Reductive Elimination of α-Phosphinozirconocene Iminoacyl Complexes: First Evidence of Neutral η^1-Imine Zirconocene. Synthesis of Bi- or Tricyclic β-Phosphino Imines

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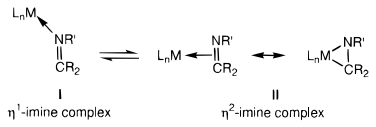
Received February 17, 1999

Abstract: Phosphinozirconocene complexes react with isocyanides to give unprecedented bi- or tricyclic β-phosphino imines through three successive and controlled steps. Spectroscopic and chemical evidence for the formation of the first neutral η^1-imine zirconocene complexes in the reductive elimination reaction sequence is presented.

Introduction

Reductive elimination reactions are among the most valuable processes to form carbon−carbon bonds in organic synthesis.[1] More specifically, the readily available metallacycles incorporating group 4 elements[2] would be useful tools for ring formation through a carbon−carbon coupling. However, intramolecular coupling reactions of group 4 iminoacyl complexes, yielding the corresponding free imines, are rather rare and mainly involve titanium complexes.[3,4] The mechanism of these reactions still remains unclear, although a concerted reductive elimination step that initially leads to an η^1-imine intermediate complex of the type **I** has already been postulated.[3a] However, none of the previous reports described isolation and characterization of η^1-imine zirconocene complexes. Addition of isocyanides on organozirconocenes is known to give the corresponding iminoacyl complexes after insertion into a zirconium−carbon bond.[5,6] These compounds have been conveniently converted, for example, to aldehydes[2a,5a] or nitriles.[7] We report herein a powerful one-pot synthesis of unprecedented bi- or tricyclic β-phosphino imines from α-phosphino cyclic organozirconocenes and isocyanides through a process involving three successive and controlled steps: a regioselective Zr−C isocyanide insertion reaction, followed by a carbon−carbon coupling reaction to form a neutral η^1-imine zirconocene complex,[8] and subsequent reductive elimination of zirconocene fragment "Cp_2Zr". The synthesis and X-ray analysis of the first β-amino indenophosphine are also described.



Results and Discussion

Treatment of a toluene solution of the α-phosphinozirconaindene **1**[9] with the isocyanide Me_3SiCH_2NC (**2a**) at room temperature for 15 min leads to the η^2-iminoacyl complex **3a** (Scheme 1), as clearly shown by ^{13}C NMR.[10] The signal at 200.7 ppm is typical for a Zr−C═N unit.[11] The disappearance of the characteristic deshielded chemical shift of the Zr−C(sp^2) aryl carbon of the indene moiety in **1** at 184.9 ppm to give a new signal resonance in **3a** at 121.5 ppm, classical for an aryl-C(sp^2) carbon atom, demonstrates the regioselective insertion of **2a** into the intracyclic Zr−C(sp^2) bond in **1** at the opposite side of the phosphino group. An X-ray crystallography study was

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(4) (a) Probert, G. D.; Whitby, R. J.; Coote, S. J. *Tetrahedron Lett.* **1995**, *36*, 4113. (b) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *Tetrahedron Lett.* **1994**, *35*, 1445. A formal reductive elimination/ring contraction reaction has been described from treatment of a 1-zircona-2-azacyclopentene with ^{t}BuNC and MeOH to form a C−N bond. Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1743.

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(7) Buchwald, S. L.; LaMaire, S. *Tetrahedron Lett.* **1987**, *28*, 295.

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(9) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P.; Dupuis, L.; Pirio, N.; Meunier, P. *Chem. Commun.* **1997**, 279.

(10) ^{13}C NMR assignments were deduced by inverse gradient δ $^1H-\delta$ ^{13}C {^{13}C,^{31}P} HMQC and $^{31}P-^1H$ INEPT NMR experiments.

(11) For characteristic signals of iminoacyl groups, see: Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583. Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. *Organometallics* **1987**, *6*, 2556. Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

10.1021/ja990502g CCC: $18.00 © 1999 American Chemical Society
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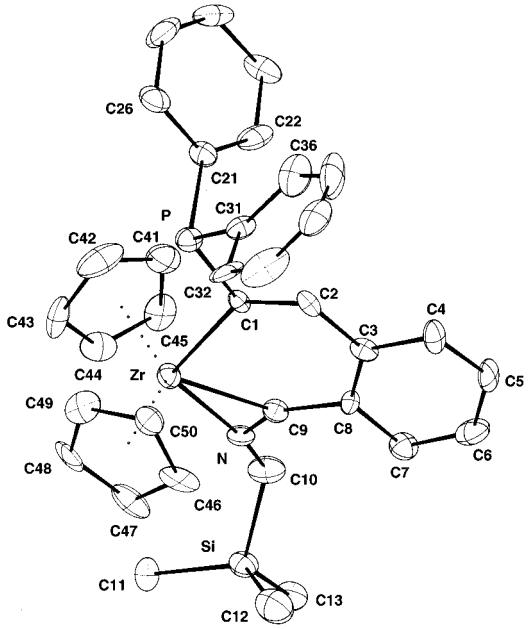
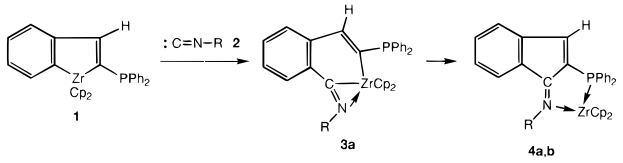
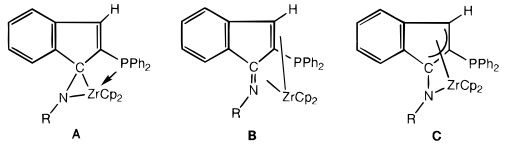


Figure 1. X-ray crystal structure of **3a** (CAMERON drawing with thermal ellipsoids at 50% probability; Cp groups were omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr−C(1) 2.368(8), Zr−C(9) 2.163(8), Zr−N 2.229(7), N−C(9) 1.278(11), P−C(1) 1.841(9), N−Zr−C(1) 107.5(3), N−Zr−C(9) 33.8(3), Zr−N−C(9) 70.3(5), Zr−C(9)−N 76.0(5).

Scheme 1. Synthesis of η^1-Imino Complexes **4a** and **4b** (**a**, R = CH_2SiMe_3; **b**, R = 2,6-$Me_2C_6H_3$)



undertaken to complete the characterization of **3a** (Figure 1, Table 1). The orange η^2-iminoacyl complex **3a** smoothly rearranges at room temperature after 7 days in benzene to give a stable green complex, **4a**, formed in quantitative yield, as monitored by ^{31}P NMR by the disappearance of the signal due to **3a** (δ = 2.0 ppm) on behalf of a new signal at 16.2 ppm (Scheme 1). Iminoacyl group 4 complexes are known to rearrange to form stable zirconocene η^2-imine complexes.[12] These derivatives, better described as metallaaziridines, undergo coupling reactions with unsaturated organic compounds to cleanly form metallacyclic compounds.[13] In marked contrast to the reactivity observed for metallaaziridine complexes, **4a** does not give any reaction with acetylenic systems or nitriles. Moreover, ^{13}C NMR experiments[10] showed the chemical shift corresponding to the carbon atom of the C−N skeleton at 118.9 (J_{CP} = 25.1 Hz) ppm, which is far deshielded compare to the signals observed for metallaaziridines in the range of 40−60 ppm (Table 2).[12,13] The carbon atom directly bonded to the phosphine moiety has shifted from 190.8 (J_{CP} = 95.5 Hz) ppm in **3a**, typical for a C(sp^2) in α position of a zirconocene fragment, to 110.4 (J_{CP} = 42.2 Hz) ppm in **4a**, in accord with a vinyl C(sp^2) in indene derivatives. Therefore, the NMR data and the chemical reactivity of **4a** are not consistent with η^2-imine zirconocene complex structure **II**. It is important to note that molecular modeling (MM2 parameters, CAChe system) shows the impossibility for compound **4a** to adopt the η^2-π-bonded-imine zirconocene structure **A**, with the phosphorus atom of the phosphino group coordinated on the metal fragment. On the basis of the chemistry described with zirconocene



complexes, two other structures may be envisaged for **4a**. The first one is the *s-trans* diene complex **B**, investigated by Erker et al.,[14] and the second one is the η^1-imine-η^3-allyl form **C**, which could be proposed by analogy with the postulated intermediate in carbonylation of zirconacyclopentenes.[15] In the view of the NMR data, contributions of these structures cannot be totally ruled out, even if it seems unreasonable to postulate form **B** in our case as a possible stable complex, as the isolated product **4a** possesses in its skeleton two efficient ligands, a phosphine and an imine, with good geometry for both to interact with the zirconocene metal fragment. Indeed, we tentatively propose for **4a** an η^1-imine zirconocene complex structure stabilized intramolecularly by the phosphino group linked to the indene moiety. This assumption came from the additional following points: (i) ^{13}C NMR data are more consistent with this latter structure. Indeed, the ^{13}C NMR chemical shift of the imino carbon atom in **4a** is between that of the C−N carbon atom signal in η^2-imine complex structure **II** and that of free imine compounds. (ii) Previous mechanistic studies[3a,13] have shown that the initial intermediate in the reductive elimination process yielding free imines is an η^1-imine complex. (iii) The green color observed appears to be characteristic for zirconocene species stabilized by two neutral two-electron-donating ligands.[16] (iv) Experiments have demonstrated that Cp_2Zr^{II} species formed in the reductive elimination of α-alkynyl-substituted zirconacyclopentenes were trapped as alkyne complexes stabilized by PMe_3.[17] Formation of **4a** may result from a carbon−carbon coupling reaction between the iminoacyl unit and the intracyclic vinyl group of the indene moiety; the η^2-imine zirconocene complex should not be ruled out, as it may be involved in the previous step of the formation of **4a,** but in the presence of the phosphine coordinating group the η^1-imine form is thermodynamically favored over the η^2-imino form. The same reaction performed with **1** and the isocyanide **2b** gave the green η^1-imine zirconocene complex **4b** (Scheme 1); transient formation of **3b** was not detected during the course of the reaction. The same NMR characteristic features described for **4a** were observed for **4b**. In marked contrast to **4a**, **4b** slowly rearranges to give the first β-phosphino indenoimine, **5b** (Scheme 2). This rearrangement can be monitored by ^{31}P NMR, which shows the disappearance of the signal due to **4b** (δ = 8.7 ppm) on behalf of a signal at −23.9 ppm, strongly indicative of the presence of a free phosphino group in **5b**. The ^{13}C NMR spectrum of **5b**

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Table 1. Crystal Data and Data Collection Parameters for Compounds **3a**, **6b**, and **8b**

	3a	**6b**	**8b**
asymmetric unit	$C_{35}H_{36}NPSiZr$	$C_{29}H_{24}NPS$	$C_{29}H_{26}NPS$
molecular weight	620.96	449.55	451.57
ρ_{calcd} (g cm^{-3})	1.36	1.28	1.30
μ (cm^{-1})	4.69	2.17	2.18
*F*000	638.41	944.93	476.46
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1$	$P2_1/n$	$P\bar{1}$
a (Å)	11.579(2)	9.162(2)	9.959(2)
b (Å)	26.073(4)	24.451(3)	10.942(2)
c (Å)	10.051(2)	11.237(2)	11.242(2)
β (deg)	89.943(2)	112.55(2)	102.16(2)
V (Å^3)	3029.9(3)	2324.9(3)	1156.2(3)
Z	4	4	2
crystal size	0.5 × 0.2 × 0.1	0.6 × 0.4 × 0.4	0.2 × 0.1 × 0.1
crystal shape	plate	parallelepiped	parallelepiped
crystal color	light orange	light red	orange yellow
no. of measured reflections	19 214	14 311	6809
no. of independent reflections	8918	3648	3484
merging *R* value	0.050	0.035	0.049
refinement on	F_{obs}	F_{obs}	F_{obs}
hydrogen atoms	calculated and not refined	calculated and not refined	calculated and not refined
R[a]	0.045	0.029	0.050
R_w[b]	0.051	0.029	0.056
Flack parameter[c]	0.015(5)	−	−
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^3)	2.90; −0.91	1.22; −0.86	0.41; −0.50
GOF (S)[d]	1.06	1.04	1.01
weighting scheme[e]	Chebyshev	Chebyshev	Chebyshev
parameters used	1.79, −0.234, 1.07	1.47, −1.58, 1.15, −0.664, 0.196	1.37, −1.26, 0.751, −0.562
absorbance correction	none	none	none
no. of reflections used [$I > 2\sigma(I)$]	8267	2999	2507
no. of parameters used	704	294	294

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. [c] Reference 25. [d] Goodness of fit = $[\sum(|F_o - F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$. [e] $W = [\text{weight}][1 - \Delta F/6\sigma F)^2]^2$ where weight is calculated from the following expression: weight = $1/\sum(r = 1, n)\text{ArTx}(X)$, where Ar are the coefficients for the Chebyshev polyniomal Tr(X) with $X = F_c/F_c(\text{max})$. See: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698−699.

exhibits a doublet at 168.7 (J_{CP} = 16.6 Hz) ppm, characteristic for the cyclic imino carbon,[10] whereas the chemical shift of the sp^2 carbon atom of the indene moiety directly bonded to the phosphino group shifted from 106.8 (J_{CP} = 37 Hz) to 144.1 (J_{CP} = 14.6 Hz) ppm. Therefore, a quite similar and significant deshielding effect is detected on both the imino carbon ($\Delta\delta$ = 32.5 ppm) and the C(sp^2) atom bonded to phosphorus ($\Delta\delta$ = 37.3 ppm) when moving from the proposed η^1-imino zirconocene complex **4b** to the free β-phosphino indenoimine **5b**. Mass spectrometry (DCI *m*/*z* 417 [M$^+$]) supports the removal of the metal fragment in **5b**. The structure of **5b** was fully corroborated by X-ray diffraction studies conducted on the corresponding sulfide compound **6b** (Figure 2, Table 1).

Interestingly, addition of HCl·OEt$_2$ (2 equiv) on a toluene solution of **4a** or **4b** gave the unexpected β-aminophosphine, **7a** or **7b**, respectively (Scheme 2). The structure of the sulfide adduct of **7b**, i.e., **8b**, was confirmed by X-ray analysis (Figure 3, Table 1). It has long been demonstrated in late-transition-metal chemistry that imine coordination-type complexes **I** and **II** may exist as an equilibrium.[18] In group 4 metallocene chemistry, the complexes of type **I** have never been isolated; they rearrange to the more stable σ-bonded η^2-imine zirconocene complexes **II**. Then, it is reasonnable to postulate that, in the presence of HCl, it is the metallaaziridine forms **9a**,**b** which react to give derivatives **10a**,**b**, which in turn rearrange to the final products **7a**,**b** (Scheme 2).[19,20]

To generalize the reductive elimination reaction process for the synthesis of new classes of P,N ligands, we have extended this sequence of reactions with isocyanides on another type of cyclic zirconaphosphine complex, i.e., the tricyclic system **11**.[21]

Insertion of isocyanide **2a** occurs chemoselectively on the Zr−C(sp^3) bond, leading to the stable iminoacyl complex **12a** (Scheme 3). ^{13}C NMR strongly supports the assigned structure; in particular, the signal of the quaternary aromatic carbon directly linked to zirconium is, as expected, deshielded at δ = 168.6 ppm, demonstrating that the insertion reaction of the isocyanide reagent occurs now at the same side of the phosphine moiety. Chemical evidence of the formation of **12a** can be found when it is reacted with HCl·OEt$_2$: the substituted phospholane **13a** (Scheme 3) arising from the selective cleavage of the Zr−C(sp^2) bond is quantitatively isolated and fully characterized.[22]

As in the case of the reaction of **1** with **2b**, **11** reacts with the isocyanide **2b** to give the stable tetracyclic zirconocene imine complex **14b**. Once again, the NMR data and the chemical reactivity (no reaction of **14b** with acetylenic compounds and nitriles) are not consistent with an η^2-imine zirconocene complex structure, **II**, for **14b** but are in agreement with an η^1-imine-type coordination, **I**. The complex **14b** slowly rearranges into the new tricyclic β-phosphino imine **15b** (Scheme 3) upon stirring at room temperature overnight. Compound **15b** presents characteristic NMR data for such a species. Mass spectrometry

(18) Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Chapters 20.1 and 21.2 and references therein.

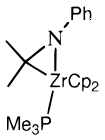
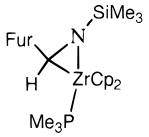
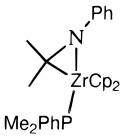
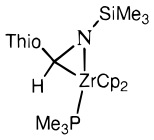
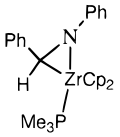
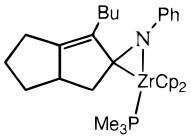
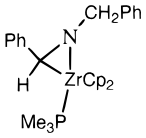
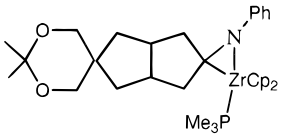
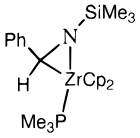
(19) If the participation of the η^2-imine zirconocene structure is reasonable to explain the synthesis of **7a**,**b**, the formation of this intermediate in the preparation of **5b** is more questionable, as it has been demonstrated that it is possible to displace a titanium metal center from its unreduced imine group by addition of external ligands, see ref 3c,d.

(20) It is of interest to note that addition of HCl on **5b** does not give **7b**.

(21) Zablocka, M.; Cénac, N.; Igau, A.; Donnadieu, B.; Majoral, J.-P.; Skowronska, A.; Meunier, P. *Organometallics* **1996**, *15*, 5436.

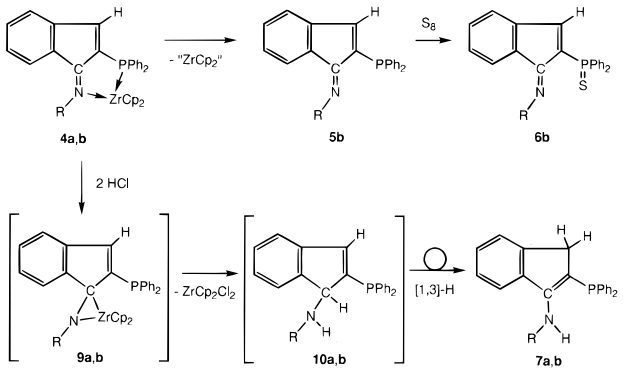
(22) NMR data of **13a** are in full agreement with those of similar compounds, see: Zablocka, M.; Igau, A.; Cenac, N.; Donnadieu, B.; Dahan, F.; Majoral, J.-P.; Pietrusiewicz, M. K. *J. Am. Chem. Soc.* **1995**, *117*, 8083.

Table 2. δ ^{13}C (ZrCN)[a] Spectroscopic Data of η^2-Imine Zirconocene Complexes $Cp_2Zr(\eta^2\text{-}CRR'{=}NR'')$(phosphine)

Product	δ ^{13}C (ZrCN) (J_{CP})	Ref	Product	δ ^{13}C (ZrCN) (J_{CP})	Ref
	41.4 (18.6)	13a		46.4 (16.4)	13d
	42.2 (18.0)	13c		52.6 (12.7)	13d
	46.8 (14.6)	13d		67.5 (15.4)	13e
	57.3 (13.6)	13d		54.3 (18.6)	12
	56.1 (12.8)	13d			

[a] NMR spectra taken in benzene-d_6. Chemical shifts in ppm, coupling constants (between parentheses) in Hz. Fur = furyl, Thio = thiophene.

Scheme 2. Reactivity of η^1-Imino Complexes **4a** and **4b** (**a**, R = CH_2SiMe_3; **b**, R = 2,6-$Me_2C_6H_3$)



(DCI, *m*/*z* 370 [$M^+ + 1$]) is in agreeement with the proposed structure. An analogous reaction performed with **11** and the isocyanide **2c** affords the tricyclic phosphinoimine **15c**. In this case, the formation of the η^1-imine derivative **14c** was detected only by ^{31}P NMR (**14c**, δ = 1.8; **15c**, δ = 12.6 ppm).

Structures of types **B** and **C** can be rejected for compounds **14b**,**c** (no carbon−carbon double bond acting as ligand), which are formed through the same type of mechanism involved for the preparation of **4a**,**b** *and* which present NMR data similar to those detected for **4a**,**b**. Moreover, a careful examination of the ^{13}C NMR data for the imino group >C=N− for compounds **4b** and **5b** on one hand and **14b** and **15b** on the other hand shows the same variation of chemical shifts when moving from **4b** to **5b** and from **14b** to **15b**, and close chemical shifts were observed for **4b** and **14b** on one hand and **5b** and **15b** on the other hand (**4b**, δ C=N 136.2 (J_{CP} = 27.5 Hz); **5b**, δ C=N 168.7 (J_{CP} = 16.6 Hz); **14b**, δ C=N 125.0 (J_{CP} = 17.0 Hz); **15b**, δ C=N 175.0 (J_{CP} = 14.4 Hz)).

All these observations are in agreement with our proposal to reject also structures **B** and **C** for compounds **4a**,**b** and to suggest an η^1-imine zirconocene complex structure for **4a**,**b** and **14b**,**c**.

In conclusion, we presented a number of arguments allowing us to propose that the mechanism of the reductive elimination reaction involving phosphorus−zirconium heterocyclic reagents and isocyanides and leading to new elaborated P,N ligands follows three steps: (i) insertion reaction of the isocyanide reagent to give the corresponding iminoacyl complex, (ii) carbon−carbon coupling reaction to form an η^1-imine zirconocene complex intramolecularly stabilized by a phosphino group, and (iii) elimination of the metal fragment "Cp_2Zr" to give the corresponding β-phosphino imine derivative. Ligand-induced reductive elimination in titanium chemistry has been demonstrated;[3c,d] thus, it is reasonable to postulate here the key role played by the phosphino group located in the close environment of the metal in the course of the metal center displacement step (iii). Each intermediate involved in the reaction sequence has been fully characterized by X-ray analysis and/or NMR spectroscopy analysis. This reductive elimination process extends the scope of the zirconocene-induced coupling reactions, allowing us to synthesize a variety of new bicyclic or tricyclic phosphorus−nitrogen-containing ligands, and opens new strategies for the preparation of chiral ligands and catalysts for a large number of reactions.[23]

Experimental Section

General Procedure, Methods, and Materials. All manipulations were performed under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox.

(23) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2108. Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Krüger, C.; Pfaltz, A. *Chem. Eur. J.* **1997**, *3*, 887. Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2897.

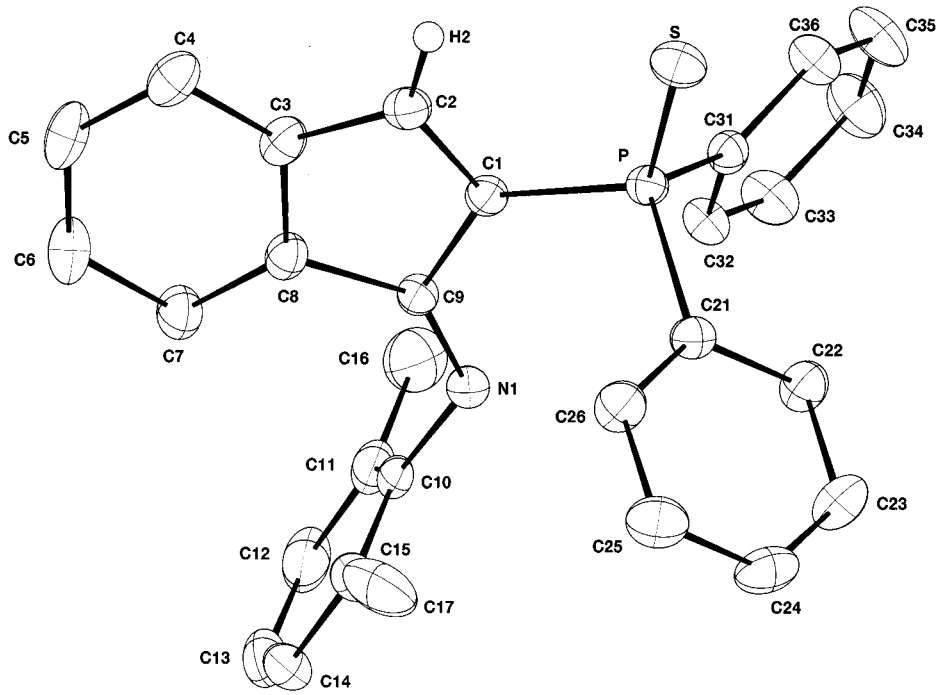


Figure 2. X-ray crystal structure of **6b** (CAMERON drawing with thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): N−C(9) 1.274(2), P−C(1) 1.8109(16), C(1)−C(9) 1.500(2), C(1)−C(2) 1.342(2), C(9)−N-C(10) 120.24(13), N−C(9)−C(1) 124.08(14), C(1)−C(9)−C(8) 105.04(13).

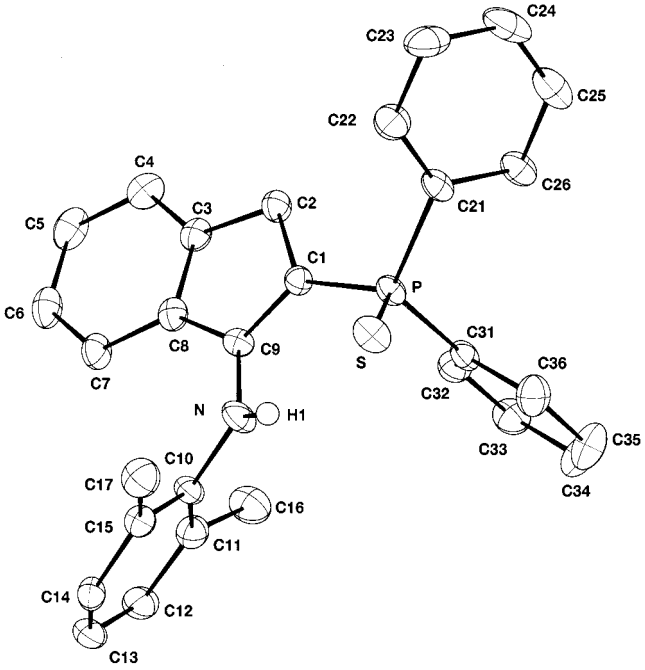


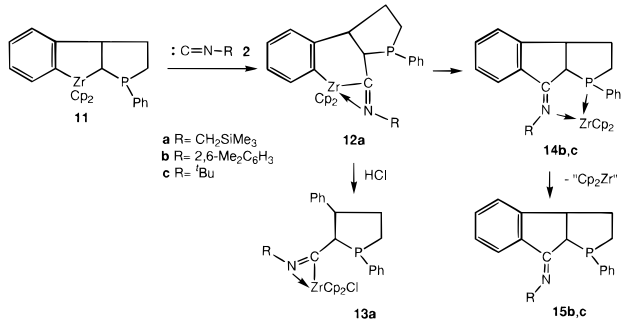
Figure 3. X-ray crystal structure of **8b** (CAMERON drawing with thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): N−C(9) 1.358(4), P−C(1) 1.764(3), C(1)−C(9) 1.374-(4), C(1)−C(2) 1.505(4), C(9)−N-C(10) 128.5(3), N−C(9)−C(1) 125.1(3), C(1)−C(9)−C(8) 108.7(3).

Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, diethyl ether), lithium aluminum hydride (pentane), sodium (toluene), or CaH_2 (CH_2Cl_2). Deuterated NMR solvents were treated with $LiAlH_4$ (C_6D_6) and CaH_2 ($CDCl_3$), distilled, and stored under argon. Complexes **1**[9] and **11**[21] were prepared according to literature procedure.

Trimethylsilylmethyl isocyanide, 2,6-dimethylphenyl isocyanide, and *tert*-butyl isocyanide were used as received from Aldrich Chemical Co.

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 (^1H, ^{13}C) or H_3PO_4 (^{31}P) references, respectively. Mass spectra were obtained on a Nermag R10-10H and performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS.

Scheme 3. Synthesis of β-Phosphino Imines **15b** and **15c**



Experimental Procedure. 3a. To a solution of **1** (0.189 g, 0.372 mmol) in toluene (5 mL) was added trimethylsilylmethyl isocyanide (**2a**) (0.052 mL, 0.372 mmol) at room temperature. The mixture was stirred for 15 min and then evaporated to dryness. The solid residue was extracted with a mixture of 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 **3a** as a yellow solid in 76% yield (0.176 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.0 (s) ppm. ^1H NMR (C_6D_6): δ −0.01 (s, 9H, $SiMe_3$), 3.52 (s, 2H, CH_2), 5.68 (s, 10H, Cp), 6.98−7.37 (m, 11H, CH_{arom}), 7.79−7.86 (m, 3H, CH_{arom}), 8.09 (d, 1H, J_{HP} = 22.5 Hz, PCCH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −1.2 (s, $SiMe_3$), 49.4 (s, CH_2), 108.1 (d, J_{CP} = 2.4 Hz, Cp), 121.5 (s, ZrC*C*), 123.9, 126.4 and 128.4 (s, CH_{arom}), 129.0 (d, J_{CP} = 6.2 Hz, *o*-PPh_2 or *m*-PPh_2), 132.9 and 134.9 (s, CH_{arom} and *p*-PPh_2), 135.1 (d, J_{CP} = 18.5 Hz, *o*-PPh_2 or *m*-PPh_2), 142.4 (d, $^1J_{CP}$ = 27.2 Hz, *i*-PPh_2), 149.6 (d, $^3J_{CP}$ = 9.6 Hz, ZrCC*C*), 151.5 (d, $^2J_{CP}$ = 8.7 Hz, ZrC*C*H), 190.8 (d, $^1J_{CP}$ = 95.5 Hz, ZrCP), 200.7 (d, $^3J_{CP}$ = 5.7 Hz, ZrCN) ppm. MS (FAB): *m*/*z* 619 [M^+]. Anal. Calcd for $C_{35}H_{36}PNSiZr$: C, 67.69; H, 5.84; N, 2.25. Found: C, 67.51; H, 5.77; N, 2.27.

4a. In an NMR tube, complex **3a** (0.050 g, 0.080 mmol) was dissolved in C_6D_6 (1 mL). After 7 days at room temperature, complex

4a was formed in almost quantitative yield, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.2 (s) ppm. ^1H NMR (C_6D_6): δ −0.15 (s, 9H, $SiMe_3$), 3.91 (d, 1H, J_{HH} = 14.7 Hz, C*H*H), 4.93 (d, 1H, J_{HH} = 14.7 Hz, C*H*H), 5.16 (s broad, 5H, Cp), 5.83 (s broad, 5H, Cp), 6.18 (d, 1H, $^3J_{HP}$ = 4.4 Hz, =CH), 7.21−8.26 (m, 14H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −0.8 (s, $SiMe_3$), 55.9 (s, CH_2), 99.6 (s, =CH), 107.4 (s, Cp), 108.0 (s, Cp), 110.4 (d, J_{CP} = 42.2 Hz, HC=*C*P), 118.3, 119.2, 122.2 and 123.1 (s, CH_{arom}), 118.9 (d, J_{CP} = 25.1 Hz, C=N), 124.8 (d, J_{CP} = 11.6 Hz, *C*CN), 129.0−130.5 (m, *o*-PPh_2 and *m*-PPh_2), 133.2 (s broad, *p*-PPh_2), 144.3 (d, $^3J_{CP}$ = 11.4 Hz, *C*CC=N) ppm. *i*-PPh_2 not observed.

4b. To a solution of **1** (0.194 g, 0.383 mmol) in C_6D_6 (5 mL) was added 2,6-dimethylphenyl isocyanide (**2b**) (0.050 g, 0.383 mmol) at room temperature. The resulting green solution was stirred at room temperature for 15 min, leading to the formation of complex **4b** in almost quantitative yield, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 8.7 (s) ppm. ^1H NMR (C_6D_6): δ 1.95 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 5.19 (d, 5H, J_{HP} = 1.2 Hz, Cp), 5.65 (d, 5H, J_{HP} = 1.1 Hz, Cp), 6.43 (d, 1H, J_{HP} = 4.5 Hz, =CH), 6.57−8.08 (m, 17H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.1 (s, CH_3), 23.2 (s, CH_3), 99.0 (s, =CH), 106.8 (d, J_{CP} = 37 Hz, HC=*C*P), 108.3 (s, Cp), 110.0 (s, Cp), 118.4, 119.9, 121.0, 122.5 and 124.7 (s, CH_{arom}), 128.8−134.6 (m, CH_{arom}, *o*-PPh_2, *m*-PPh_2, and *p*-PPh_2), 132.2 and 133.7 (s, *C*CH_3), 136.2 (d, J_{CP} = 27.5 Hz, C=N), 142.9 (d, J_{CP} = 11.1 Hz, *C*CN), 155.5 (s, *C*CC=N) ppm. *i*-PPh_2 and *C*CCH_3 not observed.

5b. To a solution of **1** (0.599 g, 1.18 mmol) in toluene (10 mL) was added 2,6-dimethylphenyl isocyanide (**2b**) (0.155 g, 1.18 mmol) at room temperature. A change of color from brown to green was observed. The mixture was stirred for 15 min and then evaporated to dryness. The orange solid residue was extracted with pentane (25 mL) and filtered. Compound **5b** was obtained as an orange solid in 67% yield (0.330 g) after solvent removal. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −23.9 (s) ppm. ^1H NMR (C_6D_6): δ 1.87 (s, 6H, CH_3), 6.42−7.66 (m, 18H, CH_{arom} and =CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.6 (s, CH_3), 121.9, 124.2, 125.0, 128.3, 128.8 and 129.1 (s, CH_{arom}), 125.1 (s, *C*CH_3), 129.3 (d, J_{CP} = 11.1 Hz, *o*-PPh_2 or *m*-PPh_2), 132.0 (s, *p*-PPh_2), 135.0 (d, J_{CP} = 20.2 Hz, *o*-PPh_2 or *m*-PPh_2), 137.5 (d, $^1J_{CP}$ = 9.6 Hz, *i*-PPh_2), 144.1 (d, J_{CP} = 14.6 Hz, HC=*C*P), 145.5 (s, *C*CC=N), 146.4 (s, H*C*=CP), 150.1 (s, *C*C=N), 168.7 (d, J_{CP} = 16.6 Hz, C=N) ppm. *C*CCH_3 not observed. MS (DCI): *m*/*z* 417 [M^+]. Anal. Calcd for $C_{29}H_{24}PN$: C, 83.42; H, 5.79; N, 3.35. Found: C, 83.27; H, 5.70; N, 3.48.

6b. To a solution of **5b** (0.200 g, 0.479 mmol) in THF (10 mL) was added an excess of sulfur (0.614 g, 2.395 mmol) at room temperature. The mixture was stirred for 1 h and then evaporated to dryness. The solid residue was extracted with pentane (50 mL) and filtered. The volatiles were removed, and the resulting solid residue was transferred to a SiO_2 chromatography column. Elution with a mixture dichloromethane/pentane (1/4) gave a red band, from which compound **6b** was isolated in 82% yield (0.176 g) after solvent removal. Mp: 160−161 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 32.6 (s) ppm. ^1H NMR (C_6D_6): δ 1.66 (s, 6H, CH_3), 6.38−7.16 (m, 13H, CH_{arom}), 8.12−8.24 (m, 4H, CH_{arom}), 8.41 (d, 1H, J_{HP} = 11.5 Hz, =CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.6 (s, CH_3), 124.0, 124.6, 125.4 and 128.6 (s, CH_{arom}), 124.8 (s, *C*CH_3), 128.9 (d, J_{CP} = 11.4 Hz, *o*-PPh_2 or *m*-PPh_2), 130.4, 131.6 and 132.2 (s, CH_{arom} and *p*-PPh_2), 133.5 (d, J_{CP} = 11.6 Hz, *o*-PPh_2 or *m*-PPh_2), 135.6 (d, J_{CP} = 89.3 Hz, HC=*C*P or *i*-PPh_2), 136.6 (d, J_{CP} = 85.6 Hz, HC=*C*P or *i*-PPh_2), 142.6 (d, J_{CP} = 16.2 Hz, *C*CC=N), 149.8 (s, *C*C=N), 157.6 (d, J_{CP} = 10.7 Hz, H*C*=CP), 166.0 (d, J_{CP} = 7.1 Hz, C=N) ppm. *C*CCH_3 not observed. MS (DCI): *m*/*z* 450 [M^+ + 1]. Anal. Calcd for $C_{29}H_{24}PNS$: C, 77.47; H, 5.38; N, 3.11. Found: C, 77.52; H, 5.17; N, 3.20.

7a. A solution of complex **3a** (0.250 g, 0.402 mmol) in toluene (10 mL) was stirred at room temperature for 7 days. A color change from yellow to green was observed. HCl (1 M in Et_2O) (0.804 mL, 0.804 mmol) was then added at −78 °C. Immediately, the color of the solution changed from green to orange. The reaction mixture was then evaporated to dryness, and the resulting solid residue was extracted with pentane (25 mL) and filtered. Compound **7a** was obtained as a yellow solid in 60% yield (0.097 g) after solvent removal. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −26.7 (s) ppm. ^1H NMR (C_6D_6): δ −0.01 (s, 9H, $SiMe_3$), 3.29 (s, 2H, CH_2), 3.33 (s, 2H, CH_2), 6.22 (s, 1H, NH), 7.03−7.58 (m, 14H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −2.4 (s, $SiMe_3$), 37.8 (d, J_{CP} = 12.0 Hz, *C*H_2CP), 39.3 (d, J_{CP} = 3.8 Hz, *C*H_2SiMe_3), 102.2 (d, J_{CP} = 8.2 Hz, C=CP), 119.2, 124.8, 126.6 and 126.7 (s, CH_{arom}), 128.5 (s, *p*-PPh_2), 129.0 (d, J_{CP} = 6.0 Hz, *o*-PPh_2 or *m*-PPh_2), 133.7 (d, J_{CP} = 18.4 Hz, *o*-PPh_2 or *m*-PPh_2), 140.2 (d, J_{CP} = 8.7 Hz, *C*=CP), 146.8 (s, *C*CH_2), 158.2 (d, J_{CP} = 25.6 Hz, *C*C=CP) ppm. *i*-PPh_2 not observed. MS (DCI): *m*/*z* 402 [M^+ + 1]. Anal. Calcd for $C_{25}H_{28}PNSiP$: C, 74.77; H, 7.02; N, 3.48. Found: C, 74.68; H, 6.91; N, 3.52.

7b. To a solution of **1** (0.162 g, 0.319 mmol) in toluene (5 mL) was added 2,6-dimethylphenyl isocyanide (**2b**) (0.042 g, 0.319 mmol) at room temperature. The mixture was stirred for 15 min at room temperature. HCl (1 M in Et_2O) (0.640 mL, 0.640 mmol) was then added to the resulting green solution at −78 °C. Immediately, the color of the solution changed from green to orange. The reaction mixture was then evaporated to dryness, and the solid residue was extracted with pentane (25 mL) and filtered. Compound **7b** was obtained as a yellow solid in 73% yield (0.098 g) after solvent removal. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.2 (s) ppm. ^1H NMR (C_6D_6): δ 2.14 (s, 6H, CH_3), 3.31 (s, 2H, CH_2), 6.08 (d, 1H, J_{HP} = 4.7 Hz, NH), 6.57−7.91 (m, 17H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.3 (s, CH_3), 38.6 (s, CH_2), 103.0 (d, J_{CP} = 7.0 Hz, C=CP), 124.7, 126.7, 126.8 and 127.2 (s, CH_{arom}), 128.8 (d, J_{CP} = 10.4 Hz, *o*-PPh_2 or *m*-PPh_2), 129.1, 129.2 and 129.7 (s, *p*-PPh_2 and CH_{arom}), 134.0 (d, J_{CP} = 18.7 Hz, *o*-PPh_2 or *m*-PPh_2), 137.8 (s, *C*CH_3), 139.4 (d, $^1J_{CP}$ = 7.3 Hz, *i*-PPh_2), 139.7 (s, *C*CCH_3), 141.3 (d, J_{CP} = 6.1 Hz, *C*=CP), 147.1 (s, *C*CH_2), 155.1 (d, J_{CP} = 18.7 Hz, *C*C=CP) ppm. MS (DCI): *m*/*z* 420 [M^+ + 1]. Anal. Calcd for $C_{29}H_{26}PN$: C, 83.03; H, 6.24; N, 3.33. Found: C, 82.93; H, 6.17; N, 3.40.

8b. To a solution of **7b** (0.150 g, 0.357 mmol) in THF (10 mL) was added an excess of sulfur (0.457 g, 1.785 mmol) at room temperature. The mixture was stirred for 1 h and then evaporated to dryness. The solid residue was extracted with diethyl ether (50 mL) and filtered. The volatiles were removed from the solution, and the resulting solid residue was transferred to a SiO_2 chromatography column. Elution with dichloromethane gave a red band, from which compound **8b** was isolated in 65% yield (0.104 g) after solvent removal. Mp: 158−159 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 31.9 (s) ppm. ^1H NMR (C_6D_6): δ 2.34 (s, 6H, CH_3), 3.28 (d, 2H, J_{HP} = 2.6 Hz, CH_2), 6.73−7.27 (m, 13H, CH_{arom}), 8.02−8.07 (m, 4H, CH_{arom}), 9.54 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.4 (s, CH_3), 40.6 (d, J_{CP} = 10.5 Hz, CH_2), 90.0 (d, J_{CP} = 101.4 Hz, C=CP), 122.3, 124.7, 127.3 and 128.0 (s, CH_{arom}), 128.9 (d, J_{CP} = 5.2 Hz, *o*-PPh_2 or *m*-PPh_2), 129.1 and 131.5 (s, *p*-PPh_2 and CH_{arom}), 132.6 (d, J_{CP} = 11.0 Hz, *o*-PPh_2 or *m*-PPh_2), 136.2 (d, $^1J_{CP}$ = 86.7 Hz, *i*-PPh_2), 137.6 (s, *C*CH_3), 139.3 (s, *C*CCH_3), 140.9 (d, J_{CP} = 12.9 Hz, *C*=CP), 146.0 (d, J_{CP} = 11.8 Hz, *C*CH_2), 159.1 (d, J_{CP} = 9.5 Hz, *C*C=CP) ppm. MS (DCI): *m*/*z* 452 [M^+ + 1]. Anal. Calcd for $C_{29}H_{26}PNS$: C, 77.07; H, 5.79; N, 3.09. Found: C, 77.14; H, 5.67; N, 3.12.

12a. To a solution of **11** (0.211 g, 0.460 mmol) in toluene (5 mL) was added trimethylsilylmethyl isocyanide (**2a**) (0.064 mL, 0.460 mmol) at −20 °C. The mixture was allowed to reach room temperature and stirred for an additional 2 h, leading to an orange solution. The solution was then evaporated to dryness, and the resulting solid residue was extracted with a mixture of 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 **12a** as a yellow solid in 82% yield (0.216 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.3 (s) ppm. ^1H NMR (C_6D_6): δ 0.11 (s, 9H, $SiMe_3$), 1.50−2.40 (m, 4H, CH_2), 2.91 (d, 1H, J_{HP} = 7.1 Hz, CHP), 3.16 (dt, 1H, J_{HP} = 10.5 Hz, J_{HH} = $J_{HH'}$ = 2.3 Hz, CH), 3.80 (broad, 2H, CH_2Si), 5.52 (s, 5H, Cp), 5.67 (s, 5H, Cp), 7.05−7.55 (m, 9H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.1 (s, $SiMe_3$), 24.8 (d, J_{CP} = 13.8 Hz, CH_2P), 46.0 (d, J_{CP} = 22.9 Hz, CHP), 47.2 (d, J_{CP} = 7.4 Hz, CH_2), 58.0 (d, J_{CP} = 2.7 Hz, CH), 40.2 (s, CH_2Si), 107.2 (s, Cp), 107.6 (s, Cp), 122.9, 124.1 and 128.7 (s, CH_{arom}), 129.24 (broad, *o*-PPh and *p*-PPh), 131.8 (d, $^3J_{CP}$ = 17.3 Hz, *m*-PPh), 139.0 (d, $^1J_{CP}$ = 29.0 Hz, *i*-PPh), 144.3 (s, CH_{arom}), 150.7 (s, C_{arom}), 168.6 (s, Zr−C_{arom}), 227.9 (s, C=N) ppm. Anal. Calcd for $C_{31}H_{36}PNSiZr$: C, 64.99; H, 6.33; N, 2.44. Found: C, 64.85; H, 6.28; N, 2.50.

13a. To a solution of **12a** (0.286 g, 0.500 mmol) in toluene (5 mL) was added 1 equiv of HCl (1 M in Et_2O, 0.5 mL, 0.500 mmol) at −78

°C. The solution was then warmed to room temperature and stirred for an additional 1 h. The resulting solution was evaporated to dryness to give **13a** as a yellow solid in 91% yield (0.276 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.4 (s) ppm. ^1H NMR (C_6D_6): δ 0.03 (s, 9H, $SiMe_3$), 2.22−2.63 (m, 5H, $2CH_2$ and CH), 3.43 (dd, 1H, J_{HH} = 2.9 Hz, J_{HP} = 12.5 Hz, PCH), 3.80 (broad, 1H, CH_2Si), 4.07 (broad, 1H, CH_2Si), 6.29 (s, 5H, Cp), 6.31 (s, 5H, Cp), 7.17−7.70 (m, 10H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.0 (s, $SiMe_3$), 24.3 (d, J_{CP} = 24.9 Hz, CH_2P), 34.7 (s, CH_2Si), 41.8 (s, CH_2), 50.4 (s, CH), 56.5 (d, J_{CP} = 21.1 Hz, CHP), 109.5 (s, Cp), 109.6 (s, Cp), 126.8, 128.5, and 128.7 (s, CH_{arom}), 129.1 (d, $^2J_{CP}$ = 6.1 Hz, *o*-PPh), 129.4 (s, *p*-PPh), 131.7 (d, $^3J_{CP}$ = 19.3 Hz, *m*-PPh), 140.5 (d, $^1J_{CP}$ = 27.4 Hz, *i*-PPh_2), 142.3 (s, *C*CH), 229.7 (d, J_{CP} = 15.1 Hz, C═N). Anal. Calcd for $C_{31}H_{37}PNSiClZr$: C, 61.10; H, 6.11; N, 2.29. Found: C, 61.12; H, 5.92; N, 2.31.

14b. To a solution of **11** (0.184 g, 0.400 mmol) in toluene (5 mL) was added 2,6-dimethylphenyl isocyanide (**2b**) (0.052 g, 0.400 mmol) at −20 °C. The mixture was allowed to reach room temperature and stirred for an additional 90 min, leading to a red solution. The solution was then evaporated to dryness to give **14b** as a red solid in 92% yield (0.200 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.1 (s) ppm. ^1H NMR (C_6D_6): δ 1.73−2.39 (m, 4H, CH_2), 1.83 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 3.17 (d, 1H, J_{HH} = 6.1 Hz, CH), 3.68 (m, 1H, CHP), 5.12 (s, 5H, Cp), 5.62 (s, 5H, Cp), 6.90−7.56 (m, 12H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.0 (s, CH_3), 19.3 (s, CH_3), 25.4 (d, J_{CP} = 16.0 Hz, CH_2P), 34.2 (s, CH_2), 50.6 (s, CH), 56.5 (d, J_{CP} = 20.6 Hz, CHP), 106.1 (s, Cp), 107.4 (s, Cp), 117.4 (d, J_{CP} = 3.5 Hz, *C*CN), 125.0 (d, J_{CP} = 17.0 Hz, CN), 125.2, 126.1, 127.7 and 128.7 (s, CH_{arom}), 128.9 (broad, *o*-PPh and *p*-PPh), 129.4 and 129.7 (s, CH_{arom}), 130.7 (d, $^3J_{CP}$ = 15.2 Hz, *m*-PPh), 132.2 (s, *C*CH_3), 134.7 (d, J_{CP} = 2.0 Hz, *C*CH_3), 136.3 (s, CH_{arom}), 141.3 (d, $^1J_{CP}$ = 29.5 Hz, *i*-PPh), 147.6 (d, J_{CP} = 2.2 Hz, *C*CH), 149.3 (s, *C*CCH_3) ppm. Anal. Calcd for $C_{35}H_{34}PNZr$: C, 71.14; H, 5.79; N, 2.37. Found: C, 71.08; H, 5.82; N, 2.40.

15b. To a solution of **11** (0.239 g, 0.520 mmol) in toluene (5 mL) was added 2,6-dimethylphenyl isocyanide (**2b**) (0.068 g, 0.520 mmol) at −20 °C. The reaction mixture was stirred overnight at room temperature to give a red solution. Solvents were evaporated to dryness, and the solid residue was extracted with pentane (30 mL) and filtered. Compound **15b** was obtained as an orange solid in 72% yield (0.138 g) after solvent removal. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.1 (s) ppm. ^1H NMR (C_6D_6): δ 1.18−2.31 (m, 4H, CH_2), 2.17 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 3.46 (dd, 1H, J_{HH} = 3.4 Hz, J_{HP} = 6.8 Hz, PCH), 3.63 (m, 1H, CH), 6.39−7.30 (m, 11H, CH_{arom}), 8.36 (d, 1H, J_{HH} = 7.5 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.0 (s, CH_3), 20.2 (s, CH_2), 23.1 (d, J_{CP} = 17.1 Hz, CH_2P), 33.4 (d, J_{CP} = 4.4 Hz, CH_2), 49.6 (s, CH), 55.1 (d, J_{CP} = 26.8 Hz, CHP), 123.5, 123.8, 124.0, 127.7, 128.5, 129.1 and 133.0 (s, CH_{arom}), 129.2 (d, $^2J_{CP}$ = 3.5 Hz, *o*-PPh), 129.8 (s, *p*-PPh), 130.2 (d, $^3J_{CP}$ = 12.8 Hz, *m*-PPh), 139.2 (d, $^3J_{CP}$ = 28.2 Hz, *i*-PPh_2), 140.4 (s, *C*C═N), 151.8 (d, J_{CP} = 1.6 Hz, *C*CC═N), 152.0 (s, *C*Me), 175.0 (d, J_{CP} = 14.4 Hz, C═N) ppm. MS (DCI/NH_3): *m*/*z* 370 [M^+ + 1]. Anal. Calcd for $C_{25}H_{24}PN$: C, 81.27; H, 6.54; N, 3.79. Found: C, 81.19; H, 6.50; N, 3.82.

15c. To a solution of **11** (0.202 g, 0.440 mmol) in toluene (5 mL) was added *tert*-butyl isocyanide (**2c**) (0.370 g, 0.440 mmol) at −20 °C. The reaction mixture was stirred at room temperature for 5 h to give a yellow solution. Solvents were evaporated to dryness, and the solid residue was extracted with diethyl ether (20 mL) and filtered. Compound **15c** was obtained as a yellow powder in 62% yield (0.088 g) after solvent removal. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.5 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.43 (s, 9H, CH_3), 1.21−2.12 (m, 4H, CH_2), 2.51 (m, 1H, PCH), 4.13 (m, 1H, CH), 7.22−7.58 (m, 8H, CH_{arom}), 7.79 (d, 1H, J_{HH} = 7.6 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.1 (d, J_{CP} = 15.6 Hz, CH_2P), 31.3 (d, J_{CP} = 5.5 Hz, CH_3), 32.4 (d, J_{CP} = 4.7 Hz, CH_2), 48.1 (d, J_{CP} = 23.1 Hz, CHP), 49.4 (s, CH), 56.3 (d, J_{CP} = 1.8 Hz, *C*CH_3), 122.6, 123.4, 127.5 and 128.2 (s, CH_{arom}), 128.3 (d, $^2J_{CP}$ = 3.6 Hz, *o*-PPh), 130.8 (s, *p*-PPh), 131.5 (d, $^3J_{CP}$ = 17.6 Hz, *m*-PPh), 138.9 (d, J_{CP} = 28.7 Hz, *i*-PPh), 142.8 (s, *C*C═N), 148.0 (s, *C*CC═N), 167.0 (d, J_{CP} = 16.4 Hz, C═N) ppm. MS (DCI/NH_3): *m*/*z* 322 [M^+ + 1]. Anal. Calcd for $C_{21}H_{24}PN$: C, 78.47; H, 7.52; N, 4.35. Found: C, 78.37; H, 7.60; N, 4.37.

X-ray Analysis of 3a, 6b, and 8b. For whole compounds, the X-ray diffraction analyses were carried out at low temperature (T = 160 K) on a STOE IPDS equipped with an Oxford Cryosystems cooler device and using Mo Kα radiation (λ = 0.710 73 Å). Crystal decay was monitored by measuring 200 reflections by image, and the final unit cell was obtained by the least-squares refinement of a setting of 5000 reflections.

Only statistical fluctuations were observed in the intensity monitors over the course of the data collection; no absorption corrections were applied on the data.

The three structures were solved by using direct methods (SIR92)[24] and refined by least-squares procedures on F_{obs}; H atoms were located on difference Fourier maps, but they were introduced in calculation in idealized positions (d_{C-H} = 0.96 Å) with isotropic thermal parameters fixed at 20% higher than those of the carbon to which they were connected, and their atomic coordinates were recalculated after each cycle of refinement. Exceptions to this were some specific H atoms, H(2) for **6b** and the hydrogen of the amine function of **8b**, which have been isotropically refined.

Concerning the structure **3a**, the crystal forms twin motifs in the wrong orthorhombic system of space group $P2_12_12_1$; the data have been indexed and resolved in monoclinic system $P2_1$, and the refinement was performed by using a specific twin operator. The absolute configuration of **3a** was assigned on the basis of refinement of Flack's parameter, x,[25] which is the fractional contribution of $F(-h)$ to the calculated structure, to the amplitude, as given in the following formula:

$$F_c^2 = (1 - x)F(h)^2 + xF(-h)^2$$

This parameter is sensitive to the polarity of the structure and was found to be close to 0, which clearly indicated the good choice of the enantiomer refined.

For whole models, refinements 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 structures factors. In the last cycles of refinement, a scheme of ponderation was used,[26] and the models reached convergence with the following formula:

$$R = \sum(||F_o| - |F_c||)/\sum|F_o|$$

$$R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$$

The calculation were performed with the aid of the CRYSTALS programs[27] running on a PC, and the molecules were drawn with CAMERON,[28] with thermal ellipsoids fixed at the 50% probability level. The atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[29]

Acknowledgment. Financial support of this work by the CNRS (France) and KBN (Poland) is gratefully acknowledged. V.C. thanks the Spanish Ministerio de Educacion y Cultura for a postdoctoral fellowship.

Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA990502G

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