Intramolecular Cyclization of Dinitriles via Zirconocene(IV)−Phosphorus Exchange Reactions: Synthesis of σ^3,λ^3-1-Phospha- and σ^3,λ^3-1,4-Diphospha-2,6-diazines

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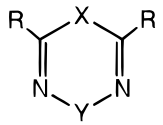
Dinitrile cyclization reactions leading to new six-membered heterocycles 1-σ^3,λ^3-phospha-2,6-diazines **3a**,**b** and 1,4-σ^3,λ^3-diphospha-2,6-diazines **6**, **7,** and **8** are presented. These syntheses involve dinitrile derivatives, Schwartz reagent $[Cp_2ZrHCl]_n$, and phosphorus compounds as promoted cyclization reagents. An X-ray crystal structure of the 1,4-σ^3,λ^3-diphospha-2,6-diazine **8** is reported.

Intramolecular cyclizations of olefins and acetylenes have been achieved by a variety of transition metal complexes in either a catalytic or a stoichiometric manner with respect to the metal.[1] In contrast there have been only a few reports on intramolecular cyclization reactions where a nitrile group participates as one of the coupling partners, and a single example of alkyne−nitrile coupling mediated by group 4 metallocene compounds has been described.[2] Furthermore to our knowledge transition metal-induced cyclization of *dinitrile* derivatives has not yet been described.[3] In our continued investigation in the studies of interactions between group 4 elements and main group elements,[4] we have developed a cyclization process promoted by zirconocene−phosphorus exchange reaction starting from dinitrile derivatives and leading to new types of mono- and disubstituted dihydrodiazine heterocycles. Despite the importance of diazines in the area of drug development and from the biochemical point of view,[5] the corresponding heterosubstituted diazines of type **I** are rare, and no general and convenient route to these derivatives from simple precursors is available.[6]



I

Results and Discussion

Dinitrile derivatives **1a**,**b** were treated with 2 equiv of the Schwartz reagent $[Cp_2ZrHCl]_n$ at 0 °C for 1 h in CH_2Cl_2 to form the corresponding bis(aldimido) complexes **2a**,**b**.[7] Addition of halogenated or pseudohalogenated phosphines $PhPX_2$ (X= Cl, Br, CN) to the reaction mixture gave via an unprecedented cyclization−exchange reaction[8] the new heterocycles σ^3,λ^3-1-phospha-2,6-diazines **3a**,**b** in 42−47% yield after workup (Scheme 1). The parent ions detected, $[M + 1]^+$, in mass spec-

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(8) Exchange reactions involving zirconocene complexes with Zr−C bonds and various main group elements are known; see for example ref 2, and: Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365, and references therein. However none of the reactions involve a transmetalation/cyclization from bis(aldimido) complexes incorporating two independent Zr−N bonds.

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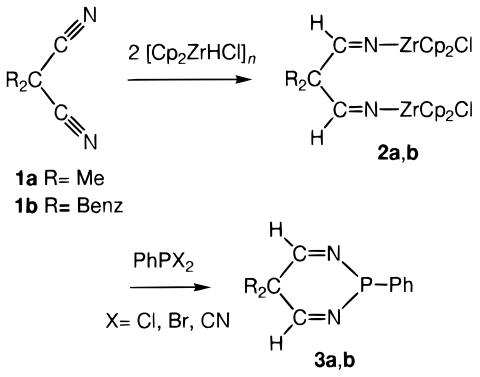
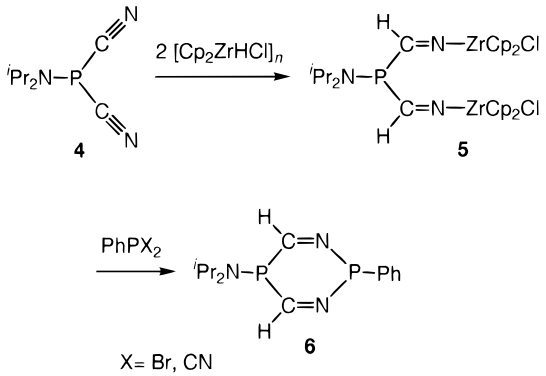
Scheme 1. Cyclization Reaction of Dinitrile Compounds 1a,b



Scheme 2. Cyclization Reaction of 4: Synthesis of 1,4-σ^3,λ^3-Diphospha-2,6-diazine 6



trometry were in agreement with the general formulas [$R_2C(HCN)_2P-Ph$] for **3**. Structures of the prepared compounds were unambiguously determined by ^1H and ^{13}C NMR. Along with the signals corresponding to the substituents on sp^3-carbon and phosphorus atoms of the heterocycles, each phospha-2,6-diazine **3a**,**b** exhibited for the two aldimido −CH═N− fragments a doublet in the 8.0−8.5 ($^3J_{HP}$ = 25 Hz) region in ^1H NMR and a signal at 167 ppm in the range expected for a cyclic imino function in ^{13}C NMR. IR data are also instructive, as one characteristic band appeared at 1580−1640 cm^{-1} which can be assigned to the C═N stretching mode of **3**.

The observation of this unusual transmetalation/cyclization reaction of dinitriles prompted us to carry out initial exploration on the generality of this reaction sequence. We found that the course of the reaction is dramatically dependent on the nature of the phosphorus-coupling reagent.

Thus the cyclization reaction was extended to the dicyanophosphine **4** using the same experimental conditions as for the preparation of diazines **3a**,**b**. Treatment of **4** (1 equiv) in CH_2Cl_2 with 2 equiv of Schwartz reagent $[Cp_2ZrHCl]_n$ at 0 °C for 1 h gave quantitatively the dizirconated compound **5** (Scheme 2). Surprisingly, exchange reactions on **5** with a number of dichlorophosphines $RPCl_2$ (R = Ph, Me, $^iPr_2N$) led to numerous unidentified products, and polymers were formed. In marked contrast the treatment of **5** with $PhPBr_2$ in CH_2Cl_2 at room temperature afforded the new σ^3,λ^3-1,4-diphospha-2,6-diazines **6** obtained after workup in 21% yield [δ ^{31}P 25.0 ($P-N^iPr_2$) and 70.7 (P−Ph) ppm]. Interestingly the use of the corresponding dicyanophosphine $PhP(CN)_2$ as promoted-cyclization reagent allowed us to obtain **6** in 52% isolated yield. This increase in isolated product **6** was probably due to the combination of two effects: (i) the ability for nitrile derivatives to act as η^1-coordinated ligands on zirconocene(IV) derivatives;[9] thus a possible precoordination of the nitrile fragments of the phosphorus reagent $PhP(CN)_2$ during the exchange reaction step which would give a higher yield of **6** may be envisaged; and (ii) a significative difference in solubility between **6** and the metal fragments, namely, $Cp_2Zr(CN)Cl$, compared to $Cp_2Zr(Br)Cl$, which allows separation by extraction in a more efficient way the product from the metal fragment in the reaction mixture. Mass spectroscopy analysis (parent ion at 294 $[M + 1]^+$) was in agreement with the general formulas [$^iPr_2N-P(HCN)_2P-Ph$] for **6**. The ^1H NMR spectrum exhibited besides the signals corresponding to the protons of the diisopropylamino and the phenyl groups a doublet of doublets at 8.78 ($^2J_{HP}$ = 38.2 Hz, $^3J_{HP}$ = 38.4 Hz) ppm, while the ^{13}C NMR spectrum displayed a doublet of doublets at 165.6 ($^1J_{CP}$ = 45.9 Hz, $^3J_{CP}$ = 9.1 Hz) ppm characteristic of the aldimido groups HC═N.[7]

Interestingly the cyclization reaction also occurred with low coordinated phosphorus coupling reagent. For example, successive additions of 2 equiv of $[Cp_2ZrHCl]_n$ followed by 2 equiv of the chlorophosphaimine Cl−P═N−Ar (Ar = 2,4,6-$^tBu_3C_6H_2$) to **1a** in CH_2Cl_2 led to the fully characterized diazine **7** (Scheme 3). Under the same experimental conditions, **4** gave the corresponding σ^3,λ^3-1,4-diphospha-2,6-diazine **8** in 91% isolated yield (Scheme 3). The structure of **8** was unambiguously determined by X-ray crystallography. The CAMERON drawing of **8** is depicted in Figure 1 together with significant bond lengths and angles. The heterocycle **8** adopts a boat conformation with phosphorus substituents in equatorial position. Synthesis of **8** may involve first a substitution reaction on one of the two N−Zr bonds with elimination of Cp_2ZrCl_2 and transient formation of **9**; then a [1,2] addition of the second equivalent of the chlorophosphaimine on the resulting P═N double bond[10] to give **10** occurred, followed by intramolecular cyclization with elimination of a second equivalent of Cp_2ZrCl_2.

In summary, we have developed a straightforward synthesis of unprecedented dihydrodiazine compounds, namely, 1-σ^3,λ^3-phospha- and 1,4-σ^3,λ^3-diphospha-2,6-diazines, from stepwise hydrozirconation and Zr/P exchange reactions. Extension of this cyclization process of dinitrile derivatives via a bis(aldimido) zirconocene to the synthesis of various diazines incorporating other main group elements as well as the study of the properties of the phosphadiazines already prepared is under way.

Experimental Section

General Procedure, Methods, and Materials. All manipulations were performed under an argon atmosphere, either

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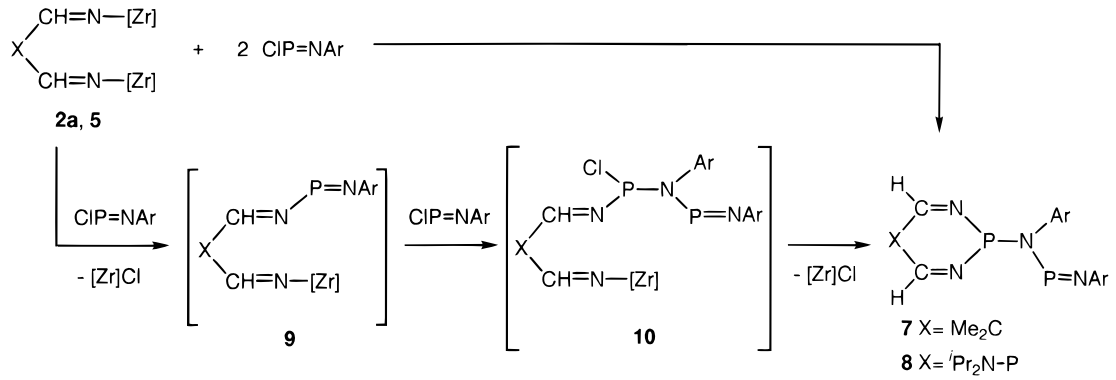
(10) A [1,2] addition of the chlorophosphaimine Cl−P═N−Ar (Ar = 2,4,6-$^tBu_3C_6H_2$) on an iminophosphine P═N double bond has already been reported: Larré, C.; Mahieu, A.; Igau, A.; Majoral, J.-P. *J. Organomet. Chem.* **1995**, *493*, 133.

Scheme 3. Synthesis of Phospha-2,6-diazines 7 and 8 (Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, [Zr] = ZrCp$_2$Cl)



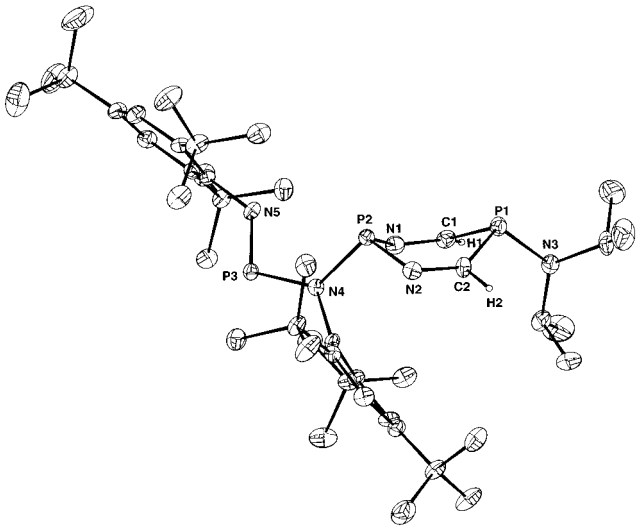


Figure 1. X-ray crystal structure of **8** (CAMERON drawing with thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.834 (4), P(1)−C(2) 1.844 (4), C(2)−N(2) 1.266 (4), C(1)−N(1) 1.269 (5), N(1)−P(2) 1.722 (3), N(2)−P(2) 1.720 (3), P(1)−C(1)−N(1) 127.8 (3), P(1)−C(2)−N(2) 126.1 (3), C(1)−P(1)−C(2) 94.0 (2), N(1)−P(2)−N(2) 102.6 (1), P(2)−N(2)−C(2) 121.7 (3), P(2)−N(1)−C(1) 120.1 (3).

on a high-vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from lithium aluminum hydride (pentane) or CaH_2 (CH_2Cl_2). Deuterated NMR solvents were treated with $LiAlH_4$ (C_6D_6) and CaH_2 (CD_2Cl_2, $CDCl_3$), distilled, and stored under argon. $[Cp_2ZrHCl]_n$[11] (Schwartz's reagent) and Cl−P=N−Ar[12] were prepared according to a literature procedure.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker MSL 400, WM-250, AC-200, and AC-80 Fourier transform spectrometers. The ^{13}C NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra. Positive chemical schifts are given downfield relative to Me_4Si (^{1}H, ^{13}C) or H_3PO_4 (^{31}P) references, respectively. IR spectra were recorded on an IBM IR/30S Fourier transform spectrometer. Mass spectra, obtained on a Nermag R10−10H, and elemental analysis were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS.

Experimental Procedure. Compound 3. In a typical experiment, a suspended solution of $[Cp_2ZrHCl]_n$ (0.563 g, 2.183 mmol) and **1** (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 **2** in nearly quantitatively yield, as assigned by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. **2a**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 8.49 (s, 2H, CH=N), 6.31 (s, 10H, Cp), 6.13 (s, 10H,Cp), 1.11 (s, 6H, CH_3); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 167.4 (s, CH=N), 115.8 (s, Cp), 112.8 (s, Cp), 43.8 (s, *C*CH_3), 22.9 (s, CH_3). **2b**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 8.70 (s, 2H, CH=N), 7.40−7.25 (m, 10H, Ph), 6.34 (s, 10H, Cp), 6.03 (s, 10H,Cp), 3.06 (s, 4H, CH_2); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 176.3 (s, CH=N), 139.8, 132.2, 131.7, 130.6, 130.0, 128.3 (Ph), 115.9 (s, Cp), 112.8 (s, Cp), 44.6 (s, *C*CH_2), 42.9 (s, C*C*H_2). **2** was used without further treatment. A solution of **2** (0.763 g, 1.092 mmol) in CH_2Cl_2 (8 mL) was added dropwise at 0 °C to a solution of $PhPX_2$ (X = Cl, Br, CN) (1.092 mmol) in CH_2Cl_2 (4 mL). After 1.5 h of stirring at room temperature, the volatiles were removed in vacuo and the product **3** was extracted with pentane (3 × 10 mL) and isolated as a yellow powder. **3a** was obtained in respectively 42% ($PhPCl_2$) and 47% ($PhPBr_2$, $PhPCN_2$) isolated yield. **3a**: IR (KBr) 1636 cm^{-1} ($\nu_{C=N}$); ^{31}P{^{1}H} NMR (82 MHz, $CDCl_3$) δ 51.8; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01 (d, 2H, $^3J_{HP}$ = 25.2 Hz, CH=N), 7.67−7.38 (m, 5H, Ph), 1.49 (s, 3H, CH_3), 1.07 (d, 3H, $^5J_{HP}$ = 2.2 Hz, CH_3); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2 (s, CH=N), 131.1 (d, $^2J_{CP}$ = 20.7 Hz, *o*-Ph), 129.7 (s, *p*-Ph), 128.4 (d, $^3J_{CP}$ = 7.3 Hz, *m*-Ph), 38.7 (d, $^3J_{CP}$ = 25.4 Hz, *C*CH_3), 23.7 (s, CH_3), 17.9 (d, $^4J_{CP}$ = 4.5 Hz, CH_3), *i*-Ph not observed; MS (DCI/NH_3) *m*/*z* 205 ([M + H]$^+$). Anal. Calcd for $C_{11}H_{15}N_2P$: C 64.69, H 6.42. Found: C 65.77, H 6.35.

The treatment for **3b** did not allow us to separate the final product from traces of metal fragment, which prevented us from giving precise isolated yields, which are however close to those obtained for **3a**. **3b**: IR (KBr) 1652 cm^{-1} ($\nu_{C=N}$); ^{31}P{^{1}H} NMR (82 MHz, $CDCl_3$) δ 48.5; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.23 (d, 2H, $^3J_{HP}$ = 24.0 Hz, CH=N), 7.40−7.09 (m, 15H, Ph), 3.18 (s, 2H, CH_2), 2.95 (d, 2H, $^5J_{HP}$ = 1.5 Hz, CH_2); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.7 (d, $^2J_{CP}$ = 2.2 Hz, CH=N), 136.4, 134.0, 133.8, 133.5, 133.3, 133.1, 131.8, 131.5, 131.3, 130.5, 130.4, 130.2, 129.9, 129.3, 128;8, 128.6, 128.4, 128.2, 128.0, 127.1, 127.0 (Ph), 46.5 (d, $^3J_{CP}$ = 26.4 Hz, *C*CH_2), 42.4 (s, CH_2), 40.6 (d, $^4J_{CP}$ = 8.3 Hz, CH_2); MS (DCI/CH_4) *m*/*z* 385 ([M + C_2H_5]$^+$), 357 ([M + H]$^+$).

6: A suspended solution of $[Cp_2ZrHCl]_n$ (0.563 g, 2.183 mmol) and **4** (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 **5** in nearly quantitatively yield as assigned by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy: ^{31}P{^{1}H} NMR (82 MHz, C_6D_6) δ 52.0; ^{1}H NMR (200 MHz, C_6D_6) δ 10.08 (d, 2H, $^2J_{HP}$ = 61.8 Hz, CH=N), 6.15, 6.10, 6.03, 5.96 (s, 5H, Cp), 3.42 (m, 2H, CHNP), 1.43 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CH_3); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 181.5 (d, $^1J_{CP}$ = 30.1 Hz, CH=N), 110.5 (s, Cp), 53.4 (s, CHNP), 24.0 (s, CH_3). **5** was used without further treatment and was added dropwise at 0 °C to a solution of $PhPX_2$ (X = Br, CN) (1.092 mmol) in CH_2Cl_2 (4 mL). After 1.5 h of stirring at room temperature,

(11) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
(12) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *12*, 1715.

the volatiles were removed in vacuo and the product **6** was extracted with pentane (3 × 10 mL) and isolated as a yellow powder in 21% ($PhPBr_2$) and 52% ($PhPCN_2$) isolated yield: IR (KBr) 1589 cm^{-1} ($\nu_{C=N}$); $^{31}P\{^1H\}$ NMR (82 MHz, C_6D_6) δ 70.7 (s, PPh), 25.0 (s, PN^iPr_2); ^1H NMR (200 MHz, C_6D_6) δ 8.78 (dd, 2H, $^2J_{HP} = {}^3J_{HP} = 38.4$ Hz, CH=N), 7.20 (m, 5H, Ph), 2.86 (sept d, 2H, $^3J_{HP} = 11.1$ Hz, $^3J_{HH} = 6.6$ Hz, $(CH_3)_2CHN$), 0.90 (d, 12H, $^3J_{HH} = 6.6$ Hz, $(CH_3)_2CHN$); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 165.6 (dd, $^1J_{CP} = 45.9$ Hz, $^2J_{CP} = 9.1$ Hz, CH=N), 133.9 (d, $^1J_{CP} = 23.3$ Hz, *i*-Ph), 132.2 (d, $^2J_{CP} = 18.9$ Hz, *o*-Ph), 130.0 (s, *p*-Ph), 129.0 (d, $^3J_{CP} = 5.9$ Hz, *m*-Ph), 52.4 (d, $^2J_{CP} = 18.3$ Hz, $(CH_3)_2CHN$), 25.1 (d, $^3J_{CP} = 5.6$ Hz, $(CH_3)_2CHN$); MS (DCI/CH_4) *m*/*z* 322 ($[M + C_2H_5]^+$), 294 ($[M + H]^+$). Anal. Calcd for $C_{14}H_{21}N_3P_2$: C 57.33, H 7.22. Found: C 57.07, H 7.34.

7: A suspended solution of $[Cp_2ZrHCl]_n$ (0.384 g, 1.487 mmol) and **1a** (0.070 g, 0.744 mmol) in CH_2Cl_2 (4 mL) was stirred for 1 h at 0 °C to give **2a**. Then the reaction mixture was cooled to −78 °C, and Cl−P=N−Ar (Ar = 2,4,6-$^tBu_3C_6H_2$) (0.712 g, 2.183 mmol) in CH_2Cl_2 (4 mL) was added dropwise to **2a**. The solution was stirred for an additional 1.5 h at room temperature. Then removal of the solvent in vacuo and extraction with pentane (2 × 10 mL) gave **7** (0.478, 0.706 mmol) as a red powder in 95% isolated yield: $^{31}P\{^1H\}$ NMR (82 MHz, $CDCl_3$) δ 296.5 (s, P=N), 130.0 (s, P−N); ^1H NMR (200 MHz, $CDCl_3$) δ 8.11 (d, 2H, $^3J_{HP} = 25.6$ Hz, CH=N); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 167.5 (d, $^2J_{CP} = 6.0$ Hz, CH=N), 23.3, 17.7 (s, $C(CH_3)_2$). Anal. Calcd for $C_{41}H_{66}N_4P_2$: C 72.74, H 9.83. Found: C 72.87, H 9.67.

8: A suspended solution of $[Cp_2ZrHCl]_n$ (0.854 g, 3.275 mmol) and **4** (0.300 g, 1.638 mmol) in CH_2Cl_2 (4 mL) was stirred for 1 h at 0 °C to give **5**. Then the reaction mixture was cooled to −78 °C, and Cl−P=N−Ar (Ar= 2,4,6-$^tBu_3C_6H_2$) (1.067 g, 3.275 mmol) in CH_2Cl_2 (4 mL) was added dropwise to **5**. The solution was stirred for 1 h at 0 °C and an additional 1.5 h at room temperature. Removal of the solvent in vacuo and extraction with pentane (2 × 10 mL) gave **8** (1.141 g, 1.490 mmol, 91%) as an orange powder: IR (KBr) 1599 cm^{-1} ($\nu_{C=N}$); $^{31}P\{^1H\}$ NMR (82 MHz, C_6D_6) δ 292.7 (s, P=N), 81.8 (d, $^3J_{PP} = 6.1$ Hz, P−N−Ar), 34.7 (d, $^3J_{PP} = 6.1$ Hz, PN^iPr_2); ^1H NMR (200 MHz, C_6D_6) δ 8.55 (dd, 2H, $^2J_{HP} = {}^3J_{HP} = 37.7$ Hz, CH=N); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 164.4 (dd, $^1J_{CP} = 45.4$ Hz, $^2J_{CP} = 24.9$ Hz, CH=N); MS (DCI/NH_3) *m*/*z* 766 ($[M + H]^+$). Anal. Calcd for $C_{44}H_{74}N_5P_3$: C 68.99, H 9.74. Found: C 68.73, H 9.55.

X-ray Analysis of 8. Yellow crystals suitable for X-ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of **8**. Crystal data for $C_{44}H_{74}N_5P_3$: $M_r = 762$, yellow block-shaped crystals (0.42 × 0.13 × 0.25), orthorhombic, space group $P2_12_12_1$, with $a = 10.260(1)$ Å, $b = 14.570(1)$ Å, $c = 31.122(2)$ Å, $V = 4652.4(2)$ Å^3, $Z = 4$, $\rho_c = 1.10$ g cm^{-3}, $F(000) = 1657$, μ(Mo Kα) = 1.56 cm^{-1}, 24360 measured reflections; a total of 7017 unique reflections have been measured with a R(average)= 0.044, $\theta_{max} = 24.2$. The data were collected at low temperature ($T = 160$ K) on a STOE imaging plate diffraction system (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with an Oxford Cryosystems cooler device; 200 exposures were obtained with $0° < \varphi < 200°$ with the crystal oscillated through 1.0° in φ. A crystal decay has been monitored by measuring 200 reflections per image, and the final unit cell parameters were obtained by the least-squares refinement of a set of 5000 reflections. Any fluctuations were observed for the intensity monitors over the course of the data collection. No absorption corrections were applied on the data. The structure was solved by using direct methods (SIR92)[13] and refined by least-squares procedures on F_o. All H atoms were located on difference Fourier maps, but they were introduced in the calculation as idealized positions ($d_{C-H} = 0.96$ Å). Their fractional atomic coordinates were recalculated after each cycle of refinement. Isotropic thermal parameters fixed at 20% higher than those of the carbon to which they are connected were assigned except aldimine H atoms labeled H(1) and H(2), which have been isotropically refined. The absolute configuration was assigned on the basis of the refinement of the Flack's enantiopole parameter, X[1,4] which shows the fractional contribution of $F_c(-h)$ in relation to $F_c(h)$ as depicted in the formula $F_c = [(1 - x)F(h)2 + xF(-h)2]$. This parameter is sensitive to the polarity of the structure and was found to be close to [$x = 0.01(9)$], which clearly indicated the correctness of the enantiomer choice. All non-hydrogens atom were anisotropically refined. Procedures of least-squares refinement were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are respectively the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles, where weights are calculated from the following expression: $w = [\text{weight}][1 - (\Delta(F)/6\sigma(F)]^2$.[15] The model reached convergence with the formulas $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. The final $R(R_w)$ values were 0.038(0.045) for 5379 observed reflections with the criterion [$I > 3\sigma(I)$] and 478 variables refined. Calculations were performed with CRYSTALS programs[16] running on a PC, and the drawing of the molecules with thermal ellipsoids at the 50% probability level was realized with the aid of CAMERON.[17] The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[18]

Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, U.K., on quoting the full journal citation.

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Supporting Information Available: Details of the X-ray structure determination, tables of positional parameters, and anisotropic thermal parameters for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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