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N-phosphonio formamidine derivatives: Synthesis, characterization, X-ray crystal structures, and deprotonation reactions

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ABSTRACT

A simple and efficient method for the preparation of *N*-phosphonio formamidine derivatives of the general formula $[R''_2N{-}C(H){=}N{-}P(R')R_2]^+X^-$ is described. The data recorded in solution and the single crystal X-ray studies revealed that these compounds are best described by the combination of the two mesomeric *N*-phosphonio formamidine $[R''_2N{-}C(H){=}N{-}P(R')R_2]^+$ and iminium phosphazene $[R''_2N{=}C(H){-}N{=}P(R')R_2]^+$ forms. Formamidine phosphorus ylides $^iPr_2N{-}C(H){=}N{-}P(CH_2)R_2$ were prepared after addition of ^{t}BuLi at −78 °C from the corresponding *N*-phosphonio compounds. $[(PhCN)_2Pd(Cl)_2]$ was reacted with $^iPr_2N{-}C(H){=}N{-}P(CH_2)^iPr_2$ to form the dimeric complex $[(^iPr_2N{-}C(H){=}N{-}P(CH_2)^iPr_2)Pd(Cl)(\mu\text{-}Cl)]_2$ which was structurally characterized by X-ray analysis. The deprotonation reactions conducted on $[^iPr_2N{-}C(H){=}N{-}PPh_3]^+X^-$ occurred via an intramolecular rearrangement to give the cyanamide compound $^iPr_2N{-}C{\equiv}N$ and PPh_3; transient formation of the amino-phosphazene-carbene $^iPr_2N{-}C{-}N{=}PPh_3$ was not observed.

Mots clés :
Phosphonium
Ylures
Palladium
Formamidines
Réaction de déprotonation

RÉSUMÉ

Une méthode simple et efficace de synthèse de dérivés *N*-phosphonio formamidines de formule générale $[R''_2N{-}C(H){=}N{-}P(R')R_2]^+X^-$ est décrite. Les données enregistrées en solution et les analyses par diffraction des rayons X sur un monocristal révèlent que ces composés peuvent être décrits par la combinaison des deux formes mésomères *N*-phosphonio formamidine $[R''_2N{-}C(H){=}N{-}P(R')R_2]^+$ et iminium phosphazène $[R''_2N{=}C(H){-}N{=}P(R')R_2]^+$. Les ylures de phosphore formamidines $^iPr_2N{-}C(H){=}N{-}P(CH_2)R_2$ ont été préparés à partir du composé *N*-phosphonio correspondant après addition de ^{i}BuLi à −78 °C. $[(PhCN)_2Pd(Cl)_2]$ réagit avec $^iPr_2N{-}C(H){=}N{-}P(CH_2)^iPr_2$ pour former le complexe dimère $[(^iPr_2N{-}C(H){=}N{-}P(CH_2)^iPr_2)Pd(Cl)(\mu\text{-}Cl)]_2$ dont la structure a été déterminée par diffraction des rayons X. Les réactions de déprotonation réalisées sur $[^iPr_2N{-}C(H){=}N{-}PPh_3]^+X^-$ suivent un processus de réarrangement intramoléculaire pour donner le composé cyanamide $^iPr_2N{-}C{\equiv}N$ et PPh_3 ; la formation transitoire du carbène amino-phosphazène $^iPr_2N{-}C{-}N{=}PPh_3$ n'a pas été observée.

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1. Introduction

Phosphonium salts are readily available at low cost, stable to oxygen and to moisture, and therefore can be stored under air atmosphere for long periods of time without any detectable deterioration. Their excellent thermal and chemical stability and their non-toxicity make phosphonium derivatives very attractive, and therefore the scope of their applications is large [1]. They have been extensively used as intermediates in organic syntheses as in Wittig reactions [2]. Phosphonium cation-based ionic liquids (ILs) offer in some chemical transformations superior properties than the nitrogen cation-based ILs [3]. The range of applications of these interesting materials, recently investigated, includes their use as extraction solvents, chemical synthesis solvents, electrolytes in batteries and super-capacitors, and in corrosion protection [4]. The most prominent catalytic application of these compounds is phase-transfer catalysis [5]. It has also been demonstrated that phosphonium salts can be used interchangeably with the corresponding phosphines in a broad spectrum of processes ranging from catalytic applications (palladium-catalyzed couplings, acylations of alcohols, and Baylis-Hillman reactions) to stoichiometric transformations (reductions of disulfides and azides) [6]. Phosphonium salts are good activating agents for performing cross-coupling palladium catalyzed arylation [7]. This class of phosphorus compounds was evaluated as powerful catalysts in the Halex reaction [8] which is, to date, one of the best and least expensive ways to introduce fluorine into a molecule. A number of successful applications of phosphonium salts as organocatalysts have been described recently [9] but the Lewis acidic nature of the phosphonium salt catalysts in organic reactions has not yet been fully evaluated.

We have previously reported the synthesis of *N*−phosphino formamidines of general structure $^{i}Pr_2N{-}C(H){=}N{-}PR_2$ [10]. Considering the increasing interest devoted to phosphonium compounds, we decided to broaden our research field to the development of a new class of functionalized phosphonium compounds, the *N*-phosphonio formamidines of the general formula $[^{i}Pr_2N{-}C(H){=}N{-}P(R')R_2]^{+}X^{-}$. These compounds have been structurally characterized by X-ray diffraction analyses. Their behavior in the presence of a large variety of organic and inorganic bases has been investigated.

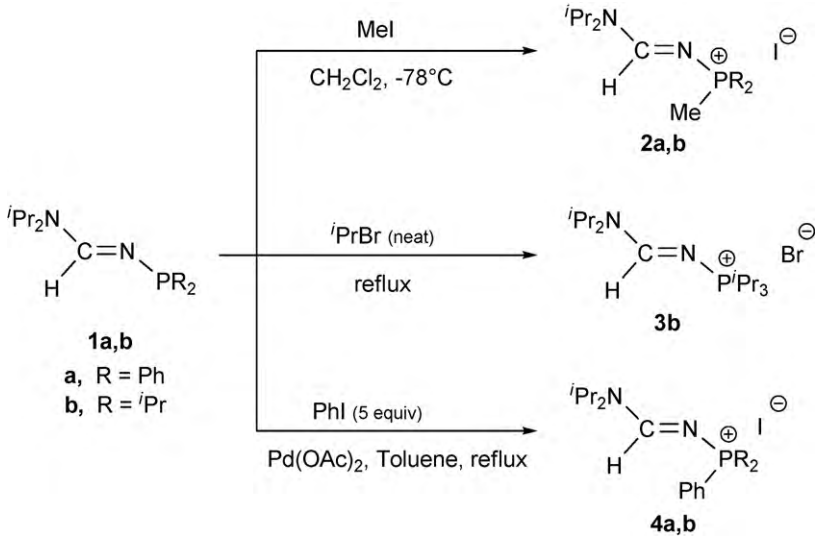
2. Results and discussion

N-phosphonio formamidines **2a**,**b** were prepared in good yields in a one-pot procedure after treatment of the corresponding *N*−phosphino formamidines **1a**,**b** derivatives with MeI in CH_2Cl_2 at −78 °C (Scheme 1). After 18 hours at reflux in neat 2-bromopropane, the *N*-phosphonio formamidine **3b** was obtained from the corresponding formamidine precursor **1b** in quantitative yield based on ^{31}P NMR spectroscopy. The phosphorus-arylation reaction conducted in the presence of $Pd(OAc)_2$ as catalyst on formamidines **1a**,**b** affording the *N*-phosphonio formamidines **4a**,**b** was adapted from a procedure described by Migita and al. [11][1]. Spectroscopic features allow for complete identification of *N*-phosphonio formamidines **2a**,**b**, **3b** and **4a**,**b**.

Mass spectrometry analyses allowed us to identify the molecular peak $[M{-}X]^{+}$ (X = I or Br) for all the compounds **2a**,**b**, **3b** and **4a**,**b**. FT-IR spectra of these compounds displayed an absorption band between 1597 and 1616 cm^{-1} corresponding to the ν(C=N) stretching of the formamidine pattern. The ^{31}P NMR chemical shifts for *N*-phosphonio formamidines **2a**,**b**, **3b** and **4a**,**b** are consistent with the characteristic shifts measured for tetracoordinated phosphorus σ^4-P fragments ($\delta \approx 30$–32 ppm [R = Ph], $\delta \approx 52$–56 ppm [R = *i*Pr]) [10]. The ^{1}H and ^{13}C NMR spectra of the *N*-phosphonio formamidines showed the presence of the proton and the carbon of the formamidine framework >N−C(H)=N− in the range of 7.9–8.8 ppm and 158–160 ppm and confirmed the presence of the different alkyl and aryl groups attached to the phosphorus atom. Moreover, the low magnitude of the $^{2}J_{CP}$ coupling constant observed between the imino carbon atom and the phosphorus fragment ($3.4 < {}^{2}J_{CP} < 7.7$ Hz) is characteristic for tetracoordinated σ^4-P *N*-phosphorus formamidino derivatives [12]. 2D HMBC ^{1}H-^{15}N and HMQC ^{31}P-$^{15}N\{^{1}H\}$ NMR experiments monitored on **2b**, **3b** and **4a**,**b** allowed us to identify the chemical shift of the imino nitrogen atom of the formamidine fragment (δ ^{15}N – 235–250.0 ppm with a $^{2}J_{NP}$ ranging from 28 to 38 Hz) which correlates with the corresponding phosphorus atom. It is interesting to note that the chemical shifts of the imino and amino nitrogen atoms in the formamidine pattern are closer to each other in the *N*-phosphonio formamidines **2b**, **3b** and **4a**,**b** ($\Delta\delta$ $^{15}N < 40$ ppm) than the ones recorded for *N*−phosphino formamidines **1a**,**b** ($\Delta\delta$ $^{15}N > 60$ ppm). This reflects a more pronounced delocalisation of the π-electrons in the *N*-phosphonium formamidine derivatives (Table 1).

Suitable crystals of compounds **2b** and **4a** were grown and the single-crystal X-ray diffraction studies revealed an *E*-formamidine arrangement for both compounds (Figs. 1 and 2). The compounds exhibit very similar structural geometry with a pyramidal phosphorus atom and a planar amino nitrogen atom $^{i}Pr_2N$−. The C1−N1 and N1−P1 bond distances of 1.31–1.33 and 1.60–1.61 Å respectively, fall in the range between carbon−nitrogen [13] and nitrogen-phosphorus double and single bonds. There is not a significant difference between the C1−N1 and C1−N2 bond lengths, which denotes a strong electronic delocalisation along the formamidine NC(H)N moiety. In comparison with the structure of the *N*−phosphino formamidine **1a**, the N2−C1−N1 angle value in **2b** and **4a** of 123–124° is not affected by the quaternarization reaction of the phosphorus atom, however, we observed a significant opening of the C1−N1−P1 bond angle up to 126° (Table 2). In marked contrast to the structure of **1a** which shows a strong localization of the >C1=N1− double bond in the formamidine pattern, the structural parameters of **2b** and **4a** suggest that the *N*-phosphonio formamidine derivatives **2a**,**b**, **3b** and **4a**,**b** are best

[1] The isolated yield of **4b** (28%) was not optimized. According to ^{31}P NMR, the product was formed in 75% yield.



Scheme 1. Formation of *N*-phosphonio formamidines **2a**,**b**, **3b** and **4a**,**b**.

Table 1
NMR Spectroscopic data for *N*-phosphonio formamidines **1a,b, 2a,b, 3b and 4a,b**.

Products	δ ^{31}P	δ $^{1}H_{CH=N}$ ($^{3}J_{HP}$)	δ $^{13}C_{C=N}$ ($^{2}J_{CP}$)	δ ^{15}N ($^{1}J_{NP}$; N–P)	δ ^{15}N $^{i}Pr_2N$
1a	54.3	8.14 (18.9)	158.6 (52.7)	−182.2 (44.6)	−243.9
1b	90.0	7.88 (17.4)	158.2 (47.9)	−177.8 (39.4)	−240.1
2a	32.2	8.25 (21.8)	159.3 (7.7)	\	\
2b	56.6	8.41 (19.7)	159.7 (3.4)	−239.6 (37.1)	−216.9
3b	56.0	8.74 (17.1)	160.3 (4.5)	−245.8 (37.7)	−215.6
4a	30.3	7.88 (21.0)	157.8 (6.8)	−235.4 (27.8)	−211.9
4b	51.9	8.75 (17.4)	160.1 (6.4)	−250.5 (32.5)	−213.4

described by the combination of the mesomeric *N*-phosphonio formamidine **A1** and iminium phosphazene **A4** forms depicted in Fig. 3.

Then, we studied the reactivity of compounds **2a**,**b** towards bases. As expected with methyl phosphonium derivatives, deprotonation reactions on **2a**,**b** in THF at −78 °C with ^{t}BuLi led to the formation of the corresponding phosphorus ylides giving rise to signals at δ ^{31}P 40.5 (**5a**, R = Ph) and 60.7 (**5b**, R = ^{i}Pr) ppm (Scheme 2). We were not able to isolate these compounds because of their extreme sensitivity to traces of proton sources to give back the

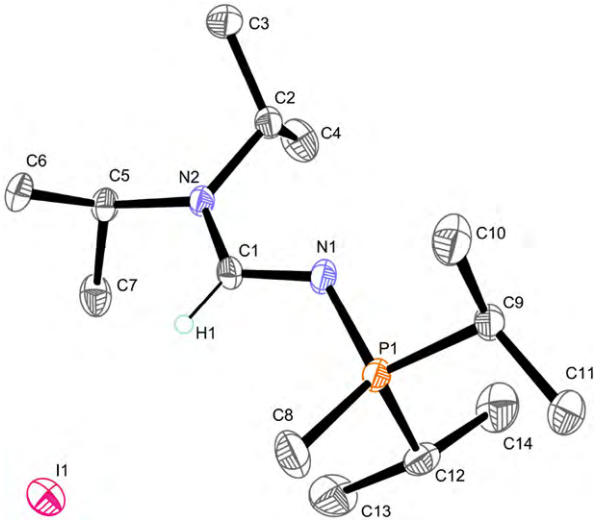


Fig. 1. Molecular structure of **2b**. Hydrogen atoms have been omitted for clarity except for the formamidine hydrogen atom H1.

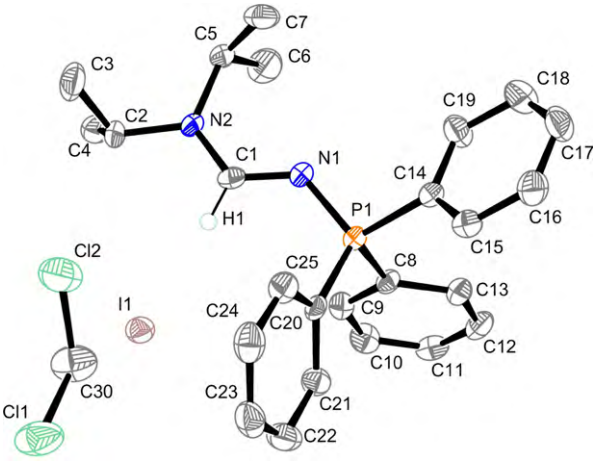


Fig. 2. Molecular structure of **4a**. Hydrogen atoms have been omitted for clarity except for the formamidine hydrogen atom H1.

Table 2
Selected bond lengths [Å] and angles [°] for compounds **1a**, **2b** and **4a**.

	1a	2b	4a
Distances (Å)			
C1–N1	1.289 (3)	1.326 (6)	1.309 (3)
C1–N2	1.341 (3)	1.313 (6)	1.311 (3)
N1–P1	1.697 (2)	1.609 (4)	1.605 (2)
Angles (°)			
N2–C1–N1	123.5 (2)	122.5 (4)	123.7 (2)
C1–N1–P1	115.7 (2)	126.2 (4)	126.45 (19)

starting phosphonium compounds. The phosphorus ylide **5b** was reacted with $[(PhCN)_2Pd(Cl)_2]$ to form complex **6**. The dimeric palladium complex **6** was also prepared in mild conditions starting from **2b**, after addition at room temperature of Ag_2O as a base and $[(PhCN)_2Pd(Cl)_2]$ (Scheme 2). The corresponding silver-ylide intermediate was identified by ^{31}P NMR at 70.6 ppm with a set of signals in the ^1H NMR spectrum at 0.49 ($^2J_{HP}$ = 10.7 Hz) and 8.48 ($^3J_{HP}$ = 21.1 Hz) ppm for the ylidic protons P=CH_2 and the formamidine proton, respectively. The dimeric palladium complex **6** was fully characterized by mass spectrometry, 1D and 2D ^{31}P, ^1H, ^{13}C NMR.

Mass spectrometric analysis is in full agreement with a dimeric structure for **6**. The ^1H and ^{13}C NMR spectra of **6** revealed the presence of the proton and the carbon of the formamidine framework >N–C(H)=N– at 8.94 ($^3J_{HP}$ = 19.8 Hz) and 159.4 ($^2J_{CP}$ = 2.5 Hz) ppm, respectively. In addition to the signals corresponding to the isopropyl substituents connected to the phosphorus atom, the methylene fragment of the ylidic function P–CH_2 appears at 1.74 ($^2J_{HP}$ = 6.8 Hz) ppm in the ^1H NMR spectrum and at –17.7 ($^1J_{CP}$ = 31.7 Hz) ppm in the ^{13}C NMR spectrum, shifted to low frequencies in comparison with the chemical shift of the methyl group in **2b**. X-ray quality crystals for **6** were obtained from a CH_2Cl_2/Et_2O solution at 4 °C (Table 3).

Table 3
Selected bond lengths [Å] and angles [°] for **6**.

Distances (Å)			
C1–N1	1.283 (6)	Pd1–Cl1	2.2845 (15)
C1–N2	1.346 (6)	Pd1–Cl2	2.3397 (15)
N1–P1	1.616 (4)	Pd1–Cl2'	2.4339 (13)
C14–P1	1.769 (5)	Pd1'–Cl2	2.4338 (13)
Pd1–C14	2.004 (5)		
Angles (°)			
N2–C1–N1	121.3 (5)	C14–Pd1–Cl2	90.18 (15)
C1–N1–P1	127.0 (4)	C14–Pd1–Cl2'	175.71 (14)
N1–P1–C8	104.6 (2)	Cl2–Pd1–Cl1	178.93 (6)
P1–C14–Pd1	119.4 (3)	Cl1–Pd1–Cl2'	92.99 (5)
C14–Pd1–Cl1	89.48 (15)	Cl2–Pd1–Cl2'	87.29 (5)

The single crystal X-ray study confirmed the dimeric structure of the ylide complex **6** (Fig. 4). The palladium atoms adopt a square planar geometry. The C14–Pd1–Cl2 and Cl1–Pd1–Cl2' bond angles of, respectively, 90.2 and 93.0° are very similar. The Pd1–Cl2 bond length (2.3397 Å) is slightly longer than the Pd1–Cl1 bond length (2.2845 Å). This slight distortion is not detected in solution as a single set of signals has been observed for the P–CH_2 fragment in the ^{31}P, ^1H, and ^{13}C NMR spectra. The P1–C14 bond length of 1.769 Å is comparable with the value recorded in the starting compound **2b** for the phosphorus–methyl bond (1.782 Å). The Pd1–C14 bond length of 2.004 Å is one of the shortest recorded to date compared to those generally reported in the literature which are in the average range of 2.03 and 2.19 Å [14]. The structural characteristic of the formamidine pattern >N2–C1(H)=N1– regarding the strong localization of the C1=N1 double bond of 1.283 Å with a significative difference of 0.063 Å between the C1–N1 and C1–N2 bond lengths resembles to the one observed for the *N*-phosphino formamidine **1a** but the C1–N1–P1 bond angle of 126.2° in **6** is typical of tetracoordinated *N*-phosphorus formamidine derivatives.

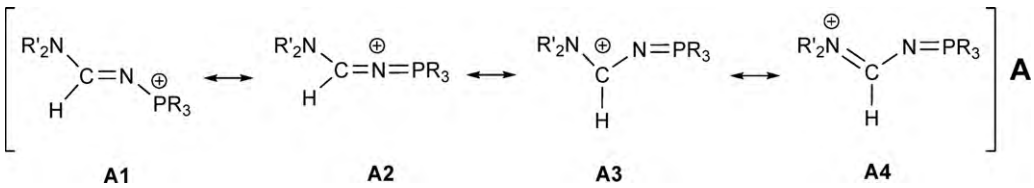
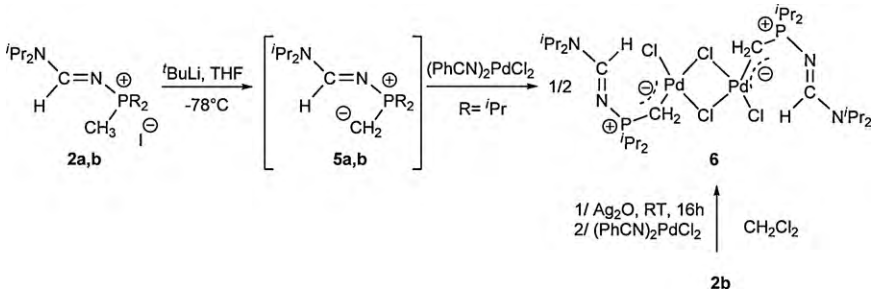


Fig. 3. Most representative mesomeric forms of *N*-phosphonio formamidine derivatives **A**.



Scheme 2. Deprotonation reaction of **2a**,**b** and formation of complex **6**.

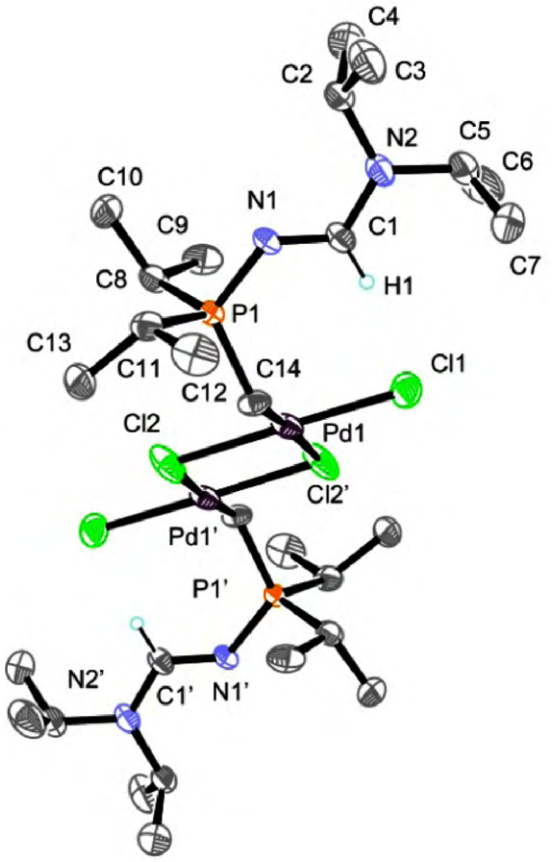


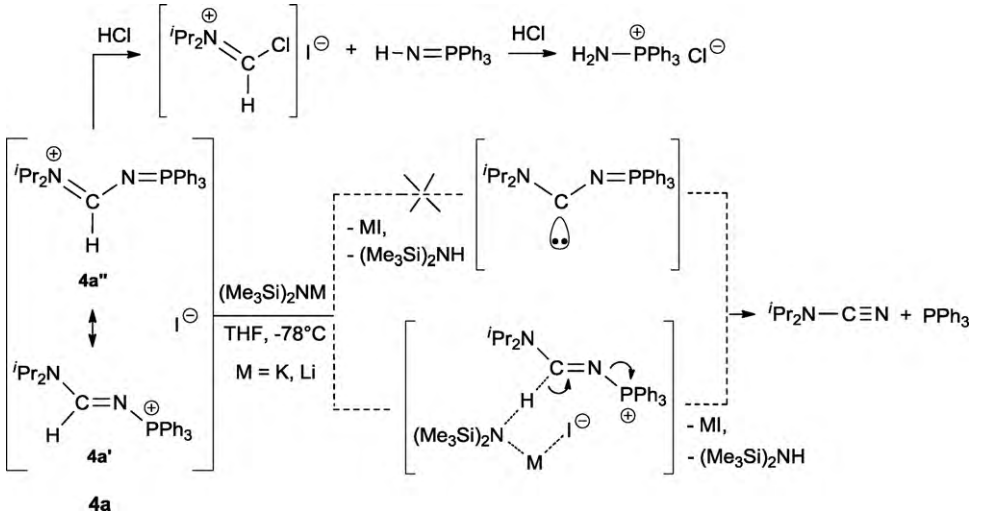
Fig. 4. Molecular structure of **6**. Hydrogen atoms have been omitted for clarity except for the formamidine hydrogen atom H1.

N-phosphonio formamidines of the general structure $[R'_2N–C(H)=N–PR_3]^+X^-$ as **3b** (R = ^{i}Pr) and **4a** (R = Ph) should be good precursors to prepare the corresponding amino-iminophosphorane carbene derivatives $R'_2N–C–N=PR_3$ [15]. A large variety of bases such as ^{t}BuOK, $^i Pr_2NLi$ (LDA), ^{t}BuLi, NaH, $(Me_3Si)_2NM$ (M = K or Li) and mesityllithium (MesLi) have been tested on **3b** without any success. Addition at –78 °C of amides $MN(SiMe_3)_2$ (M = K or Li) to **4a** gave by ^{31}P NMR a signal at –4.0 ppm corresponding to PPh_3. The ^{1}H NMR spectrum displayed a set of signals at 1.27 (d, $^3J_{HH}$ = 6.5 Hz) and 3.23 (h, $^3J_{HH}$ = 6.5 Hz) ppm corresponding to diisopropylcyanamide $^i Pr_2N–C\equiv N$ (Scheme 3).

Identification of PPh_3 and $^i Pr_2N–C\equiv N$ after deprotonation of **4a** and elimination of MI (M = K, Li) cannot be rationalized via the transient formation of the amino-iminophosphorane carbene $^i Pr_2N–C–N=PPh_3$. A concerted mechanism should be invoked in this reaction which induces the abstraction of the proton of the formamidine function with concomittant cleavage of the phosphorus-nitrogen bond. The same reaction recorded in the presence of trapping reagents confirmed that the carbene $^i Pr_2N–C–N=PPh_3$ does not form during the deprotonation reaction of **4a**. It is interesting to note that the proposed mechanism for the formation of PPh_3 and $^i Pr_2N–C\equiv N$ in the deprotonation reactions of **4a** involves the mesomeric phosphonium form **4a'**. In marked contrast, formation of $[Ph_3P–NH_2]Cl$ [16] as the major phosphorus product after addition of HCl to **4a** can be reasonably rationalyzed via the protonation of the basic nitrogen site of the iminophosphorane fragment of the iminium mesomeric form **4a"** followed by the cleavage of the carbon-nitrogen bond to give $Ph_3P=N–H$ and the corresponding stable iminium compound $[^i Pr_2N=C(H)Cl]I$. Addition of a second equivalent of HCl led to the observed amino phosphonium product $[Ph_3P–NH_2]Cl$.

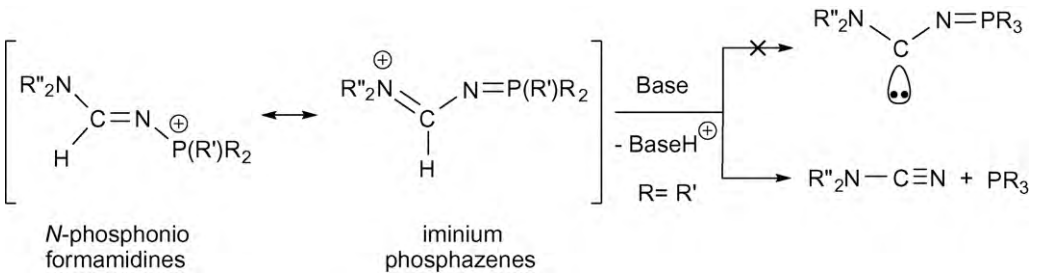
3. Conclusion

We have prepared in good yields a large variety of *N*-phosphonio formamidine derivatives of the general formula $[R"_2N–C(H)=N–P(R')R_2]^+X^-$. The data recorded in solution and the structural parameters of the X-ray analysis revealed that these compounds are best described



Scheme 3. Deprotonation reaction of the *N*-phosphonio formamidine **4a**.

by the combination of the mesomeric *N*-phosphonio formamidine and iminium phosphazene forms.



Deprotonation reactions with ^{t}BuLi on the *N*-phosphonio formamidines $[^{i}Pr_2N{-}C(H){=}N{-}P(CH_3)R_2]^{+}X^{-}$ (R = Ph, ^{i}Pr) led to the formation of the corresponding phosphorus ylides $^{i}Pr_2N{-}C(H){=}N{-}P(CH_2)R_2$. The phosphorus ylide $^{i}Pr_2N{-}C(H){=}N{-}P(CH_2)^{i}Pr_2$ was reacted with $[(PhCN)_2Pd(Cl)_2]$ to give the dimeric complex $[(^{i}Pr_2N{-}C(H){=}N{-}P(CH_2)^{i}Pr_2)Pd(Cl)(\mu\text{-}Cl)]_2$ structurally characterized by X-ray analysis. The reactivity of different organic and inorganic bases on $[^{i}Pr_2N{-}C(H){=}N{-}PR_3]^{+}X^{-}$ (R = Ph, ^{i}Pr) did not lead to the corresponding carbene derivatives $^{i}Pr_2N{-}C{-}N{=}PR_3$. Instead, with R = Ph, the deprotonation reaction occurred via an intramolecular rearrangement to give the cyanamide compound $^{i}Pr_2N{-}C{\equiv}N$ and PPh_3. This new class of *N*-phosphonio compounds $[R"_2N{-}C(H){=}N{-}P(R')R_2]^{+}X^{-}$ will be evaluated as organocatalysts in different organic reactions.

4. Experimental section

All reactions were conducted under an inert atmosphere of dry argon using standard Schlenk-line techniques. Solvents were dried and degassed by standard methods before use. NMR spectra were recorded on a Bruker AV 500, AV 300, DPX 300 or AC200 spectrometers. Chemicals shifts for ^{1}H and ^{13}C are referenced to residual solvent resonances used as an internal standard and reported relative to $SiMe_4$. ^{31}P and ^{15}N NMR chemical shifts are reported relative to external aqueous 85% H_3PO_4 (^{31}P) and CH_3NO_2 (^{15}N) respectively. Melting points were obtained using an Electrothermal Digital Melting Point apparatus and are uncorrected. Mass spectra were recorded on a TSQ7000 Thermo Electron mass spectrometer.

4.1. Preparation of $^{i}Pr_2N{-}C(H){=}N{-}PPh_2(Me)^{+},I^{-}$ (**2a**)

MeI (0.19 mL, 3.05 mmol) was added dropwise to a solution of *N*-phosphino formamidine (**1a**) (0.95 g, 3.05 mmol) in CH_2Cl_2 (10 mL) at −78 °C under argon. The reaction mixture was stirred for 5 minutes at room temperature. The solvent was removed under vacuum, the resulting white powder was washed with pentane (3 × 15 mL). Yield: 90% (1.25 g). M.p. 140–142 °C. FT-IR: ν 1612 cm^{-1}. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 32.2 (s) ppm. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 1.36 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, NCHC*H*$_3$), 1.47 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NCHC*H*$_3$), 2.74 (d, $^{2}J_{HP}$ = 13.2 Hz, 3H, PC*H*$_3$), 4.04 (h, $^{3}J_{HH}$ = 6.8 Hz, 1H, NC*H*CH$_3$), 4.50 (h, $^{3}J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 7.26–7.37 (m, 2H, *H*$_{Ph}$), 7.65–7.71 (m, 4H, *H*$_{Ph}$), 7.75–7.86 (m, 4H, *H*$_{Ph}$), 8.25 (d, $^{3}J_{HP}$ = 21.8 Hz, 1H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ 14.2 (d, $^{1}J_{CP}$ = 63.3 Hz, PCH$_3$), 20.0 (s, NCHCH$_3$), 22.9 (s, NCHC*H*$_3$), 47.4 (s, NCHCH$_3$), 48.2 (s, NCHCH$_3$), 125.6 (d, $^{1}J_{CP}$ = 103.4 Hz, *i*-P*C*$_{Ph}$), 130.1 (d, J_{CP} = 12.8 Hz, *C*H$_{Ph}$), 132,1 (d, J_{CP} = 10.6 Hz, *C*H$_{Ph}$), 134.4 (d, $^{4}J_{CP}$ = 3.1 Hz, *p*-*C*H$_{Ph}$), 159.3 (d, $^{2}J_{CP}$ = 7.7 Hz, *C*H=N) ppm. $C_{20}H_{28}IN_2P$ (454.10): calcd. C 52.87, H 6.21, N 6.17; found C 53.62, H 6.15, N 5.95. MS m/z: 327 [M − I]$^{+}$.

4.2. Preparation of $^{i}Pr_2N{-}C(H){=}N{-}P^{i}Pr_2(Me)^{+},I^{-}$ (**2b**)

MeI (0.19 mL, 3.05 mmol) was added dropwise to a solution of *N*−phosphino formamidine (**1b**) (0.75 g, 3.05 mmol) in CH_2Cl_2 (10 mL) at −78 °C under argon. The reaction mixture was stirred for 5 minutes at room temperature. The solvent was removed under vacuum, the resulting white powder was washed with pentane (3 × 15 mL). Yield: 82% (0.97 g). M.p. 124−126 °C. FT-IR: ν 1616 cm^{-1}. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 56.6 (s) ppm. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 1.19 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HP}$ = 16.5 Hz, 6H, PCHC*H*$_3$), 1.21 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HP}$ = 16.5 Hz, 6H, PCHC*H*$_3$), 1.29 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, NCHC*H*$_3$), 1.32 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, NCHC*H*$_3$), 1.98 (d, $^{2}J_{HP}$ = 11.4 Hz, 3H, PC*H*$_3$), 2.42 (hd, $^{3}J_{HH}$ = 7.1 Hz, $^{2}J_{HP}$ = 10.3 Hz, 2H, PC*H*CH$_3$), 4.09 (h, $^{3}J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 4.16 (h, $^{3}J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 8.41 (d, $^{3}J_{HP}$ = 19.7 Hz, C*H*=N) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ 4.1 (d, $^{1}J_{CP}$ = 46.1 Hz, PCH$_3$), 15.4 (d, $^{2}J_{CP}$ = 3.9 Hz, PCHCH$_3$), 19.7 (s, NCHCH$_3$), 22.5 (s, NCHCH$_3$), 24.3 (d, $^{1}J_{CP}$ = 66.3 Hz, P*C*HCH$_3$), 47.2 (s, NCHCH$_3$), 52.2 (s, NCHCH$_3$), 159.7 (d, $^{2}J_{CP}$ = 3.4 Hz, CH=N) ppm. NMR ^{15}N{^{1}H} (40.6 MHz, d^{8}-toluene): δ = −216.9 (s, N^{i}Pr2), −239.6 (d, $^{1}J_{NP}$ = 37.1 Hz, C=N−P) ppm. $C_{14}H_{32}IN_2P$ (386.14): calcd. C 43.53, H 8.35, N 7.25; found C 43.86, H 8.72, N 7.02 MS m/z: 259 [M − I]$^{+}$.

4.3. Preparation of $^{i}Pr_2N{-}C(H){=}N{-}P^{i}Pr_3^{+},Br^{-}$ (**3b**)

N−phosphino formamidine (**1b**) (0.91 g, 3.73 mmol) was dissolved in 2-bromopropane (5 mL, 53.26 mmol). The reaction mixture was heated at reflux for 18 hours. 2-bromopropane was removed under vacuum, the resulting white powder was washed with pentane (3 × 15 mL). Yield: 86% (1.18 g). M.p. 115−117 °C. FT-IR: ν 1597 cm^{-1}.

$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 56.0 (s) ppm. NMR ^1H (300.1 MHz, $CDCl_3$): δ 1.27 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 15.4 Hz, 18H, PCHCH_3), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 2.99 (hd, $^3J_{HH}$ = 7.2 Hz, $^2J_{HP}$ = 11.7 Hz, 2H, PC*H*CH$_3$), 4.13 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 4.25 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 8.74 (d, $^3J_{HP}$ = 17.1 Hz, C*H*=N) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 16.6 (d, $^2J_{CP}$ = 2.9 Hz, PCHCH_3), 19.6 (s, NCHC*H*3), 22.6 (s, NCHC*H*3), 23.2 (d, $^1J_{CP}$ = 54.1 Hz, P*C*HCH$_3$), 46.4 (s, N*C*HCH$_3$), 51.3 (s, N*C*HCH$_3$), 160.3 (d, $^2J_{CP}$ = 4.5 Hz, H*C*=N) ppm. $^{15}N\{^1H\}$ NMR (50.7 MHz, $CDCl_3$): δ = –215.6 (d, $^3J_{NP}$ = 9.4 Hz, N^{i}Pr2), –245.8 (d, $^1J_{NP}$ = 37.7 Hz, C=N–P) ppm. $C_{16}H_{36}BrN_2P$ (366.18): calcd. C 52.31; H 9.88; N 7.63; found C 52.58; H 9.95; N 7.35. DCI MS (CH_4) m/z: 287 $[M–Br]^+$.

4.4. Preparation of ^{i}Pr$_2$N–C(H)=N–PPh$_3^+$,I$^-$ (4a)

PhI (1.680 mL, 14.99 mmol) and $Pd(OAC)_2$ (0.067 g, 0.30 mmol) were added to a solution of *N*-phosphino formamidine **1a** (3.0 mmol) in toluene (10 mL). The reaction mixture was heated at reflux for 18 hours. The solvent was removed under vacuum, the resulting white powder was washed with pentane (3 × 15 mL). Yield: 80% (1.24 g). M.p. 170–172 °C. FT-IR: ν 1603 cm^{-1}. $^{31}P\{^1H\}$ NMR (121.5 MHz; $CDCl_3$): δ 30.3 (s) ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 1.32 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 1.55 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 4.13 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 4.44 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 7.64–7.82 (m, 15H, H_{Ph}), 7.88 (d, $^3J_{HP}$ = 21.0 Hz, 1H, H*C*=N) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 19.9 (s, NCHCH_3), 23.1 (s, NCHCH_3), 48.5 (s, N*C*HCH$_3$), 51.8 (s, N*C*HCH$_3$), 122.7 (d, $^1J_{CP}$ = 101.9 Hz, *i*-PC$_{Ph}$), 130.1 (d, J_{CP} = 12.8 Hz, *C*H$_{Ph}$), 132.8 (d, J_{CP} = 10.6 Hz, *C*H$_{Ph}$), 134.7 (d, $^4J_{CP}$ = 2.3 Hz, *p*-*C*H$_{Ph}$), 157.8 (d, $^2J_{CP}$ = 6.8 Hz, HC=N) ppm. $^{15}N\{^1H\}$ NMR (50.7 MHz, CD_2Cl_2): δ –211.9 (d, $^3J_{NP}$ = 12.5, N^{i}Pr2), –235.4 (d, $^1J_{NP}$ = 27.8 Hz, C=N–P) ppm. $C_{25}H_{30}IN_2P$ (516.12): calcd. C 58.15; H 5.86; N 5.42; found C 58.46; H 5.99; N 5.23. DCI MS (CH_4) m/z: 389 $[M–I]^+$.

4.5. Preparation of ^{i}Pr$_2$N–C(H)=N–P^{i}Pr$_2$(Ph)$^+$,I$^-$ (4b)

PhI (1.680 mL, 14.99 mmol) and $Pd(OAC)_2$ (0.067 g, 0.30 mmol) were added to a solution of *N*-phosphino formamidine **1b** (3.0 mmol) in toluene (10 mL). The reaction mixture was heated at reflux for 18 hours. The solvent was removed under vacuum, the resulting white powder was washed with pentane (3 × 15 mL). Yield: 28% (0.38 g). M.p. 147–149 °C. FT-IR: ν 1600 cm^{-1}. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 51.9 (s) ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 1.17 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 16.8 Hz, 6H, PCHCH_3), 1.23 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 16.8 Hz, 6H, PCHCH_3), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 6H, NCHCH_3), 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 3.52 (m, 2H, PC*H*CH$_3$), 4.31 (m, 1H, NC*H*CH$_3$), 4.40 (m, 1H, NC*H*CH$_3$), 7.65–7.74 (m, 5H, H_{Ph}), 8.75 (d, $^3J_{HP}$ = 17.4 Hz, 1H, H*C*=N) ppm. ^{13}C {^1H} NMR (75.5 MHz, $CDCl_3$): δ 15.5 (d, $^2J_{CP}$ = 2.9 Hz, PCHCH_3), 15.7 (d, $^2J_{CP}$ = 2.7 Hz, PCHCH_3), 19.8 (s, NCHCH_3), 22.7 (s, NCHCH_3), 22.7 (d, $^1J_{CP}$ = 5.5 Hz, P*C*HCH$_3$), 23.4 (d, $^1J_{CP}$ = 4.3 Hz, P*C*HCH$_3$), 47.0 (s, N*C*HCH$_3$), 52.0 (s, N*C*HCH$_3$), 120.9 (d, $^1J_{CP}$ = 97.5 Hz, *i*-PC$_{Ph}$), 129.4 (d, J_{CP} = 11.5 Hz, *C*H$_{Ph}$), 132.1 (d, J_{CP} = 8.2 Hz, *C*H$_{Ph}$), 133.4 (d, $^4J_{CP}$ = 2.7 Hz, *p*-*C*H$_{Ph}$), 160.1 (d, $^2J_{CP}$ = 6.4 Hz, H*C*=N) ppm. $^{15}N\{^1H\}$ NMR (50.7 MHz, CD_2Cl_2): δ –213.4 (d, $^3J_{NP}$ = 9.0, N^{i}Pr2), –250.5 (d, $^1J_{NP}$ = 32.5 Hz, C=N–P) ppm. $C_{19}H_{34}IN_2P$ (448.15): calcd. C. 50.90, H 7.64, N 6.25; found C. 51.44, H 7.89, N 6.12. DCI MS (CH_4) m/z: 321 $[M–I]^+$.

4.6. Preparation of complex [^{i}Pr$_2$N–C(H)=N–P^{i}Pr$_2$(CH$_2$)PdCl$_2$]$_2$ (6)

Ag_2O (0.512 g, 2.21 mmol) was added to a solution of phosiumfam **2b** (0.854 g, 2.21 mmol) in CH_2Cl_2 (30 mL) at room temperature. After 16 hours stirring, $(PhCN)_2PdCl_2$ (0.424 g, 1.10 mmol) was added to the reaction mixture, which was stirred for 24 hours. The solvent was removed under vaccuum and the crude product was purified on column chromatography using Et_2O as eluent. Complex **6** was obtained as a red powder which was recrystalized from a CH_2Cl_2/Et_2O solution at 4 °C. Yield: 25% (0.24 g). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 64.6 (s) ppm. ^1H NMR (300.1 MHz, $CDCl_3$): δ 1.24 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 11.4, 6H, PCHCH_3), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NCHCH_3), 1.46 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 11.4 Hz, 6H, PCHCH_3), 1.74 (d, $^2J_{HP}$ = 6.8 Hz, 2H, PCH_2), 2.45 (h d, $^3J_{HH}$ = 7.2 Hz, $^2J_{HP}$ = 11.9 Hz, 2H, PC*H*CH$_3$), 3.79 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 4.35 (h, $^3J_{HH}$ = 6.9 Hz, 1H, NC*H*CH$_3$), 8.94 (d, $^3J_{HP}$ = 19.8 Hz, C*H*=N) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ –17.7 (d, $^1J_{CP}$ = 31.7 Hz, PCH$_2$), 15.8 (d, $^2J_{CP}$ = 3.5 Hz, PCHCH_3), 16.5 (s, PCHCH_3), 19.7 (s, NCHC*H*3), 23.2 (s, NCHCH_3), 25.0 (d, $^1J_{CP}$ = 65.4 Hz, P*C*HCH$_3$), 46.1 (s, N*C*HCH$_3$), 50.1 (s, N*C*HCH$_3$), 159.4 (d, $^2J_{CP}$ = 2.5 Hz, HC=N) ppm. DCI MS (NH_3) m/z: 888 $[M + NH_3]^+$.

5. X-ray analysis

Data of compounds **4a** and **6** were collected at low temperature (180 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Instrument Cooler Device. Data of compound **2b** were collected at low temperature (180 K) on a IPDS STOE diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92 [17], and refined by means of least-squares procedures on a F2 with the aid of the program SHELXL97 [18] included in the softwares package WinGX version 1.63 [19]. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography [20]. All hydrogens atoms were geometrically placed and refined by using a riding model. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: w = 1/[σ2(Fo2) + (aP)2 + bP] where P = (Fo2+2Fc2)/3. Drawing of molecule are performed with the program ORTEP32 [21] with 30% probability displacement ellipsoids for non-hydrogen atoms.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.crci.2010.06.017.

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