2PCl [R = Ph (**4**), *t*Bu (**5**)] to **30** leads to the formation of a multitude of phosphorus products from which the cyanophosphanes R_2PCN [$\delta^{31}P$ = −33.2 (R = Ph), 16.9 (R = *t*Bu) ppm] were identified. The chlorophosphane $(iPr_2N)_2PCl$ (**5**) did not react with **30**; however, addition of the corresponding more-electrophilic phosphenium reagent $(iPr_2N)_2POTf$ (**17**) to **30** in CH_2Cl_2 at −78 °C afforded the expected stable N-σ^3,λ^3-phosphadiimine compound **31** isolated in 77% yield [$\delta^{31}P$ = 47.0 (PCH=N) and 90.2 (CH=NP) ppm]. In the ^1H NMR spectrum the signal of the PCH=N fragments is shifted to high field at δ = 9.40 ppm. In the ^{13}C NMR spectrum the compound exhibits a characteristic chemical shift at δ = 177.2 ppm in the region observed for the other β-dialdimine derivatives described in this paper.

Addition of acid chlorides RC(O)Cl (R = Me, Ph, *t*Bu) to **30** gave a mixture of phosphorus-containing products (by ^{31}P NMR spectroscopy) which were not identified.

In order to confirm the spectroscopic assignments of compound **31** and to have a better insight into the structure of the diimine derivative prepared, X-ray diffraction studies was carried out on **32** (Figure 4) obtained after addition of sulfur to **31**. All the ^1H and ^{13}C NMR spectroscopic data are consistent with a dialdimine structure for **32**. The X-ray analysis confirms the presence of the two CH=N aldimine functions with the phosphorus substituents $P(NiPr_2)_2$ linked to the imino nitrogen atom. Protons H(11) and H(21) of the aldiimido function and the thiophosphanyl groups $P(S)(NiPr_2)_2$ are in a *cis*-configuration about the C=N double bonds. The bond lengths and angles are in agreement with a C-N double bond for the imine function and compare well with those obtained for the structurally characterized *N*-phosphaaldimido compounds **9**, $iPr_2N-P(CH=N)_2P-N(Ar)P=N(Ar)$[6a] and $(iPr_2N)_2P-CH=N-P(NiPr_2)_2$.[5]

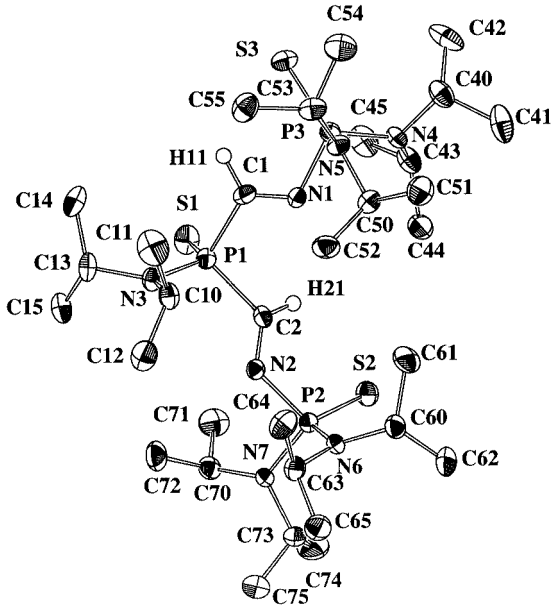


Figure 4. X-ray crystal structure of **32** (CAMERON drawing with thermal ellipsoids at 50% probability): selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.822(5), P(1)−C(2) 1.826(4), C(1)−N(1) 1.267(5), C(2)−N(2) 1.257(5), P(1)−N(3) 1.641(4), N(1)−P(3) 1.742(4), N(2)−P(2) 1.734(3), P(1)−C(2)−N(2) 124.3(3), N(3)−P(1)−C(1) 110.2(2), C(2)−N(2)−P(2) 118.9(3), N(3)−P(1)−C(2) 110.4(2), C(1)−N(1)−P(3) 118.3(3), P(1)−C(1)−N(1) 122.6(3)

It should be added that *N*-zirconated compounds **24a,b** and **30** can also be prepared in quantitative yield by the addition of Schwartz's reagent **1** to the corresponding mono-zirconated complexes **3a,b** and **14**, respectively.

Conclusion

In summary, we have developed a straightforward synthesis of mono- and β-dialdimido *N*-functionalized derivat-

ives from a hydrozirconation reaction with the Schwartz reagent $[Cp_2ZrHCl]_n$ (**1**) and the corresponding nitrile compounds of the type $X(CN)_2$, followed by a substitution reaction of the zirconocene fragment with the corresponding electrophile E^+ (E = PR_2, RC(O), Me_2NCH_2). We showed that replacing the organic fragment, X = CR_2 (R = Me, Benz), by a phosphanyl group, X = $P(NiPr_2)_2$, has a dramatic effect on the efficiency of the exchange reaction of the zirconocene fragment with electrophiles. Up to now, we have not rationalized this observation as the electronic and steric factors that govern the reactivity of electrophiles on imino-zirconocene complexes are by no means fully understood. We have prepared various unprecedented β-dialdimido systems, such as the σ^3,λ^3-*N*-phosphaimine products **25**−**27** and **31**. Further work dealing with their electronic and coordinative properties as well as their reactivity is currently underway.

Experimental Section

General Remarks: All manipulations were performed under an argon atmosphere, either on a vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, toluene, benzene, diethyl ether), lithium aluminium hydride (pentane), or CaH_2 (CH_2Cl_2). Deuterated NMR solvents were treated with $LiAlH_4$ (C_6D_6, [D_8]THF) and CaH_2 (CD_2Cl_2), distilled, and stored under argon. Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker MSL-400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Chemical shifts are given downfield relative to Me_4Si (^1H,^{13}C) or H_3PO_4 (^{31}P) respectively. ^{13}C NMR assignments were confirmed by inverse gradient δ^1H-$\delta^{13}C\{^{13}C,^{31}P\}$ HMQC and $^{31}P-^1H$ INEPT NMR experiments. Elemental and mass spectrum analyses obtained on a Nermag R10−10H were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. $(iPr_2N)P(CN)_2$,[6b] $R_2C(CN)_2$ [9] (R = Me, Benz), $(iPr_2N)_2PCl$,[10] $(iPr_2N)_2POTf$[11] and $[Cp_2Zr(H)(Cl)]_n$ [12] (Schwartz's reagent) were prepared according to literature procedures. Ph_2PCl, *t*BuC(O)Cl and $[CH_2NMe_2]Cl$ were purchased from Aldrich and used without further purification.

Typical Procedure for the Preparation of *N*-Zirconaimino *gem*-Nitrile Derivatives 3a and 3b: Compound **2a** (0.100 g, 1.062 mmol) was added to a suspension of $[Cp_2Zr(H)(Cl)]_n$ (**1**) (0.274 g, 1.062 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h to give a clear yellow solution. The resulting monohydrozirconated compounds were characterized and used without further treatment. In an identical experiment conducted in CD_2Cl_2, **3a** was identified by ^1H and ^{31}P NMR experiments as the sole product of the reaction.

3a: IR (KBr): $\tilde{\nu}$ = 2237 cm^{-1} (ν_{CN}), 1668 cm^{-1} ($\nu_{CH=N}$); ^1H NMR (CD_2Cl_2): δ = 1.43 (s, 6 H, CH_3), 6.18 (s, 10 H, Cp), 8.23 (s, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 25.1 (s, CH_3), 43.8 [s, $C(CH_3)_2$], 113.4 (s, Cp), 118.0 (s, CN), 167.6 (s, CH=N) ppm. MS (DCI/CH_4): *m*/*z* = 351 $[M + H]^+$, 379 $[M + C_2H_5]^+$.

3b: IR (KBr): $\tilde{\nu}$ = 2243 cm^{-1} (ν_{CN}), 1599 cm^{-1} ($\nu_{CH=N}$); ^1H NMR ($CDCl_3$): δ = 3.14 (s, 2 H, CH_2), 3.15 (s, 2 H, CH_2), 5.56 (s, 10 H, Cp), 7.38 (s, 5 H, C_6H_5), 7.40 (s, 5 H, C_6H_5), 8.30 (s, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.9 (s, CH_2), 52.3 [s, $C(CH_2-C_6H_5)_2$], 111.2 (s, Cp), 119.2 (s, CN), 128.0 (s, *p*-Ph), 128.7 (s, *m*-Ph), 130.4 (s, *o*-Ph), 134.7 (s, *i*-Ph), 162.1 (s, CH=N) ppm. MS (DCI/CH_4): *m*/*z* = 504 $[M + H]^+$, 532 $[M + C_2H_5]^+$.

Typical Procedure for the Preparation of *N*-Phosphaimino *gem*-Nitrile Derivatives 6 and 8: A stoichiometric amount of the corresponding chlorophosphanes [Ph_2PCl (**4**), $(iPr_2N)_2PCl$ (**5**)] was added to a solution of **3a**,**b** in CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred for 2 h and then evaporated to dryness. The solid residue was extracted with pentane (3 × 20 mL). Removal of the volatiles gave the corresponding products **6** and **8**.

6: Yellow powder, 164 mg (0.584 mmol, 55%) prepared from 374 mg of **3a** (1.062 mmol) and 191 μL of **4** (1.062 mmol). ^1H NMR ($CDCl_3$): δ = 1.48 (s, 6 H, CH_3), 7.33−7.47 (m, 11 H, CH=N and Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.9 (s, CH_3), 40.1 [s, $C(CH_3)_2$], 122.0 (s, CN), 128.7 (d, $^2J_{C,P}$ = 13.9 Hz, *o*-Ph), 129.7 (s, *p*-Ph), 132.5 (d, $^3J_{C,P}$ = 21.4 Hz, *m*-Ph), 137.8 (d, $^1J_{C,P}$ = 14.8 Hz, *i*-Ph), 164.8 (s, CH=N) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 48.4 ppm. MS (DCI/CH_4): *m*/*z* = 281 $[M + H]^+$, 310 $[M + C_2H_5]^+$.

8: Yellow powder, 422 mg (0.924 mmol, 91%) prepared from 512 mg of **3b** (1.015 mmol) and **5** (1.015 mmol). IR (KBr): $\tilde{\nu}$ = 1587 cm^{-1} ($\nu_{CH=N}$), 2240 cm^{-1} (ν_{CN}). ^1H NMR ($CDCl_3$): δ = 0.99 [d, $^2J_{H,H}$ = 6.6 Hz, 12 H, $(CH_3)_2CH$], 1.16 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $(CH_3)_2CH$], 3.08 (d, $^5J_{H,P}$ = 3.4 Hz, 2 H, CH_2), 3.23 (s, 2 H, CH_2), 3.39 [sept d, $^3J_{H,H}$ = 6.6, $^3J_{H,P}$ = 11.0 Hz, 4 H, $(CH_3)_2CH$], 7.29 (s, 5 H, Ph), 7.39 (s, 5 H, Ph), 7.89 (d, $^3J_{H,P}$ = 18.9 Hz, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.0 [s, $CH_3)_2CH$], 24.2 [s, $(CH_3)_2CH$], 41.9 (s, CH_2), 43.2 (s, CH_2), 45.7 [d, $^2J_{C,P}$ = 12.5 Hz, $(CH_3)_2CH$], 51.6 [d, $^3J_{C,P}$ = 20.2 Hz, $(C_6H_5-CH_2)C$], 120.2 (s, CN), 127.2 (s, *p*-Ph), 128.3 (s, *m*-Ph), 130.2 (s, *o*-Ph), 134.5 (s, *i*-Ph), 160.1 (d, $^2J_{C,P}$ = 31.2 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 85.1 (s, CH=N−P) ppm. MS (DCI/CH_4): *m*/*z* = 479 $[M^+ + H]$. $C_{29}H_{43}N_4P$ (478.32): calcd. C 72.77, H 9.20, N 11.71; found C 72.68, H 9.11, N 11.85.

Preparation of 7: A stoichiometric amount of Ph_2PCl (**4**) (182 μL, 1.015 mmol) was added dropwise to a solution of **3b** (512 mg, 1.015 mmol) in CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred for 1 h and then the solvents evaporated to dryness. The solid residue was dissolved in a minimum of CH_2Cl_2 (approx. 0.5 mL) and then poured into a vigorously stirred solution of pentane (40 mL). The resulting precipitate was washed twice with 20 mL of pentane and vacuum dried, giving **7** as a yellow powder in 97% yield (426 mg). ^1H NMR ($CDCl_3$): δ = 3.10 (s, 4 H, CH_2), 7.15−7.41 (m, 21 H, CH=N, and aryl groups) ppm. $^{31}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.4 (s, CH_2), 50.7 (s, Benz-*C*), 120.0 (s, CN), 127.6 (s, *o*-Benz), 128.6 (s, *m*-Benz), 128.9 (d, $^2J_{C,P}$ = 10.1 Hz, *o*-Ph), 129.3 (s, *p*-Ph), 129.9 (s, *p*-Benz), 132.8 (d, $^3J_{C,P}$ = 21.1 Hz, *m*-Ph), 134.2 (s, *i*-Benz), 163.9 (s, CH=N) ppm; *i*-Ph was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.1 ppm. MS (DCI/CH_4): *m*/*z* = 433 $[M^+ + H]$, 461 $[M^+ + C_2H_5]$.

Preparation of 9: After addition of an excess of sulfur, **7** (230 mg, 0.532 mmol) was isolated as the corresponding thiophosphane **9**. The reaction mixture was stirred for 2 h at room temperature in THF (10 mL), then **9** (91%, 225 mg) was purified by column chromatography over Florisil, eluting with pentane. ^1H NMR ($CDCl_3$): δ = 3.24 (s, 2 H, CH_2), 3.28 (s, 2 H, CH_2), 7.08−7.65 (m, 20 H, Ph), 8.77 (d, $^3J_{H,P}$ = 36.6 Hz, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.3 (s, CH_2), 54.2 [s, $(C_6H_5-CH_2)C$, 118.6 (s, CN), 127.7 (s, *o*-C_6H_5-CH_2, 128.2 (s, *p*-Ph), 128.5 (d, $^2J_{C,P}$ = 6.3 Hz, *o*-Ph), 128.6 (s, *m*-$C_6H_5-CH_2$), 130.1 (s, *p*-$C_6H_5-CH_2$), 131.9 (d, $^3J_{C,P}$ = 12.1 Hz, *m*-Ph), 133.3 (s, *i*-$C_6H_5-CH_2$) 176.1 (d, $^2J_{C,P}$ = 7.1 Hz, CH=N) ppm; *i*-Ph was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 61.2 (s, CH=N−P) ppm. MS (DCI/CH_4): *m*/*z* = 465

[M^+ +H], 493 [M^+ + C_2H_5]. $C_{29}H_{25}N_2PS$ (464.15): calcd. C 74.98, H 5.42, N 6.06; found C 75.13, H 5.61, N 5.91.

Preparation of 10a: A stoichiometric amount of the acid chloride *t*BuC(O)Cl (131 μL, 1.062 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **3a** (374 mg, 1.062 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The resulting solution was then stirred at room temperature for 4 h. Volatiles were removed in vacuo and the product was separated from the metal fragment by successive extraction of the residue with pentane (3 × 30 mL). The solvent was evaporated to dryness to give **10a** as a white powder in 92% yield (176 mg, 0.977 mmol). IR (KBr): $\tilde{\nu}$ = 1598 cm^{-1} ($\nu_{CH=N}$), 1677 cm^{-1} ($\nu_{C=O}$). ^1H NMR ($CDCl_3$): δ = 1.20 [s, 9 H, $(CH_3)_3C$], 1.49 [s, 3 H, $(CH_3)_2C$], 1.53 [s, 3 H, $(CH_3)_2C$], 7.67 (s, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.6 [s, $(CH_3)_2C$], 27.3 [s, $(CH_3)_3C$], 38.6 [s, $(CH_3)_3C$], 47.2 [s, $(CH_3)_2C$], 122.3 (s, CN), 167.1 (s, CH=N), 193.1 (s, C=O) ppm. MS (DCI/CH_4): *m*/*z* = 181 [M^+ +H], 209 [M^+ + C_2H_5].

Preparation of 10b: A stoichiometric amount of *t*BuC(O)Cl (125 μL, 1.015 mmol) in 5 mL of CH_2Cl_2 was added at room temperature to a solution of **3b** (512 mg, 1.015 mmol) in 15 mL of CH_2Cl_2. The resulting solution was then stirred at room temperature for 3 h. The solvent was removed in vacuo. The product **10b** was isolated as a white powder in 67% yield (223 mg, 0.671 mmol) after column chromatography on Florisil with ethyl acetate as eluent. The product was recrystallized from CH_2Cl_2/pentane to produce colorless crystals. M.p. 128 °C. IR (KBr): $\tilde{\nu}$ = 2243 cm^{-1} ($\nu_{C=N}$), 1606 ($\nu_{CH=N}$), 1695 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$): δ = 0.96 (s, 9 H, CH_3), 3.15 (s, 4 H, $C_6H_5-CH_2$), 7.31 (s, 10 H, Ph), 7.65 (s, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.2 [s, $C(CH_3)_3$], 42.0 (s, C_6H_5-CH_2), 50.3 [s, $C(CH_3)_3$], 53.4 [s, $C(CH_2-C_6H_5)_2$], 118.7 (s, CN), 127.8 (s, *o*-Ph), 128.6 (s, *m*-Ph), 130.2 (s, *p*-Ph), 133.4 (s, *i*-Ph), 161.9 (s, CH=N), 193.1 (s, C=O) ppm. MS (DCI/CH_4): *m*/*z* = 333 [M^+ +H], 361 [M^+ + C_2H_5]. $C_{29}H_{25}N_2PS$ (332.19): calcd. C 79.48, H 7.28, N 8.43; found C 79.53, H 7.31, N 8.41.

Preparation of 11a: A stoichiometric amount of a suspension of $[CH_2NMe_2]Cl$ (100 mg, 1.062 mmol) in 5 mL of CH_2Cl_2 was added at 0 °C to a solution of **3a** (374 mg, 1.062 mmol) in 10 mL of CH_2Cl_2. The resulting solution was then stirred at room temperature for 3 h. The solvent was removed in vacuo. Successive extractions of the residue with pentane (3 × 20 mL) gave the product **11a** as a yellow powder in 73% yield (113 mg, 0.775 mmol). ^1H NMR ($CDCl_3$): δ = 1.47 [s, 6 H, $(CH_3)_2C$], 2.71 [s, 6 H, $(CH_3)_2N$], 4.56 (s, 2 H, $N-CH_2-N$), 7.82 (s, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.0 [s, $(CH_3)_2C$], 40.8 [s, $(CH_3)_2N$], 44.7 [s, $(CH_3)_2C$], 76.0 (s, $N-CH_2-N$), 123.7 (s, CN) 163.4 (s, CH=N) ppm. MS (DCI/CH_4): *m*/*z* = 154 [M^+ +H], 182 [M^+ + C_2H_5].

Preparation of 11b: A stoichiometric amount of a suspension of $[CH_2NMe_2]Cl$ (95 mg, 1.015 mmol) in 5 mL of CH_2Cl_2 was added at room temperature to a solution of **3b** (512 mg, 1.015 mmol) in 15 mL of CH_2Cl_2. The resulting solution was then stirred at room temperature for 3 h. The solvent was removed in vacuo. The solid residue was dissolved in a minimum of CH_2Cl_2 (approx. 0.5 mL) and then poured dropwise into a vigorously stirred solution of pentane (50 mL). The metal salts precipitated, filtered and the solution was evaporated to dryness to give **11b** (236 mg, 0.771 mmol) as a yellow powder in 76% yield. ^1H NMR ($CDCl_3$): δ = 2.31 [s, 6 H, $N(CH_3)_2$], 3.14 (s, 2 H, $C_6H_5-CH_2$), 3.18 (s, 2 H, $C_6H_5-CH_2$), 4.35 (s, 2 H, $N-CH_2-N$), 7.25−7.31 (m, 10 H, C_6H_5), 7.84 (s, 1 H, CH=N ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 41.2 (s, C_6H_5-CH_2), 42.1 [s, $N(CH_3)_2$], 53.4 [s, $C(C_6H_5-CH_2)_2$], 77.6 (s, $N-CH_2-N$), 119.3 (s, CN), 127.5 (s, *o*-Ph), 128.5 (s, *m*-Ph), 130.1 (s, *p*-Ph), 134.0 (s, *i*-Ph), 164.6 (s, CH=N) ppm. MS (DCI/CH_4): *m*/*z* = 306 [M^+ +H], 334 [M^+ + C_2H_5].

Typical Procedure for the Preparation of Formyl *gem*-Nitrile Derivatives 12a,b: A solution of **11a,b** in CH_2Cl_2 was passed through silica gel to give **12a**,**b**.

12a: 79% yield. ^1H NMR ($CDCl_3$): δ = 1.47 [s, 6 H, $(CH_3)_2C$], 9.46 (s, 1 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.8 [s, $(CH_3)_2C$], 45.3 [s, $(CH_3)_2C$], 123.3 (s, CN), 193.0 (s, CH=O) ppm. MS (DCI/CH_4): *m*/*z* = 98 [M^+ +H], 126 [M^+ + C_2H_5]. C_5H_7NO (332.19): calcd. C 61.84, H 7.27, N 14.42; found C 62.02, H 7.33, N 14.31.

12b: 81% yield. M.p. 139.5 °C. IR (KBr): $\tilde{\nu}$ = 2247 cm^{-1} (ν_{CN}), 1737 ($\nu_{CH=O}$). ^1H NMR ($CDCl_3$): δ = 3.06 (s, 2 H, CH_2), 3.22 (s, 2 H, CH_2), 7.24−7.41 (m, 10 H, Ph), 9.74 (s, 1 H, CH=O) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): = δ = 40.1 (s, C_6H_5-CH_2), 43.2, [s, $C(CH_2-C_6H_5)_2$], 118.2 (s, CN), 127.9 (s, *o*-Ph), 128.7 (s, *m*-Ph), 130.0 (s, *o*-Ph), 133.0 (s, *i*-Ph), 194.9 (s, C=O) ppm. MS (DCI/CH_4): *m*/*z* = 250 [M^+ +H], 278 [M^+ + C_2H_5]. $C_{17}H_{15}NO$ (249.12): calcd. C 81.90, H 6.06, N 5.62; found C 81.92, H 6.13, N 5.51.

Preparation of 14: A suspension of $[Cp_2Zr(H)Cl]_n$ (0.282 g, 1.092 mmol) and **13** (0.200 g, 1.092 mmol) in CH_2Cl_2 (8 mL) was stirred for 1 h at 0 °C. Removal of the solvent in vacuo from the clear brown reaction mixture gave **14** in nearly quantitatively yield. ^1H NMR (CD_2Cl_2, 200.1 MHz): δ = 1.24 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.28 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.46 (sept d, $^3J_{H,P}$ = 13.2, $^3J_{H,H}$ = 6.6 Hz, 2 H, CHNP), 6.17 (s, 5 H, Cp), 6.26 (s, 5 H, Cp), 9.34 (d, $^2J_{H,P}$ = 75.4 Hz, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 23.2 (s, CH_3), 53.3 (s, CHNP), 110.7, 111.0 (s, Cp), 120.8 (d, $^1J_{C,P}$ = 101.2 Hz, PCN), 171.8 (d, $^1J_{C,P}$ = 17.0 Hz, C=N) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 15.2 ppm. IR (KBr, CH_2Cl_2): $\tilde{\nu}$ = 2155 (C≡N), 1660 (CH=N) cm^{-1}.

Typical Procedure for the Preparation of *N*-Phospha *gem*-Nitrile Derivatives 15 and 16: A solution of Ph_2PCl (**4**) (216 μL, 1.200 mmol) in 5 mL of CH_2Cl_2 was added to a magnetically stirred solution of **14** (530 mg, 1.200 mmol) in CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 1 h at −78 °C then allowed to warm to 0 °C and stirred for a further hour. The solution was slowly warmed to room temperature and the solvents evaporated to dryness. The product **15** was separated from the metal salts by successive extractions with pentane (3 × 20 mL) and isolated as a yellow powder in 83% yield (368 mg, 0.996 mmol).

15: IR (KBr/CH_2Cl_2): $\tilde{\nu}$ = 1597 cm^{-1} ($\nu_{CH=N}$), 2155 ($\nu_{C\equiv N}$). ^1H NMR (C_6D_6): δ = 0.81 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 0.95 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.06 [m, 2 H, $CH(CH_3)_2$,), 6.89−7.16 (m, 4 H, Ph), 7.32−7.45 (m, 4 H, Ph), 7.58−7.66 (m, 2 H, Ph), 8.18 (dd, $^2J_{Hp}$ = 65.2, $^3J_{H,P}$ = 22.4 Hz, 1 H, CH=N) ppm. $^{31}C\{^1H\}$ (C_6D_6): δ = 24.2 [s, $(CH_3)_2CH$], 49.1 [s, $(CH_3)_2CH$], 121.0 (d, $^1J_{C,P}$ = 90.3 Hz, CN), 129.4 (s, Ph), 130.7 (d, $^2J_{C,P}$ = 27.0 Hz, *o*-Ph), 132.8 (d, $^2J_{C,P}$ = 19.7 Hz, *o*-Ph), 133.6 (d, $^3J_{C,P}$ = 11.9 Hz, *m*-Ph), 134.0 (d, $^3J_{C,P}$ = 10.9 Hz, *m*-Ph), 135 (d, $^3J_{C,P}$ = 12.6 Hz, *m*-Ph), 135.2 (d, $^3J_{C,P}$ = 13.1 Hz, *m*-Ph), 138.6 (d, $^1J_{C,P}$ = 32.8 Hz, *i*-Ph), 138.9 (d, $^1J_{C,P}$ = 22.7 Hz, *i*-Ph), 172.0 (s, CH=N) ppm. $^{31}P\{^1H\}$ (C_6D_6): δ = 18.7 (d, $^3J_{PP}$ = 34.5 Hz, P-CN), 58.1 (d, $^3J_{PP}$ = 34.5 Hz, PPh_2) ppm. MS (DCI/CH_4): *m*/*z* = 370 [M^+ +H].

16: In an identical procedure, **16** (yellow powder, 78%) was obtained from **14** (530 mg, 1.200 mmol) and one equivalent of **5** (320 mg, 1.200 mmol). IR (KBr/CH_2Cl_2): $\tilde{\nu}$ = 1596 cm^{-1} ($\nu_{CH=N}$), 2156 ($\nu_{C\equiv N}$). ^1H NMR (C_6D_6): δ = 1.09 (m, 36 H, CH_3), 3.42 [m, 6 H, $CH(CH_3)_2$], 8.71 (dd, $^2J_{H,P}$ = 72.3, $^3J_{H,P}$ = 22.5 Hz, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.7 [d, $^3J_{C,P}$ = 6.9 Hz, $(CH_3)_2CH$], 46.7 [d, $^2J_{C,P}$ = 12.2 Hz, $(CH_3)_2CH$], 47.0 [d, $^2J_{C,P}$ = 12.2 Hz, $(CH_3)_2CH$], 121.0 (d, $^1J_{C,P}$ = 90.0 Hz, CN), 168.0 (dd, $^1J_{C,P}$ = 22.7, $^2J_{C,P}$ = 4.8 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 15.6 (d, $^3J_{PP}$ = 27.1 Hz, P-CN), 91.2 (d, $^3J_{PP}$ = 27.1 Hz, PPh_2)

ppm. MS (DCI/CH_4): m/z = 416 [M^+ +H]. $C_{20}H_{43}N_5P_2$ (415.30): calcd. C 57.81, H 10.43, N 16.85; found C 57.92, H 10.54, N 16.81.

Preparation of 18: A stoichiometric amount of phosphenium salt **17** (442 mg, 1.200 mmol) in 10 mL of CH_2Cl_2 was added at −78 °C to a solution of **14** (530 mg, 1200 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at −78 °C then allowed to warm to 0 °C and stirred for a further hour. The solution was then slowly warmed room temperature. $^{31}P\{^1H\}$ NMR spectroscopy showed the presence of $(i\mathrm{Pr}_2\mathrm{N})_2$P−CN and **18** along with unidentified phosphorus polymers which were eliminated after addition of pentane (20 mL) to the crude reaction mixture and filtration of the precipitate. Treatment of the resulting solution did not allow separation of **18** from $(i\mathrm{Pr}_2\mathrm{N})_2$P−CN. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 18.6 (s, CH$_3$−CH−N−P-CN), 24.5 (d, $^3J_{C,P}$ = 5.8 Hz, CH$_3$−CH−N−P−P-CN), 24.9 (d, $^3J_{C,P}$ = 7.2 Hz, CH$_3$−CH−N−P-CN), 47.2 (s, CH−N−P-CN), 49.1 (dd, $^2J_{C,P}$ = 12.4, $^3J_{C,P}$ = 9.2 Hz, CH−N−P−P-CN), 126.8 (dd, $^1J_{C,P}$ = 116.8, $^2J_{C,P}$ = 38.0 Hz, CN) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −3.2 (d, $^1J_{PP}$ = 77.9 Hz, P-CN), 58.7 [d, $^1J_{P,P}$ = 77.9 Hz, P(NiPr$_2$)$_2$] ppm.

Preparation of 20: A stoichiometric amount of a suspension of $[CH_2NMe_2]Cl$ (112 mg, 1.200 mmol) in 5 mL of CH_2Cl_2 was added at 0 °C to a solution of **14** (530 mg, 1.200 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at 0 °C then allowed to warm to room temperature and stirred for a further hour. The solvent was removed in vacuo and the product **20** extracted with pentane (3 × 20 mL) to give a yellow powder in 72% yield (209 mg, 0.865 mmol). ^1H NMR (C_6D_6): δ = 0.96 (s, 6 H, N−CH$_3$), 1.03 [d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH(CH_3)$_2$], 2.21 (s, 2 H, CH$_2$−N), 3.15 [sept, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH(CH$_3$)$_2$], 7.80 (dt, $^2J_{H,P}$ = 61.6, $^4J_{H,H}$ = 1.3 Hz, 1 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.1 [s, CH(CH$_3$)$_2$], 42.8 (s, N−CH$_3$), 48.4 [s, CH(CH$_3$)$_2$], 85.1 (d, $^3J_{C,P}$ = 13.6 Hz, N−CH$_2$−N), 121.3 (d, $^1J_{C,P}$ = 86.8 Hz, CN), 165.7 (d, $^1J_{C,P}$ = 7.4 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 12.7 (s, P-CN) ppm. MS (DCI/CH_4): m/z = 243 [M^+ +H].

Typical Procedure for the Preparation of *N*-Zirconaimino Derivatives 24a,b: Compound **2a** (100 mg, 1.062 mmol) was added to a suspension of $[Cp_2Zr(H)(Cl)]_n$, (**1**) (548 mg, 2.124 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h then allowed to warm to room temperature and stirred for a further 1.5 h. The final product **24a** was used without further treatment. In an analogous manner **24b** was obtained from **1** (524 mg, 2.030 mmol) and **2b** (250 mg, 1.015 mmol). In identical experiments in CD_2Cl_2, **24a**,**b** were respectively identified by ^1H and ^{31}P NMR spectroscopy as the sole products of the reaction.

24a: IR (KBr): $\tilde{\nu}$ = 1624 cm^{-1} ($\nu_{CH=N}$). ^1H NMR (CD_2Cl_2): δ = 1.11 (s, 6 H, CH$_3$), 6.13 (s, 10 H, Cp), 6.31 (s, 10 H, Cp), 8.49 (s, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 22.9 (s, CH$_3$), 43.8 [s, C(CH$_3$)$_2$]; 112.8 (s, Cp), 115.8 (s, Cp), 167.4 (s, CH=N) ppm.

24b: ^1H NMR (CD_2Cl_2): δ = 3.06 (s, 4 H, CH$_2$), 6.03 (s, 10 H, Cp), 6.34 (s, 10 H, Cp), 7.25−7.40 (m, 10 H, C_6H_5), 8.70 (s, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 42.9 (s, CH$_2$), 44.6 [s, C(CH$_2$−C$_6$H$_5$)$_2$], 112.8 (s, Cp), 115.8 (s, Cp), 128.3 (s, *p*-Ph), 130.0 (s, *m*-Ph), 132.2 (s, *o*-Ph), 139.8 (s, *i*-Ph), 176.3 (s, CH=N) ppm.

Preparation of 25: Two equivalents of Ph_2PCl (**4**) (415 μL, 2.134 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **24a** (648 mg, 1.062 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and then the solvents evaporated to dryness. The solid residue was dissolved in a minimum of CH_2Cl_2 (approx. 0.5 mL) and then poured into a vigorously stirred solution of pentane (40 mL). The metal salts precipitated. After filtration, removal of the volatiles gave the corresponding product **25** as a yellow powder in 97% yield (480 mg, 1.030 mmol). IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} ($\nu_{CH=N}$). ^1H NMR ($CDCl_3$): δ = 1.28 (s, 6 H, CH$_3$), 7.30−7.43 (m, 20 H, Ph), 7.71 (d, $^3J_{H,P}$ = 22.2 Hz, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.0 [s, (CH$_3$)$_2$C], 51.0 Hz [t, $^3J_{C,P}$ = 11.1 Hz, (CH$_3$)$_2$$C$], 128.5 (d, $^2J_{C,P}$ = 6.9, *o*-Ph), 129.3 (s, *p*-Ph), 132.4 (d, $^3J_{C,P}$ = 20.7 Hz, *m*-Ph), 138.8 (d, $^1J_{C,P}$ = 14.7 Hz, *i*-Ph), 173.7 (s, CH=N) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 48.9 (s, PPh$_2$) ppm. MS (DCI/CH_4): m/z = 467 [M^+ +H]. $C_{20}H_{43}N_5P_2$ (466.17): calcd. C 74.67, H 6.05, N 6.01; found C 74.81, H 6.18, N 5.89.

Typical Procedure for the Preparation of Bis(*N*-phosphaimino) Derivatives 26 and 27: Two equivalents of Ph_2PCl (**4**) (365 μL, 2.030 mmol) in 8 mL of CH_2Cl_2 was added to a solution of **24b** (773 mg, 1.015 mmol) in CH_2Cl_2 (15 mL) at room temperature. The mixture was stirred for 1.5 h at room temperature and then the solvents evaporated to dryness. Successive extractions with pentane (3 × 20 mL) gave the corresponding product **26** as a yellow powder in 67% yield (421 mg, 0.680 mmol). In an identical procedure, **27** (664 mg, 0.934 mmol) was obtained from **24b** (773 mg, 1.015 mmol) and two equivalents of **5** (or **17**) (2.030 mmol).

26:. ^1H NMR ($CDCl_3$): δ = 3.08 (s, 4 H, CH$_2$) 7.05−7.50 (m, 20 H, Ph), 8.60 (d, $^3J_{H,P}$ = 29.1 Hz, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.4 (s, CH$_2$), 53.8 [t, $^3J_{C,P}$ = 12.4 Hz, (C$_6$H$_5$−CH$_2$)C], 126.4 (s, *o*-C$_6$H$_5$−CH$_2$), 128.1 (s, *m*-C$_6$H$_5$−CH$_2$), 128.4 (d, $^2J_{C,P}$ = 8.5 Hz, *o*-Ph), 128.6 (s, *p*-Ph), 130.4 (s, *p*-C$_6$H$_5$−CH$_2$), 132.7 (d, $^3J_{C,P}$ = 20.8 Hz, *m*-Ph), 136.7 (s, *i*-C$_6$H$_5$−CH$_2$), 137.8 (d, $^1J_{C,P}$ = 18.2 Hz, *i*-Ph), 173.2 (s, CH=N) ppm $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 49.8 (s, CH=N−P) ppm. MS (DCI/CH_4): m/z = 619 [M^+ +H]. $C_{41}H_{36}N_2P_2$ (618.24): calcd. C 79.59, H 5.86, N 4.53; found C 79.65, H 5.92, N 4.41.

27: IR (KBr): $\tilde{\nu}$ = 1601 cm^{-1} ($\nu_{CH=N}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 85.8 (s, CH=N−P) ppm. ^1H NMR ($CDCl_3$): δ = 1.02 [d, $^3J_{H,H}$ = 6.6 Hz, 24 H, (CH_3)$_2$CH], 1.17 [d, $^3J_{H,H}$ = 6.6 Hz, 24 H, (CH_3)$_2$CH], 2.80 (d, $^5J_{H,P}$ = 2.8 Hz, 2 H, CH$_2$), 3.15 (s, 2 H, CH$_2$), 3.68 (sept d, $^3J_{H,H}$ = 6.6, $^3J_{H,P}$ = 12.4 Hz, 8 H, (CH$_3$)$_2$CH], 7.28 (s, 10 H, Ph), 8.30 (d, $^3J_{H,P}$ = 2.7 Hz, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.1 [s, (CH$_3$)$_2$CH], 41.5 (s, CH$_2$) 45.4 [d, $^2J_{C,P}$ = 12.7 Hz, (CH$_3$)$_2$$C$H], 55.5 [t, $^3J_{C,P}$ = 14.6 Hz, (C$_6$H$_5$−CH$_2$)C], 125.8 (s, *p*-Ph), 127.7 (s, *m*-Ph), 130.4 (s, *o*-Ph), 137.7 (s, *i*-Ph), 169.0 (d, $^2J_{C,P}$ = 34.8 Hz, CH=N) ppm. MS (DCI/CH_4): m/z = 711 [M^+ +H]. $C_{41}H_{72}N_6P_2$ (710.53): calcd. C 69.26, H 10.21, N 11.82; found C 69.38, H 10.34, N 11.71.

Preparation of 28: Two equivalents of *t*BuC(O)Cl (265 μL, 2.124 mmol) in 5 mL of CH_2Cl_2 was added at room temperature to a solution of **24a** (648 mg, 1.062 mmol) in 15 mL of CH_2Cl_2. The resulting solution was then stirred at room temperature overnight. The solvent was removed in vacuo. The product **28** was isolated after successive extractions with pentane (3 × 20 mL) as a white oil in 94% yield (266 mg, 0.998 mmol). ^1H NMR ($CDCl_3$): δ = 0.91 [s, 6 H, (CH$_3$)$_2$C], 1.10 [s, 18 H, C(CH$_3$)$_3$], 7.73 (s, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.2 [s, (CH$_3$)$_2$C], 27.5 [s, C(CH$_3$)$_3$], 36.8 [s, C(CH$_3$)$_3$], 45.7 [s, C(CH$_3$)$_2$], 167.1 (s, CH=N), 194.1 (s, C=O) ppm. MS (DCI/CH_4): m/z = 267 [M^+ +H], 495 [M^+ + C_2H_5].

Preparation of 29: Two equivalents of a suspension of $[CH_2NMe_2]Cl$ (199 mg, 2.124 mmol) in 5 mL of CH_2Cl_2 was added at room temperature to a solution of **24a** (648 mg, 1.062 mmol) in 15 mL of CH_2Cl_2. The resulting orange solution was then stirred at room temperature for 3 h. The solvent was removed in vacuo. Successive extractions of the residue with pentane (3 × 20 mL) gave

the product **29** as a yellow oil in 61% yield (138 mg, 0.648 mmol). IR (KBr): $\tilde{\nu}$ = 1669 cm^{-1} ($\nu_{CH=N}$). ^1H NMR ($CDCl_3$): δ = 1.04 [s, 6 H, $(CH_3)_2C$], 2.57 [s, 12 H, $(CH_3)_2N$], 4.64 (s, 4 H, $N-CH_2-N$), 7.60 (s, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.3 [s, $(CH_3)_2C$], 42.3 [s, $(CH_3)_2N$], 47.8 [s, $(CH_3)_2C$], 74.5 (s, $N-CH_2-N$), 164.4 (s, CH=N) ppm. MS (DCI/CH_4): *m*/*z* = 213 [M^+ + H], 241 [$M^+ + C_2H_5$].

Preparation of 30: A suspension of $[Cp_2Zr(H)(Cl)]_n$ (0.565 g, 2.190 mmol) and **13** (0.482 g, 1.092 mmol) in CH_2Cl_2 (10 mL) was stirred for 1.5 h at 0 °C. Removal of the solvent from the clear brown reaction mixture in vacuo gave **30** in quantitative yield. ^1H NMR (C_6D_6, 200.1 MHz): δ = 1.43 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 3.42 (m, 2 H, CHNP), 6.15, 6.10, 6.03, 5.96 (s, 5 H, Cp), 10.08 (d, $^2J_{H,P}$ = 61.8 Hz, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 24.0 (s, CH_3), 53.4 (s, CHNP), 110.5 (s, Cp), 181.5 (d, $^1J_{C,P}$ = 30.1 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ = 52.0 ppm. IR: ν(C=N) = 1647, 1624 cm^{-1}.

Preparation of 31: Two equivalents of **17** (831 mg, 2.184 mmol) in 6 mL of CH_2Cl_2 was added to a magnetically stirred solution of **30** (763 mg, 1.092 mmol) in CH_2Cl_2 at −78 °C. The reaction mixture was stirred for 1 h at −78 °C then allowed to warm to 0 °C and stirred for a further hour. The solution was slowly warmed up to room temperature and the solvents evaporated to dryness. The product **31** was separated from the metal salts by successive extractions with pentane (3 × 20 mL) and isolated as a yellow powder in 77% yield (545 mg, 0.841 mmol). ^1H NMR (C_6D_6): δ = 1.21 (d, $^3J_{H,H}$ = 6.6 Hz, 30 H, CH_3), 1.22 (d, $^3J_{H,H}$ = 6.9 Hz, 30 H, CH_3), 3.29 (m, 2 H, CH−N−P−C), 3.50 (m, 8 H, CH−N−P−N), 9.40 (dd, $^2J_{H,P}$ = 53.0, $^3J_{H,P}$ = 27.2 Hz, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 25.0 [s, $(CH_3)_2CH$], 46.7 [d, $^2J_{C,P}$ = 7.7 Hz, $(CH_3)_2CH$], 47.0 [d, $^2J_{C,P}$ = 7.7 Hz, $(CH_3)_2CH$], 177.2 (dd, $^1J_{C,P}$ = 16.9, $^2J_{C,P}$ = 11.6 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 47.0 (t, $^3J_{P,P}$ = 15.1 Hz, P−CH=N), 90.2 (d, $^3J_{P,P}$ = 15.1 Hz, CH=N−P) ppm. MS (DCI/CH_4): *m*/*z* = 648 [M^+ +H], 676 [$M^+ + C_2H_5$]. $C_{32}H_{72}N_7P_3$ (647.51): calcd. C 59.32, H 11.20, N 15.13; found C 59.43, H 11.29, N 15.07.

Preparation of 32: Addition of an excess of sulfur (5−10 equiv.) to a CH_2Cl_2 solution (10 mL) of **31** (487 mg, 0.752 mmol) gave **32** (93%, 520 mg), which was isolated after column chromatography on silica gel 60 (70−230 mesh ASTM) with pentane/THF (9:1) as eluent. The product was recrystallized from hexane at 4 °C to produce yellow crystals. M.p. 136−137 °C. ^1H NMR (C_6D_6): δ = 1.36 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.40 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.43 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.45 (d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH_3), 3.73 (sept d, $^3J_{H,P}$ = 18.4, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH−N−P−C), 3.87 (sept d, $^3J_{H,P}$ = 19.0, $^3J_{H,H}$ = 6.8 Hz, 8 H, CH−N−P−N), 10.08 (ddd, $^2J_{H,P}$ = 67.0, $^3J_{H,P}$ = 44.6, $^5J_{H,P}$ = 2.1 Hz, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 22.8, 22.9, 23.9, 24.0 [s, $(CH_3)_2CH-N-P-N$], 24.7 [d, $^3J_{C,P}$ = 2.0 Hz, $(CH_3)_2CH-N-P-C$], 47.2 [d, $^2J_{C,P}$ = 5.0 Hz, $(CH_3)_2CH-N-P-C$], 47.3 [d, $^2J_{C,P}$ = 4.8 Hz, $(CH_3)_2CH-N-P-N$], 48.5 [d, $^2J_{C,P}$ = 3.8 Hz, $(CH_3)_2CH-N-P-C$], 176.5 (ddd, $^1J_{C,P}$ = 105.1, $^2J_{C,P}$ = 11.2, $^4J_{C,P}$ = 2.0 Hz, CH=N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 44.5 (t, $^3J_{PP}$ = 95.6 Hz, P−CH=N), 75.9 (d, $^3J_{PP}$ = 95.6 Hz, CH=N−P) ppm. MS (DCI/CH_4): *m*/*z* = 744 [M^+ +H], 772 [$M^+ + C_2H_5$]. $C_{32}H_{72}N_7P_3S_3$ (743.42): calcd. C 51.66, H 9.75, N 13.18; found C 51.73, H 9.91, N 13.31.

X-ray Analysis of 9, 10b, 12b and 32: For all compounds data collection was performed at low temperature on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), the final unit-cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. Numerical absorption corrections[13] were applied for each structure.The structures were solved by direct methods using SIR92,[14] and refined by least-squares procedures on F^2 with the aid of (SHELXL-97)[15] by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors, respectively. The atomic scattering factors were taken from International tables for X-ray crystallography.[16] All hydrogen atoms were located on difference Fourier maps and refined with a riding model, excepted H(31) of **9**, **10b** and **12b** and hydrogens atoms H(11) and H(21) of compound **32**, which were refined isotropically. All non-hydrogens atoms were refined anisotropically and a weighting scheme was applied in the last cycles of refinement; weights were calculated from the following formula: $w = 1/[\sigma^2(F_o^2)+(aP)^2+ bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Molecules were drawn with the program ZORTEP[17] with 50% probability displacement ellipsoids for non-hydrogen atoms.

CCDC-191017 (**9**), -191018 (**10b**), -191019 (**12b**) and -191020 (**32**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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