Dynamic Behavior of an *N*-Metalated β-Enaminoimine Complex − Preparation of *N*-Phosphanylenamine and β-Enaminoimine Derivatives

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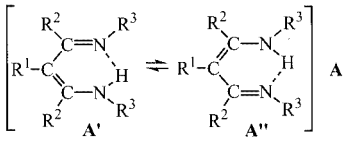
Variable-temperature NMR spectroscopy of the β-enaminoimine complex **2** showed a dynamic process which was attributed to an internal fluxional aldimido *N*-zirconated π-linear/σ-bent structure. Such an internal rearrangement has been previously proposed to occur in these systems but never observed. We have prepared a variety of (*N*-phosphanyl-β-enamino)imine ligands using the hydrozirconation/transmetalation reaction of malonodinitrile compounds $RCH(CN)_2$ (R = H, PPh_2). In addition to their potential uses in coordination chemistry, these systems are good tools for the study of intramolecular hydrogen bonding. The X-ray crystal structure of **14** at 180 K shows an unsymmetrical system with the N(H) proton localized on one of the two chelating nitrogen atoms, consistent with the existence in solution of a low barrier proton transfer process with a double-well potential.

Introduction

β-Enaminoimine derivatives have been intensively studied as members of the family of polymethine merocyanines, a fundamental group of organic dyes with a wide variety of uses. [1] Related compounds of the type **A**, also called β-diimine systems, described as "formal" six-membered rings with a chelating μ^2-H proton bridged to the nitrogen atoms, have been successfully used as ligands in coordination chemistry.[2]



Recently, we described the synthesis of the β-enaminoimine compound **2**, with a transition metal fragment bonded to the nitrogen atoms (**A**: $R^1 = R^2 = H$, $R^3 = ZrCp_2Cl$).[3] In addition to the dynamic NMR behaviour of the *N*-zirconated β-enaminoimine **2**, we present herein the preparation of *N*-phosphanylenamine derivatives and describe the formation of unsymmetrical (*N*-phosphanyl-β-enamino)imine compounds according to a hydrozirconation/transmetalation reaction sequence. We also report an X-ray crystal structure of a β-enaminoimine compound containing an unsymmetrical intramolecular hydrogen bond.

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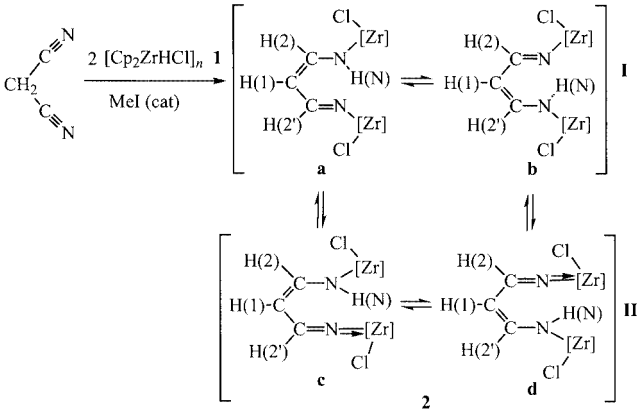
Dynamic Behavior of the *N*-Zirconated β-Enaminoimine Complex 2

Results

The *N*-metalated β-enaminoimine compound **2** was prepared by the addition of 2 equiv. of **1** to malonodinitrile in the presence of a catalytic amount of MeI (Scheme 1).[3]



Scheme 1. Description of the different conformers of the (*N*-zircona-β-enamino)imine derivative **2** at 193 K; [Zr] = $ZrCp_2$

At 293 K, 1D ^{1}H and ^{13}C NMR spectra show only one set of signals for the two CH(2/2′)−N aldimine groups, indicative of a process that rapidly interconverts the hydrogen atoms H(2) and H(2′) on the NMR time scale. An excitation-sculpted singly selective 1D TOCSY (Figure 1)[4] allows the assignment of the signal of the H(N) proton bridged by the two nitrogen atoms of the β-enaminoimine skeleton at δ = 7.10 ppm.[5]. It was clear from this experiment that the H(N) proton was involved in an exchange having a rate in the intermediate range on the NMR time scale. The NMR spectra exhibit two singlets for the Cp groups at δ = 6.35 and 6.53 ppm (^{1}H NMR, 10 H each) and δ = 116.6 and 114.5 ppm (^{13}C NMR). Lowering of the temperature from 293 to 193 K leads to a splitting of the H(N) and H(2/2′) protons, suggesting the presence of at least two conformers (Figure 1).

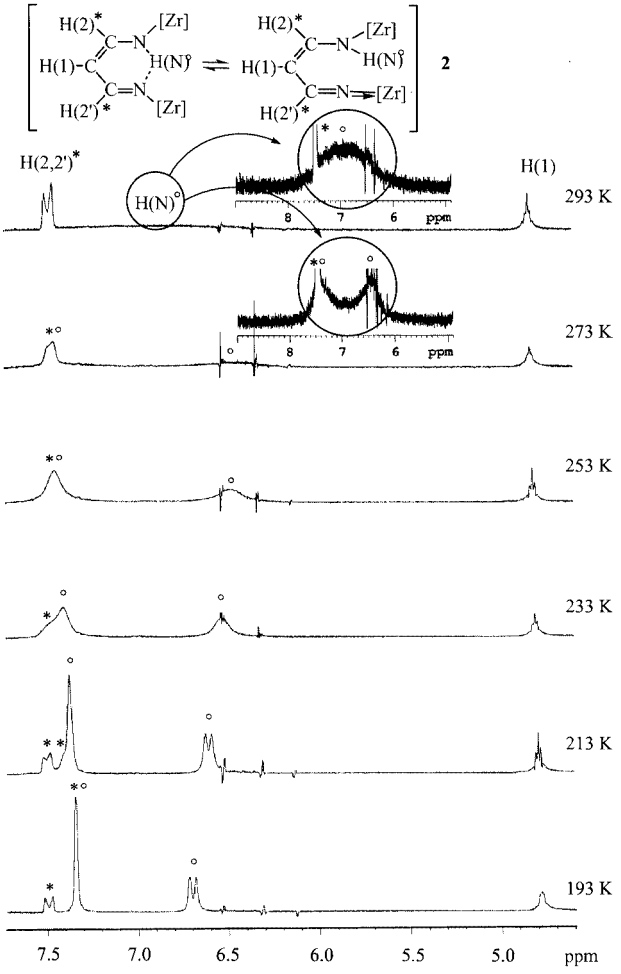


Figure 1. 1D selective TOCSY of **2** at variable temperature with excitation of H(1) (the corresponding symmetric Lewis structures are omitted for clarity); mixing time = 60 ms; [Zr] = $ZrCp_2Cl$

At 193 K the ^{1}H NMR spectrum of the CH(2/2′)−N−H(N) moiety of one of the two conformers shows a doublet of doublets at δ = 7.49 ppm [H(2/2′)] and a doublet at δ = 6.70 ppm [H(N)], with coupling constants of $^3J_{H(2/2')\text{-}H(1)}$ = 5.5 Hz and $^3J_{H(2/2')\text{-}H(N)}$ = 13.0 Hz. The ^{13}C NMR spectrum displays a peak at δ = 157.6 ppm, assigned to the aldimine carbon atom CH(2/2′). Signals due to the H(2/2′) and H(N) protons of the other conformer accidentally overlap (^{1}H at 193 K: δ = 7.34 ppm), and the outer lines of the doublets are thus no longer visible. Consequently, it was not possible to determine the different coupling constants. The ^{13}C NMR spectrum exhibits a peak at δ = 158.4 ppm [CH(2/2′)−N group]. Note that the methine CH(1) group resonances [δ = 4.78 ppm − broad peak (^{1}H); δ = 93.7 ppm (^{13}C)] and the Cp signals of **I** and **II** cannot be differentiated. The NMR spectroscopic assignments have been unambiguously confirmed by 2D NMR experiments at 193 K (gs-DQFCOSY, gs-HMQC). Note that line broadening was observed for the Cp groups, but no splitting of the signals was detected on decreasing the temperature. Exchange between the two conformers **I** and **II** was definitively established by 1D GROESY experiments (Scheme 1, Figure 2).[8]

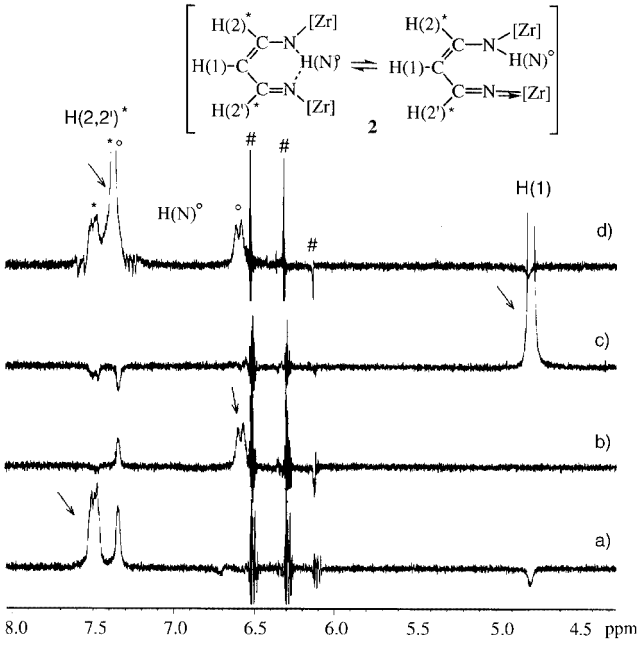


Figure 2. 1D GROESY of **2** at 193 K (the corresponding symmetric Lewis structures are omitted for clarity) with selective excitation of the site indicated by the arrow →; mixing time = 200 ms; lines denoted by # are residual signals of the Cp protons; [Zr] = $ZrCp_2Cl$

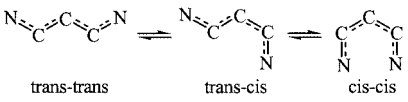
The 1D GROESY spectrum obtained on irradiation of the H(2/2′) protons of the conformer with δ = 7.49 ppm displays an exchange peak with the H(2/2′) protons of the other conformer (δ = 7.34 ppm) and an ROE enhancement (spatial proximity) with H(1) (Figure 2, a). Irradiation of the H(N) proton of the conformer with δ = 6.70 ppm gives only a positive exchange peak with the H(N) protons of the other conformer (δ = 7.34 ppm) (Figure 2, b). Finally, irradiation of the H(1) protons only gives rise to ROE enhancements with the H(2/2′) protons of conformers **I** and **II** (Figure 2, c). The GROESY spectrum obtained on irradiation of the signal at δ = 7.34 ppm follows from the experiments a), b), and c) in Figure 2 and definitively demonstrated the overlapping H(2/2′) and N(H) protons for one

conformer: in addition to an ROE enhancement with H(1), an exchange peak with the H(2/2′) protons (δ = 7.49 ppm) and with the N(H) proton (δ = 6.70 ppm) of the other conformer is also observed. The chemical shift equivalence of the H(2) and H(2′) protons in **I** and **II** is accommodated by a rapid tautomeric conversion of **a** and **b** for **I** and **c** and **d** for **II**. From the results of the dynamic NMR spectra, **2** appears to behave as a rather unconventional β-enaminoimine system. At low temperature, it is likely that we have been able to "freeze out" a dynamic process involving a fluxional structure from which each form identified is in a fast tautomeric equilibrium, namely **a** and **b** for **I** and **c** and **d** for **II**.

Discussion

The bis(*N*-zirconated) β-enaminoimine complex **2** contains the vinamidine moiety N−C−C−C−N and an *N*-metalated alkylideneamido arrangement, two types of substructures which may undergo fluxional processes.

It has been reported that β-enaminoimine derivatives with N−C−C−C−N core atoms may exist in three different configurations: "*trans-trans*", "*trans-cis*", and "*cis-cis*" [Equation (1)]. The tautomeric and conformational equilibria of these products have been found to be substituent-, solvent-, and temperature-dependent.[9]



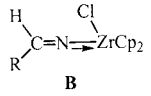
(1)

In CD_2Cl_2 at 193 K, the coupling constant of $^3J_{H(2/2')\text{-}H(1)}$ = 5.5 Hz observed for one of the conformers indicates the presence of the *cis-cis* form.[10] At 293 K the time-averaged $^3J_{H(2/2')\text{-}H(1)}$ coupling constant of 5.7 Hz implies that the second conformer exhibits the same *cis-cis* configuration for the vinamidine moiety. Moreover, the same ^{13}C NMR chemical shift observed for the CH(1) methine group indicates that the geometry around this carbon atom is retained in **I** and **II**.[11] Finally, the ROE enhancement observed for the H(1) and H(2/2′) protons of one of the conformers confirms the proximity of these protons. These NMR spectroscopic data establish conformers **I** and **II** as having a *cis-cis* configuration. Therefore, the dynamic NMR behavior observed for the *N*-zirconated β-enaminoimine complex **2** does not involve the core atoms of the β-enaminoimine system; the *cis-cis* rigidity about the N−C−C−C−N skeleton is maintained throughout the observed fluxional process.

Starting from the Lewis structure **I** for **2** (Scheme 1), two intramolecular dynamic processes may be proposed to rationalize the results of the low-temperature NMR spectra : i) rotation of the $ZrCp_2Cl$ fragments about the Zr−N bond and/or ii) a fluxional π-linear/σ-bent process involving the *N*-metalated alkylideneamido moieties in the plane containing the β-enaminoimine system −N(H)−$(CH)_2$−CH=N−.

Simple close-contact calculations carried out on complex **2**[12] revealed severe intramolecular nonbonded contacts between the Cp ring hydrogen atoms of the two metal fragments and between the Cp ring hydrogen atoms and the hydrogen atom of the H−C−N moiety of the β-iminoenamine skeleton. Because of these steric constraints, the magnitude of the rotation of the $ZrCp_2Cl$ fragments about the Zr−N bonds is limited, and therefore only a restricted rotation is observed for **2**. In metallocene complexes, restricted rotation about the bond between a metal ion and a planar amido/ketimide nitrogen atom is assumed to have a very low activation barrier; to the best of our knowledge no restricted rotation processes in such complexes has been "frozen out" by variable-temperature NMR experiments.[13,14c]

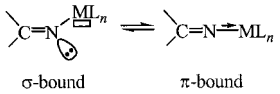
16-Electron d^0 group-4 metallocene complexes of the type Cp_2MRR' (M = Ti, Zr, Hf) have one vacant orbital available for conjugative interaction with lone pairs or π-systems at adjacent σ-bonded ligands R, R′.[15] Even though Cp_2M-N π-interactions are not maximized in group-4 amido[13] and ketimide[14] metallocene complexes, π-overlap between the LUMO of the metal fragment and the nitrogen lone pair has been commonly observed. Erker and co-workers have reported that aldimido [RCH=N−$ZrCp_2Cl$] complexes have a substantial Zr−N π-character. This was unambiguously demonstrated by an X-ray structure analysis of **B** (R = Ph), which showed a nearly linear Zr−N=CHPh unit (Zr−N−C 170.5(5)°].[15a,15b] In solution, the linear heteroallene-type structural unit in **B** (R = Ph) is of high stereochemical persistence and rigidity, and the geometric isomerization (*E*)/(*Z*) could be effected neither thermally nor photochemically. Moreover, the hydrozirconation of nitriles using the Schwartz reagent $[Cp_2ZrHCl]_n$ led to the corresponding zirconocene ketimide complexes with a *syn* stereochemistry; the metal-bound chlorine atom and the hydrogen atom of the aldimine function are positioned *syn* to the linear Zr−N−C moiety.



B

It is likely that, at room temperature, we are observing the results of the two rapid dynamic processes which involve: i) restricted rotation about the Zr−N bonds and ii) the σ-bound (**I**) and π-bound-like (**II**) *N*-zirconated conformers of the β-enaminoimine compound **2** (Scheme 1). Consistent with the studies reported in the literature, the two sets of Cp resonances observed for **2** at room temperature may be the result of restricted rotation about the Zr−N bonds, with a molecular geometry which places the chlorine atoms of the zirconocene fragments Cp_2ZrCl *syn* to the hydrogen atom of the HCN subunits. It is reasonable to propose that lowering of the temperature has the effect of "freezing out" the *N*-σ-bent-zirconated β-enaminoimine form **I** and linearising the Zr−N=C units to form the heteroallene system **II** (Scheme 1).[16] This internal fluxional *N*-zirconated π-linear/σ-bent structure [Equation (2)] was previously proposed to occur in these systems but until now

it has not been observed in coordinatively unsaturated *N*-metalated alkylideneamido complexes.

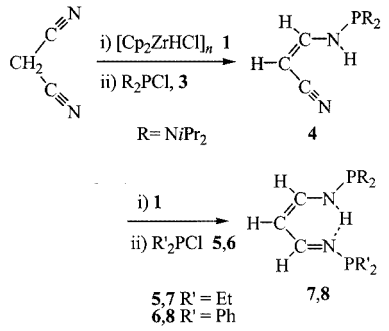


(2)

On the basis of variable-temperature ^{1}H NMR experiments, the activation barrier of the observed dynamic process attributed to the transition between bent (**I**) and linear (**II**) conformers in **2** has been calculated as $\Delta G^{\ddagger} = 13$ kcal/mol.[17]

Preparation of *N*-Phosphanylenamine and (*N*-Phosphanyl-β-enamino)imine Ligands

The next step in the preparation of β-enaminoimine ligands starting from malonodinitrile was to probe the monohydrozirconation/transmetalation reaction process. Treatment of $CH_2(CN)_2$ with 1 equiv. of the Schwartz reagent $[Cp_2Zr(H)Cl]_n$ (**1**), followed by addition of $(i\mathrm{Pr}_2N)_2PCl$ (**3**) led to the formation of the *N*-phosphanylenamine compound **4** in 66% isolated yield (Scheme 2).

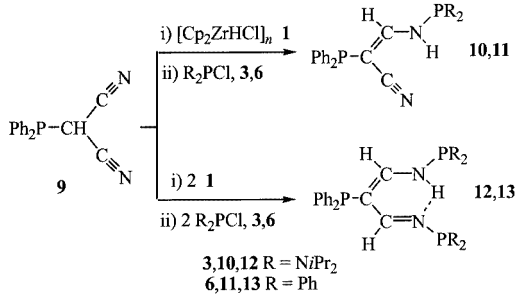


Scheme 2. Selective monohydrozirconation/transmetalation reactions of malonodinitrile and the β-nitriloeneamine compound **4**

This compound was identified by its spectroscopic properties which included strong absorptions in the IR spectrum at 1600 and 2194 cm^{-1} assigned to the C=N and C≡N stretches, respectively. The ^{31}P NMR spectrum of **4** displays a singlet at δ = 87.1 ppm. In addition to signals due to the isopropyl group, ^{1}H and ^{13}C NMR spectra display signals in the region expected for a CH= vinylic group geminal to an electron-withdrawing group [δ = 3.74 (^{1}H) and 66.1 (^{13}C) ppm] and a CH−N< enamine fragment [δ = 6.53 (^{1}H) and 150.8 (^{13}C) ppm]. The broad signal at δ = 5.30 ppm in the ^{1}H NMR is typical of an NH secondary amine. The NMR spectroscopic data establish **4** as an (*N*-phosphanyl-β-enamino)nitrile. Another hydrozirconation/transmetalation reaction on the enamine compound **4** using **1** and R′$_2$PCl [R′ = Et (**5**), Ph (**6**)] gave the expected unsymmetrical (*N*-phosphanyl-β-enamino)imine derivatives **7** and **8**, respectively (Scheme 2). IR spectra indicate the disappearance of the ν(C≡N) band in **4** and the appearance of an absorption in the region expected for the C=N functionality in β-enaminoimine systems [ν(C≡N): 1625 cm^{-1} (**7**), 1621 cm^{-1} (**8**)]. The ^{31}P NMR spectra of **7** and **8** display two singlets at δ = 53.3, 87.1 (**7**) ppm and 64.8, 89.3 (**8**) ppm. Signals in both ^{1}H and ^{13}C NMR spectra are consistent with CH=N aldimine groups [**7**: δ = 7.62 (^{1}H, overlapped) ppm, δ = 156.1, 159.8 (^{13}C) ppm; **8**: δ = 7.39, 7.91 (^{1}H) ppm, δ = 150.5, 164.5 (^{13}C) ppm] and the central methine CH fragments [**7**: δ = 4.87 (^{1}H) and δ = 97.6 (^{13}C) ppm; **8**: δ = 4.89 (^{1}H) and δ = 97.8 (^{13}C) ppm] in the β-diimine derivatives **7** and **8**. The ^{13}C NMR chemical shifts of the central methine CH fragments and the upfield shift of the broad NH signal [δ = 5.30 (**4**), 10.54 (**7**), 10.84 (**8**) ppm] in the ^{1}H NMR spectra establish **7** and **8** as having a *cis-cis* configuration, with a hydrogen-bonded chelate form in a β-diimine compound.

It is noteworthy that hydrozirconation of succinonitrile and glutaronitrile using **1** (1 and 2 equiv.) followed by an exchange reaction with Ph_2PX (X = Cl, Br, CN) led to the formation of insoluble polymeric products.

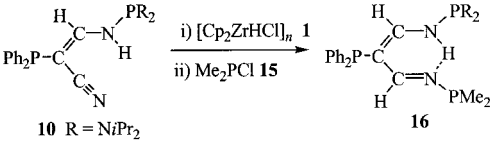
Under the same experimental conditions as those used for $CH_2(CN)_2$, the phosphanylmalononitrile **9** undergoes the same "one pot" mono- and dihydrozirconation/transmetalation reaction sequence(Scheme 3). Addition of 1 equiv. of **1** to **9** followed by addition of a stoichiometric amount of R_2PCl (**3**, **6**) to the resulting mixture affords the corresponding *N*-phosphanylenamine compounds **10** and **11**, respectively (Scheme 3).



Scheme 3. Mono-and dihydrozirconation/transmetalation reactions of the phosphanylmalonodinitrile compound **9**

The IR spectra of **10** and **11** display both C=N and C≡N stretches. The parent ion peak $[M + 1]^+$ detected in the mass spectrum of **11** is in agreement with the general formula $[C_3H_2N_2(PPh_2)_2]$. The ^{31}P NMR spectra of **10** and **11** display two singlets at δ = 8.0, 85.2 and δ = −1.6, 55.1 ppm, respectively. ^{1}H and ^{13}C NMR spectra exhibit (besides the chemical shifts corresponding to the protons and carbon atoms of the phosphanyl substituents) signals in the region expected for a CH−N< enamine fragment [**10**: δ = 7.58 (^{1}H) and δ = 159.1 (^{13}C) ppm; **11**: δ = 7.75 (^{1}H) and δ = 163.7 (^{13}C) ppm]. The broad signal at δ = 5.90 (**10**) and 8.18 (**11**) ppm in the ^{1}H NMR spectra corresponds to the NH secondary amine. The NMR spectroscopic data establish an (*N*-phosphanyl-β-enamino)nitrile skeleton in **10** and **11**.

Reaction of **9** with 2 equiv. of **1** and addition of 2 equiv. of R_2PCl (**3**, **6**) allowed isolation of the corresponding *N*-phosphanyl-β-diimines **12** and **13**, respectively (Scheme 3). The parent ion $[M + 1]^+$ detected in the mass spectrum of **13** was in agreement with the general formula $[C_3H_3N_2(PPh_2)_3]$. Infrared spectra show absorptions at 1633 cm^{-1} (**12**) and 1635 cm^{-1} (**13**) assigned to the C=N stretch of the enaminoimine fragment. In addition to signals corresponding to the phosphanyl substituents, ^1H and ^{13}C NMR spectra of **12** and **13** show the presence of the β-diimine NC(H)CC(H)N skeleton. The chemical shifts in both ^1H [δ = 7.90 (**12**) and 8.35 (**13**) ppm] and ^{13}C [δ = 161.3 (**12**) and 166.9 (**13**) ppm] NMR spectra are consistent with the CH=N aldimine and with the central methine PC fragments the signals of which appear at δ = 99.9 (**12**) and 103.4 (**13**) ppm in the ^{13}C NMR spectrum, respectively. The NMR spectroscopic data (^{13}P, ^1H, and ^{13}C) indicate symmetric ligand environments, which is consistent with a rapid tautomeric interconversion. Addition of **1** to the (*N*-phosphanyl-β-enamino)nitrile **10**, followed by a substitution reaction with Me_2PCl (**15**), gave the corresponding unsymmetrical β-enaminoimine derivative **16** in 84% yield (Scheme 4).



Scheme 4. Monohydrozirconation/transmetalation reactions of the phosphanyl-β-nitriloeneamine compound **10**

The ^{31}P NMR spectrum of **16** displays three singlets at δ = −4.6 (PPh), 40.6 (PMe), and 86.3 ($PNiPr_2$) ppm. Both CH=N aldimine groups exhibit characteristic NMR signals at δ = 7.91 and 8.29 (^1H) ppm and δ = 160.7 and 166.5 (^{13}C) ppm. The ^{13}C NMR chemical shift of the central methine CP fragment (δ = 100.5 ppm) and the upfield shift of the broad NH signal in the ^1H NMR spectrum (δ = 11.39 ppm) establish **16** as having a "*cis-cis*" configuration, with a hydrogen-bonded chelate form in a β-enaminoimine compound.

X-ray Crystal Structure of 14

To confirm the spectroscopic assignments and to have a better insight into the molecular structure of the (*N*-phosphanyl-β-enamino)imine species prepared, an X-ray diffraction study was carried out on the phosphane sulfide product **14** obtained after addition of elemental sulfur to **13** (Figure 3, Table 1).

The crystal structure of **14**, recorded at 180 K, shows discrete molecular units which do not display the C_{2v} symmetry previously observed in compound **A** [$R^1 = R^2 = H$, $R^3 = P(S)Ph_2$].[3,18] All atoms in **14** except those of the phenyl groups and the sulfur atoms S1 and S3 lie in the same plane with a maximum deviation of 0.0046 Å. The

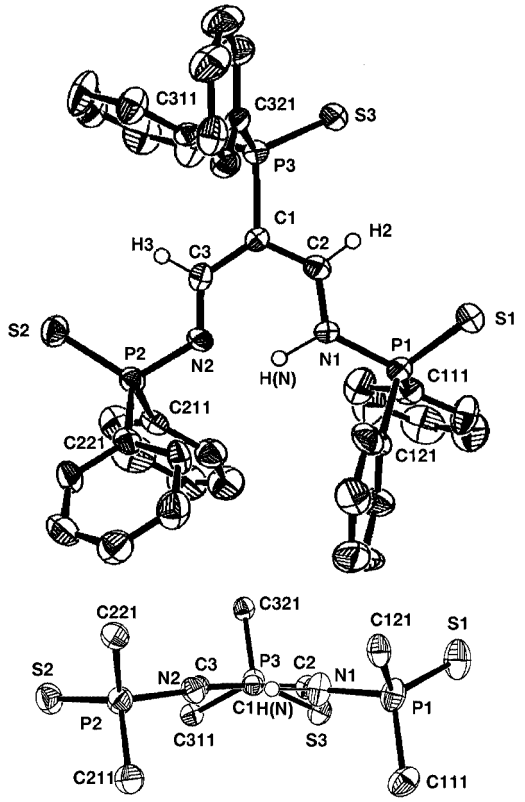


Figure 3. Two views of the molecular geometry of $Ph_2P(S)C[CHNP(S)Ph_2]_2(\mu\text{-}H)$ (**14**) as determined by X-ray diffraction

Table 1. Selected bond lengths [Å] and angles [°] for **14**

C(1)−C(2)	1.378(7)	C(1)−C(3)	1.424(7)
C(1)−P(3)	1.801(5)	C(2)−N(1)	1.351(6)
C(3)−N(2)	1.298(6)	N(1)−P(1)	1.696(5)
N(2)−P(2)	1.691(5)	P(1)−S(1)	1.926(2)
P(2)−S(2)	1.935(2)	P(3)−S(3)	1.953(2)
C(2)−C(1)−C(3)	121.0(5)	P−C(2)−N(2)	168.5(2)
C(1)−C(2)−N(1)	124.0(5)	C(1)−C(3)−N(2)	124.4(5)
P(3)−C(1)−C(2)	116.1(4)	P(3)−C(1)−C(3)	122.9(4)
C(2)−N(1)−P(1)	126.0(4)	C(2)−N(2)−P(2)	121.3(4)

presence of the N1−H1···N2 intramolecular hydrogen bond, with an N···N distance of 2.66 Å[19] and an N−H···N angle of 137°, may be responsible for the planarity of the system, together with some degree of charge delocalization. The C2−N1 [1.351(6) Å] and C3−N2 [1.298(6) Å] distances are close to the values reported for C=C−NH− and $C(sp^2)$−C=N− fragments respectively, and are representative of single and double bond lengths in such systems.[20,21] The thiophosphoryl groups $-P(S)Ph_2$ in **14** showed the expected typical structural parameters.[22]

The X-ray data recorded at 180 K showed that the β-enaminoimine compound **14** possesses an unsymmetrical intramolecular hydrogen H(N) bond with two different nitrogen chelating atoms, N1 and N2, in the solid state. However, in solution it behaves as a symmetric compound, consistent with the occurrence of a very fast tautomeric proton

exchange equilibrium. These observations can be rationalized if it is assumed that **14** possesses a low-barrier hydrogen bond with a double-well potential. This is in agreement with the mechanism of proton transfer in malonaldehyde recently proposed by Silvi and co-workers,[23] involving a two-step reaction with a concerted charge transfer from one bond to another within the planar framework of the aldehyde. This description may also be applied to the analogous β-enaminoimine systems.[24]

Conclusion

In conclusion, we have demonstrated that the bis(*N*-zirconated) β-enaminoimine system **2** shows a dynamic NMR behavior which may be reasonably attributed to a σ-bent/π-linear fluxional structure. Complex **2** is the ideal synthon to prepare unsymmetrical β-enaminoimine derivatives following the hydrozirconation/transmetalation reaction sequence. Starting with the phosphanylmalononitrile $Ph_2P-CH(CN)_2$ and using an identical reaction process, (*N*-phosphanyl-β-enamino)imine derivatives have been prepared and characterized. These compounds will be further investigated as ligands in coordination complexes.

The X-ray crystal structure of **14** at 180 K shows an unsymmetrical system, with the N(H) proton localized on one of the two chelating nitrogen atoms. This solid-state structural analysis is consistent with the existence in solution of a rapidly interconverting pair of tautomers[25] with a low-barrier proton transfer process corresponding to a double-well potential. The β-enaminoimine compounds described in this paper represent a good model for the study of intramolecular hydrogen bonding.

Experimental Section

General Remarks: All manipulations were performed under argon in a vacuum line using standard Schlenk techniques. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF and toluene), lithium aluminum hydride (pentane), or CaH_2 (CH_2Cl_2). Deuterated NMR solvents were treated with $LiAlH_4$ ([D_8]toluene, 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 with Bruker AMX-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 NMR experiments. Elemental and mass spectral analyses (obtained using a Nermag R10-10H) were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PCl}$[26] and $[Cp_2Zr(H)Cl]_n$[27] were prepared according to literature procedures. Ph_2PCl (Aldrich), Me_2PCl (Strem), Et_2PCl (Strem), MeI (Aldrich), and $CH_2(CN)_2$ (Aldrich) were purchased and used without further purification.

Preparation of 2: A solution of $CH_2(CN)_2$ (0.100 g, 1.514 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of $[Cp_2Zr(H)Cl]_n$ (0.781 g, 3.028 mmol) in CH_2Cl_2 (3 mL) at −30 °C. The reaction mixture was stirred for 30 min at room temperature and then cooled to −50 °C, at which temperature MeI (0.188 μL, 3028 mmol) in CH_2Cl_2 (5 mL) was slowly added. The solution was then stirred for an additional 2 h at room temperature. Removal of the solvent in vacuo gave **2** as an orange solid. ^1H and ^{13}C NMR recorded at 293 K: ^1H NMR (CD_2Cl_2): δ = 4.84 (br, 1 H, CH), 6.35 (s, 10 H, Cp), 6.53 (s, 10 H, Cp), 7.10 (br., 1 H, NH), 7.48 (dd, $J_{H(2)-H(1)}$ = 5.8, $J_{H(2)-H(N)}$ = 12.6 Hz, CHN) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 97.9 (s, CH), 114.5, 116.6 (s, Cp), 157.6 (s, CHN) ppm. ^1H and ^{13}C NMR of conformers **I** and **II** recorded at 193 K: ^1H NMR (CD_2Cl_2): δ = 4.78 (br, 1 H, CH), 6.30 (s, 10 H, Cp), 6.52 (s, 10 H, Cp), 6.70 [d, $J_{H(2)-H(N)}$ = 13.0 Hz, NH), 7.49 (dd, $J_{H(2)-H(1)}$ = 5.5, $J_{H(2)-H(N)}$ = 13.0 Hz, CHN) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 97.9 (s, CH), 114.8, 117.0 (s, Cp), 157.6 (s, CHN) ppm. ^1H NMR (CD_2Cl_2): δ = 4.78 (br, 1 H, CH), 6.30 (s, 10 H, Cp), 6.52 (s, 10 H, Cp), 7.34 (br, CHN and NH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 97.9 (s, CH), 114.8, 117.0 (s, Cp), 158.4 (s, CHN) ppm.

Preparation of 4: A suspension of $[Cp_2ZrHCl]_n$ (0.600 g, 2.327 mmol) in CH_2Cl_2 (3 mL) was added to a solution of malonodinitrile (2.327 mmol, 0.154 g) in CH_2Cl_2 (10 mL) at −40 °C. and the reaction mixture was allowed to warm slowly to room temperature. As soon as the reaction mixture turned clear, $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PCl}$ (0.619 mg, 2.327 mmol) in CH_2Cl_2 (2 mL) was added and the solution was stirred for 1 h at room temperature. Removal of the solvent in vacuo gave a yellow solid residue which was extracted with cold pentane (10 mL). After filtration, the volatiles were evaporated and **4** was obtained as a yellow powder. Yield: 66% (457 mg). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 87.1 (s) ppm. ^1H NMR (C_6D_6): δ = 1.03 (d, $^3J_{H,H}$ = 6.7 Hz, 24 H, CH_3), 3.24 (d sept, $^3J_{H,H}$ = 6.7, $^3J_{HP}$ = 11.8 Hz, 4 H, $CHCH_3$), 3.74 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, CHCN), 5.30 (br. d, $^3J_{H,H}$ = 15.0 Hz, 1 H, NH), 6.53 (ddd, $^3J_{HP}$ = $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 15.0 Hz, 1 H, CHNH) ppm. ^{13}C NMR (C_6D_6): δ = 24.0 (d, $^3J_{PC}$ = 7.2 Hz, CH_3), 24.6 (d, $^3J_{PC}$ = 7.2 Hz, CH_3), 45.9 (d, $^2J_{PC}$ = 12.8 Hz, $CHCH_3$), 66.1 (d, $^2J_{PC}$ = 7.5 Hz, CHCN), 118.8 (s, CN), 150.8 (d, $^2J_{PC}$ = 27.7 Hz, CHNH) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1600 (C=N), 2194 (C≡N) cm^{-1}. $C_{15}H_{31}N_4P$ (298.47): calcd. C 60.36, H 10.47, N 18.77; found C 60.48, H 10.28, N 18.56.

Typical Procedure for the Synthesis of Compounds 7 and 8: Compound **4** (0.215 g, 0.721 mmol) in CH_2Cl_2 (2 mL) was added to a suspension of $[Cp_2ZrHCl]_n$ (0.186 g, 0.721 mmol) in CH_2Cl_2 (2 mL) at −40 °C. The resulting mixture was stirred and allowed to warm slowly to room temperature. As soon as the solution turned clear, Et_2PCl (0.90 mg, 0.721 mmol) in CH_2Cl_2 (1 mL) was added. The mixture was stirred for 15 min at room temperature and then concentrated to dryness. The volatiles were removed to give **7** as an orange powder. Yield: 78% (218 mg). **7**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 64.8 (s, PEt_2), 89.3 (s, $PN\mathit{i}Pr_2$) ppm. ^1H NMR (C_6D_6): δ = 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_2CH_3), 1.05 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_2CH_3), 1.16 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, $CHCH_3$), 1.19 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, $CHCH_3$), 3.50 (d sept, $^3J_{H,H}$ = 6.7, $^3J_{HP}$ = 11.0 Hz, 4 H, $CHCH_3$), 4.87 (dd, $^3J_{H,H}$ = $^3J_{H,H}$ = 5.9 Hz, 1 H, CH), 7.55−7.74 (m, 2 H, CHN), 10.54 (br. m, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 9.5 (d, $^2J_{PC}$ = 14.5 Hz, CH_2CH_3), 24.6 (d, $^3J_{PC}$ = 7.5 Hz, $CHCH_3$), 24.8 (d, $^3J_{PC}$ = 7.5 Hz, $CHCH_3$), 25.0 (d, $^2J_{PC}$ = 12.3 Hz, CH_2CH_3), 46.3 (d, $^2J_{PC}$ = 12.5 Hz, $CHCH_3$), 97.6 (dd, $^3J_{PC}$ = $^3J_{PC}$ = 13.6 Hz, CH), 156.1 (d, $^2J_{PC}$ = 37.3 Hz, $CHNPN\mathit{i}Pr$), 159.8 (d, $^2J_{PC}$ = 27.4 Hz, CHNPEt) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1625 (C=N) cm^{-1}. $C_{19}H_{42}N_4P_2$ (388.59): calcd. C 58.72, H 10.89, N 14.42; found C 58.89, H 11.61, N 14.29. **8** [**1** (0.233 g), **4** (0.270 g), **6** (0.199 g)] isolated as an orange-yellow powder. Yield: 87% (0.380 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 53.3 (s,

PPh_2), 84.5 (s, $PNiPr_2$) ppm. ^1H NMR (C_6D_6): δ = 1.05 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, $CHCH_3$), 1.09 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, $CHCH_3$), 3·32 (dsept, $^3J_{H,H}$ = 6.7, $^3J_{HP}$ = 11.0 Hz, 4 H, $CHCH_3$), 4.89 (dddd, $^3J_{H,H}$ = $^3J_{H,H}$ = 6.7, $^4J_{HP(Ph)}$ = 4.9, $^4J_{HP(NiPr)}$ = 1.5 Hz, 1 H, CH), 7.41−7.60 (m, 10 H, Ph), 7.82−7.96 (m, 2 H, CHN), 10.84 (br. d, $^2J_{HP}$ = 9.9 Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 24.5 (d, $^3J_{PC}$ = 7.3 Hz, CH_3), 24.7 (d, $^3J_{PC}$ = 7.3 Hz, CH_3), 46.4 (d, $^2J_{C,P}$ = 12.3 Hz, *C*HCH_3), 97.8 (dd, $^3J_{C,P(Ph)}$ = 10.7, $^3J_{C,P(NiPr)}$ = 13.4 Hz, CH), 128.9 (d, $^3J_{C,P}$ = 7.0 Hz, *m*-Ph), 129.5 (s, *p*-Ph), 132.0 (d, $^2J_{C,P}$ = 20.7 Hz, *o*-Ph), 141.6 (d, $^1J_{C,P}$ = 16.6 Hz, *i*-Ph), 150.5 (d, $^2J_{C,P}$ = 33.2 Hz, *C*HNPPh), 164.5 (d, $^2J_{PC}$ = 15.1 Hz, $CHNPNiPr_2$) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1621 (C=N) cm^{-1}. $C_{27}H_{42}N_4P_2$ (484.67): calcd. C 66.91, H 8.73, N 11.56; found C 67.15, H 8.66, N 11.39.

Preparation of 9: $CH_2(CN)_2$ (0.480 g, 0.076 mmol) in THF (5 mL) was added slowly to a solution of LDA (0.779 g, 0.0726 mmol) in THF (25 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, then Ph_2PCl (1.600 g, 0.076 mmol) in THF (5 mL) was added dropwise. The mixture was slowly warmed to room temperature over 1 h, filtered, and the solvent was evaporated. The resulting solid residue was washed with Et_2O (2 × 20 mL). The volatiles were removed in a vacuum line over 5 h at 80 °C to give **9** as a yellow-brown solid.Yield: 95% (1.514 g). M.p. 83−84 °C. $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = −5.9 ppm. ^1H NMR ([D_8]THF): δ = 7.18−7.50 (m, 10 H, Ph) ppm. ^{13}C NMR ([D_8]THF): δ = 7.9 (d, $^1J_{C,P}$ = 5.8 Hz, PC), 127.4 (s, *p*-Ph), 127.9 (d, $^3J_{C,P}$ = 6.2 Hz, *m*-Ph), 128.4 (d, $^2J_{C,P}$ = 21.1 Hz, CN), 132.5 (d, $^2J_{C,P}$ = 19.4 Hz, *o*-Ph), 142.2 (d, $^1J_{C,P}$ = 11.2 Hz, *i*-Ph) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2189 (C≡N) cm^{-1}.

Preparation of 10: A solution of **9** (0.262 g, 1.046 mmol) in THF (2 mL) was added to a suspension of $[Cp_2ZrHCl]_n$ (0.270 g, 1.046 mmol) in THF (2 mL) at −40 °C. The resulting mixture was stirred and allowed to warm slowly to room temperature. As soon as the reaction mixture turned clear, $(iPr_2N)_2PCl$ (0.278 mg, 1.046 mmol) in THF (2 mL) was added. The solution was stirred for 30 min at room temperature and the solvent was then removed. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed and **10** was obtained as a yellow-orange solid. Yield: 55% (277 mg). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −8.0 (PPh_2), 85.2 ($PNiPr_2$) ppm. ^1H NMR (C_6D_6): δ = 1.01 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.05 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 3.23 (d sept, $^3J_{H,H}$ = 6.7, $^3J_{HP}$ = 11.6 Hz, 4 H, *C*HCH_3), 5.95 (br. dd, $^3J_{H,H}$ = 2.0, $^3J_{HP}$ = 15.6 Hz, 1 H, NH), 7.00−7.28 (m, 5 H, Ph), 7.58 (ddd, $^3J_{H,H}$ = 7.1, $^3J_{HP(PPh2)}$ = 15.6, $^3J_{HP(PNiPr)}$ = 9.5 Hz, 1 H, C*H*NH), 7.65−7.77 (m, 5 H, Ph) ppm. ^{13}C NMR (C_6D_6): δ = 24.4 (d, $^3J_{PC}$ = 8.2 Hz, CH_3), 24.7 (d, $^3J_{PC}$ = 8.2 Hz, CH_3), 46.2 (d, $^2J_{PC}$ = 12.3 Hz, *C*HCH_3), 76.3 (dd, $^1J_{PC}$ = 16.0, $^3J_{PC}$ = 5.8 Hz, PC), 129.2 (s, *p*-Ph), 129.3 (s, *m*-Ph), 133.5 (d, $^1J_{C,P}$ = 20.0 Hz, *o*-Ph), 139.0 (d, $^1J_{C,P}$ = 5.8 Hz, *i*-Ph), 159.1 (dd, $^2J_{C,P}$ = 21.1, $^2J_{C,P}$ = 67.3 Hz, PCCH) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1619 (C=N), 2195 (C≡N) cm^{-1}. $C_{27}H_{40}N_4P_2$ (482.65): calcd. C 67.19, H 8.35, N 11.61; found C 67.35, H 8.12, N 11.45.

Preparation of 11: A solution of **9** (340 mg, 1.356 mmol) in THF (2 mL) was added to a suspension of $[Cp_2ZrHCl]_n$ (250 mg, 1.356 mmol) in THF (2 mL) at −40 °C. The resulting mixture was stirred and allowed to warm slowly to room temperature. As soon as the solution turned clear (ca. 20 min), Ph_2PCl (300 mg, 1.356 mmol) in THF (2 mL) was added. The resulting mixture was stirred at room temperature for 30 min and then concentrated to dryness. The solid residue was extracted with CH_2Cl_2/pentane (1:5, 20 mL) and filtered. The volatiles were removed to give **11** as a white solid. Yield: 66% (391 mg). M.p. 155−156 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −1.6 ($CPPh_2$), 55.1 ($NPPh_2$) ppm. ^1H NMR (C_6D_6): δ = 7.28−7.65 (m, 20 H, Ph), 7.75 (ddd, $^3J_{H,H}$ = 14.5, $^3J_{HP(NPPh2)}$ = 10.3, $^3J_{HP(C,PPh2)}$ = 9.5 Hz, 1 H, C*H*NH), 8.18 (dd, $^3J_{H,H}$ = 4.0, $^2J_{Hp}$ = 14.5 Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 80.0 (dd, $^1J_{C,P}$ = 17.6, $^3J_{C,P}$ = 10.4 Hz, PC), 118.4 (d, $^2J_{C,P}$ = 5.0 Hz, CN), 130.3 (d, $^3J_{C,P}$ = 6.9 Hz, *m*-Ph), 130.6 (d, $^3J_{C,P}$ = 6.9 Hz, *m*-Ph), 131.6 (s, *p*-Ph), 133.6 (d, $^2J_{C,P}$ = 19.9 Hz, *o*-Ph), 134.6 (d, $^2J_{C,P}$ = 19.9 Hz, *o*-Ph), 139.9 (d, $^1J_{C,P}$ = 16.1 Hz, *i*-Ph), 140.1 (d, $^1J_{C,P}$ = 16.2 Hz, *i*-Ph), 163.7 (dd, $^2J_{C,P(C,PPh2)}$ = 70.0, $^2J_{C,P(NPPh)}$ = 37.5 Hz, *C*HNP) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1642 (C=N), 2202 (C≡N) cm^{-1}. MS (DCI/CH_4): *m*/*z* = 437 $[M + H]^+$. $C_{27}H_{22}N_2P_2$ (436.45): calcd. C 74.30, H 5.08, N 6.42; found C 74.45, H 4.94, N 6.32.

Typical Procedure for the Synthesis of Compounds 12 and 13: A solution of **9** (0.270 g, 1.078 mmol) in THF (2 mL) was added to a suspension of $[Cp_2ZrHCl]_n$ (0.556 g, 2.156 mmol) in THF (3 mL) at −40 °C. The resulting mixture was stirred and slowly warmed to room temperature. As soon as the reaction mixture turned clear (ca. 30 min), $(iPr_2N)_2PCl$ (0.574 mg, 2.156 mmol) in THF (2 mL) was added. After stirring for 4 h, the solution was concentrated to dryness. The resulting solid residue was extracted with CH_2Cl_2/pentane (1:4, 30 mL) and filtered. The volatiles were evaporated to give **16** as a yellow solid. Yield 67% (516 mg).

Data for 12: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −1.8 (PPh_2), 86.2 ($PNiPr_2$) ppm. ^1H NMR (C_6D_6): δ = 1.02 (d, $^3J_{H,H}$ = 6.6 Hz, 24 H, CH_3), 1.21 (d, $^3J_{H,H}$ = 6.6 Hz, 24 H, CH_3), 3.54 (dsept, $^3J_{H,H}$ = 6.6, $^3J_{HP}$ = 12.3 Hz, 8 H, C*H*CH_3), 6.90−7.58 (m, 10 H, Ph), 7.90 (ddd, $^3J_{H,H}$ = 7.3, $^3J_{HP(PPh)}$ = 7.3, $^3J_{HP(PniPr)}$ = 18.0 Hz, 2 H, C*H*NH), 10.35 (br. m, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 24.4 (d, $^3J_{C,P}$ = 7.0 Hz, CH_3), 24.8 (d, $^3J_{C,P}$ = 7.0 Hz, CH_3), 47.9 (d, $^2J_{PC}$ = 13.1 Hz, $CHCH_3$), 99.9 (dd, $^1J_{PC}$ = $^3J_{PC}$ = 9.3 Hz, PC), 128.1 (s, *p*-Ph), 128.7 (d, $^3J_{C,P}$ = 5.5 Hz, *m*-Ph), 133.0 (d, $^2J_{C,P}$ = 17.6 Hz, *o*-Ph), 141.0 (d, $^1J_{C,P}$ = 11.4 Hz, *i*-Ph), 161.3 (dd, $^2J_{C,P(PPh2)}$ = 36.1, $^2J_{HP(PNiPr)}$ = 20.6 Hz, CHNP) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1633 (C=N) cm^{-1}. $C_{39}H_{69}N_6P_3$ (715.05): calcd. C 65.51, H 9.72, N 11.75; found C 65.72, H 9.65, N 11.68.

Data for 13: Yield: 54% (229 mg). M.p. 126−127 °C (dec). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −3.6 ($CPPh_2$), 54.9 ($NPPh_2$) ppm. ^1H NMR (C_6D_6): δ = 7.00−8.15 (m, 30 H, Ph), 8.35 (ddd, $^3J_{H,H}$ = $^3J_{HP(C,PPh)}$ = 6.1, $^3J_{HP(NPPh)}$ = 16.9 Hz, 2 H, C*H*NH), 12.55 (tt, $^3J_{H,H}$ = $^3J_{HP(NPPh)}$ = 6.1 Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 103.4 (dt, $^1J_{C,P(CPPh)}$ = 6.3, $^3J_{C,P(NPPh)}$ = 10.3 Hz, PC), 128.4 (s, *p*-NPPh), 128.9 (d, $^3J_{C,P}$ = 5.1 Hz, *m*-CPPh), 129.0 (d, $^3J_{C,P}$ = 6.7 Hz, *m*-NPPh), 129.5 (s, *p*-CPPh), 132.2 (d, $^2J_{C,P}$ = 20.6 Hz, *o*-

Table 2. Crystallographic data for **14**

Empirical formula	$C_{39}H_{33}N_2P_3S_3$
Formula mass	718.76
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 14.804(5) Å
	b = 12.238(5) Å
	c = 20.169(5) Å
	β = 93.710(5)°
Volume	3646(2) $Å^3$
Z, calculated density	4, 1.309 mg/m^3
Absorption coefficient	0.366 mm^{-1}
F(000)	1496
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0524, $wR2$ = 0.0638
R indices (all data)	$R1$ = 0.1710, $wR2$ = 0.0901
Largest diff. peak and hole	0.279 and −0.315 e $Å^{-3}$

NPPh), 133.0 (d, $^2J_{C,P}$ = 18.6 Hz, *o*-CPPh), 139.8 (d, $^1J_{C,P}$ = 10.1 Hz, *i*-CPPh), 140.3 (d, $^1J_{C,P}$ = 13.1 Hz, *i*-NPPh), 166.9 (dd, $^2J_{C,P(C,PPh)}$ = 34.5, $^2J_{HP(NPPh)}$ = 25.5 Hz, CHNP) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1635 (C=N) cm^{-1}. MS (DCI/CH_4): *m*/*z* = 623 [M + H]$^+$. $C_{39}H_{33}N_2P_3$ (622.63): calcd. C 75.23, H 5.34, N 4.50; found C 75.41, H 5.23, N 4.33.

Preparation of 14: Treatment of **13** (362 mg, 0.581 mmol) in CH_2Cl_2 (8 mL) with an excess of sulfur at room temperature for 12 h afforded **14**, which was purified by column chromatography (silica gel, pentane/ethyl acetate, 1:4, R_f = 0.49). The product crystallized from toluene as colorless crystals. Yield: 81% (338 mg). M.p. 185−186 °C. $^{31}P\{^1H\}$ NMR (400 MHz, 233 K, [D_8]toluene): δ = 43.5 [CP(S)Ph_2], 63.2 [NP(S)Ph_2] ppm. ^1H NMR (400 MHz, 233 K, [D_8]toluene): δ = 7.46−8.04 (m, 30 H, Ph), 9.59 (ddd, $^3J_{H,H}$ = 5.8, $^3J_{HP(NPPh)}$ = 8.5, $^3J_{HP(C,PPh)}$ = 23.5 Hz, 2 H, C*H*NH), 13.59 (tt, $^3J_{H,H}$ = 5.8, $^2J_{HP(NPPh)}$ = 5.0 Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 102.8 (dt, $^1J_{C,P(C,PPh)}$ = 97.1, $^3J_{C,P(NPPh)}$ = 14.0 Hz, PC), 128.7 (d, $^3J_{C,P}$ = 13.8 Hz, *m*-Ph), 129.3 (s, *p*-Ph), 131.0 (d, $^2J_{C,P}$ = 11.5 Hz, *o*-Ph), 134.4 (d, $^1J_{C,P}$ = 96.0 Hz, *i*-Ph), 164.4 (d, $^2J_{C,P}$ = 19.7 Hz, *C*HNP) ppm. FT-IR (KBr): $\tilde{\nu}$(C=N) 1596 cm^{-1}. MS (DCI/CH_4): *m*/*z* = 719 [M + H]$^+$. $C_{39}H_{33}N_2P_3S_3$ (718.65): calcd. C 65.18, H 4.63, N 3.90; found C 65.05, H 4.45, N 3.79.

Preparation of 16: A solution of **10** (0.351 g, 0.729 mmol) in CH_2Cl_2 (2 mL) was added to a suspension of $[Cp_2ZrHCl]_n$ (0.556 g, 2.156 mmol) in CH_2Cl_2 (2 mL) at −40 °C. The resulting mixture was stirred and slowly warmed to room temperature. As soon as the reaction mixture turned clear (ca. 20 min), Me_2PCl (0.070 g, 0.729 mmol) in CH_2Cl_2 (2 mL) was added. After stirring for 15 min, the solution was concentrated to dryness. The resulting solid residue was extracted with pentane (30 mL) and filtered. The volatiles were removed to give **16** as a yellow solid. Yield: 84% (0.334 g). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −4.6 (PPh_2), 40.6 (PMe_2), 86.3 (PN*i*Pr_2) ppm. ^1H NMR (C_6D_6): δ = 1.06 (d, $^2J_{H,H}$ = 4.5 Hz, 6 H, PCH_3), 1.09 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 1.14 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 3.41 (dsept, $^3J_{H,H}$ = 6.5, $^3J_{HP}$ = 11.3 Hz, 4 H, C*H*CH_3), 6.86−7.72 (m, 10 H, Ph), 7.91 (m, 1 H, C*H*NPN*i*Pr), 8.29 (m, 1 H, C*H*NPMe), 11.39 (br. m, 1 H, NH) ppm. ^{13}C NMR (C_6D_6): δ = 18.9 (d, $^1J_{C,P}$ = 17.0 Hz, CH_3), 24.6 (d, $^3J_{C,P}$ = 8.4 Hz, CH_3), 24.7 (d, $^3J_{C,P}$ = 8.4 Hz, CH_3), 46.4 (d, $^2J_{C,P}$ = 12.8 Hz, *C*HCH_3), 100.5 (d, $^3J_{C,P}$ = 9.2 Hz, PC), 129.1 (s, *p*-Ph), 129.2 (d, $^3J_{C,P}$ = 8.0 Hz, *m*-Ph), 133.2 (d, $^2J_{C,P}$ = 17.6 Hz, *o*-Ph), 140.7 (d, $^1J_{C,P}$ = 10.9 Hz, *i*-Ph), 160.7 (dd, $^2J_{C,P(PPh2)}$ = 34.6, $^2J_{C,P(PNiPr)}$ = 28.8 Hz, CHNPN*i*Pr), 166.5 (dd, $^2J_{C,P(PPh)}$ = 35.0, $^2J_{C,P(PMe)}$ = 18.9 Hz, CHNPMe) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1593 (C=N) cm^{-1}. $C_{29}H_{47}N_4P_3$ (544.71): calcd. C 63.94, H 8.70, N 10.28; found C 63.92, H 8.56, N 10.35.

X-ray Analysis of 14: Single crystals of **14** were obtained from toluene. Data (Table 2) were collected at 180 K with an IPDS STOE diffractometer equipped with an Oxford Cryosystems Cryostream Cooler Device using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by means of a least-squares refinement performed on a set of 5000 strong reflections. No significant intensity fluctuations were observed during the data collection, indicating crystal decay was minimal. The structure was solved by Direct Methods using SIR92,[28] and refined by means of least-squares procedures on F^2 using SHELXL-97.[29] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[30] All hydrogen atoms were located in a difference Fourier map, and, with the exception of H(N), were refined using a riding model with an isotropic thermal parameter fixed at 20% greater than those of the carbon atoms to which they are connected. H(N), the hydrogen atom connected to N(1), was refined isotropically. All non-hydrogen atoms were refined anisotropically, and the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the last cycles of refinement. Molecular graphics were produced using ZORTEP,[31] with non-hydrogen atoms drawn at the 50% probability level. CCDC-196233 contains 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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[17] Rate constants were derived from band-shape analysis using the software MEXICO (available from A. D. Bain, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada). NMR parameters were optimized to match the simulated and the experimental data. Activation parameters were determined by a standard Eyring analysis.

[18] The X-ray crystallographic investigation of **A** [$R^1 = R^2 = H$, $R^3 = P(S)Ph_2$] at 293 K revealed two "half-hydrogen" atoms in the N···N region of the molecule, similar to what might be obtained by the superposition of one half molecule of **A′** on one half molecule of **A′′**.

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