



Note

N,N' and N,O chelated phosphonium cations containing aminotroponimate or aminotroponate units

Lucian-Cristian Pop^{a,b}, Nadia Katir^a, Annie Castel^{a,*}, Luminita Silaghi-Dumitrescu^{b,*,1}, Fabien Delpech^a, Ioan Silaghi-Dumitrescu^b, Heinz Gornitzka^a, Desmond MacLeod-Carey^c, Nathalie Saffon^d^a Laboratoire Hétérochimie Fondamentale et Appliquée, UMR/CNRS 5069, Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex 9, France^b Babes-Bolyai University, 1, Kogalniceanu Street, Cluj-Napoca, Romania^c Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306 Correo 22, Santiago, Chile^d Structure Fédérative Toulousaine en Chimie Moléculaire (FR2599), Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex 09, France

ARTICLE INFO

Article history:

Received 27 November 2008

Received in revised form 15 January 2009

Accepted 16 January 2009

Available online 22 January 2009

Keywords:

Phosphorus

N,N ligand

N,O ligand

Chelates

ABSTRACT

New phosphonium cations stabilized by bidentate monoanionic *N*-isopropyl-2-(isopropylamino)troponimate or 2-(isopropylamino)troponate units have been synthesized. These complexes were characterized by ³¹P, ¹H and ¹³C NMR spectroscopies, and the molecular structures were determined by X-ray crystallography. These data indicate the formation of N,N'- and N,O-chelate derivatives having three-coordinate phosphorous atoms included in planar heterobicycles. Moreover, computational studies support the presence of high delocalization of the positive charge into the π-conjugated carbon backbone and of the high-lying phosphorus lone-pair orbital.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

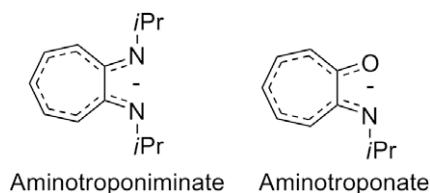
Pnictogenium cations, like other low coordinate Group 15 elements, are conspicuous by virtue of their expected ambiphilic (Lewis acid and base) properties. They have attracted steady interest since the discovery of the first stable phosphonium ion in 1964 [1] both for fundamental purposes and for applications in the design of novel catalysts [2]. The reaction of a phosphonium cation with an organometallic fragment having an appropriate leaving ligand (carbonyl, phosphine, acetonitrile) represents formally the simplest method to generate a cationic phosphonium complex and holds the promise for the generalization of this direct complexation pathway. However, known stable phosphonium cations are limited in number and in variety [3]. Likewise, the range of phosphonium ligands in cationic complexes remains confined quasi-exclusively to diamino, aminoalkoxy or dialkoxy phosphonium moieties [3], despite renewed interest in the phosphonium group as a strong π-acidic ligand in the context of the preparation of electrophilic late transition-metal catalysts [2]. Recently, the use of a β-diketiminato ligand has opened up the possibilities for the preparation of new types of stable phosphonium cations [4]. How-

ever, this approach suffers from a lack of generality since the preparation of a N,N'-chelated phosphonium cation supported by a β-diketiminato ligand hinges on the use of: (i) an electronegative substituent (e.g. C₆F₅) at the nitrogen atoms and/or (ii) of an alkyl substituent at the γ-carbon of the β-diketiminato to circumvent phosphorus substitution at this site. As a part of our ongoing studies of strategies to stabilize low-coordinate phosphorus atom [5], we identified the monoanionic ligands aminotroponimate and aminotroponate (Scheme 1) as highly promising candidates for stabilizing phosphonium ions.

Aminotroponimates ([ATI]⁻) are a well known class of ligands which have found extensive use in coordination chemistry leading to a large number of transition-metal and main-group complexes [6]. On one hand, this ligand displays heteroatom bonding and a highly conjugated 10 π-electron system that should allow charge delocalization when incorporating the pnictogenium atom in the π-electron backbone. On the other hand, and in marked contrast to the β-diketiminato scaffold, [ATI]⁻ is expected to form stable five-membered chelate rings and its anticipated fused ring structure should disfavor side reactions analogous to those observed in the β-diketiminato system. By contrast, aminotroponates ([AT]⁻), which may formally be considered as a combination of amido and carbonyl donors, have been much less investigated. Only a few aminotroponate complexes of main-group [7] and transition-metals [8] are known. However, in both cases the coordination chemistry of these ligands remains totally unexplored for

* Corresponding author. Fax: +33 5 61 55 82 04.

E-mail addresses: castel@chimie.ups-tlse.fr (A. Castel), lusi@chem.ubbcluj.ro (L. Silaghi-Dumitrescu).¹ Fax: +40 264 59 19 06.



Scheme 1.

electron-rich elements from Groups 15–17. Here we describe the synthesis, characterization and a computational study of novel chlorophosphonium cations incorporating an aminotroponimine or an aminotroponate ligand.

2. Results and discussion

Two different routes were envisaged starting from trichlorophosphine: a nucleophilic substitution reaction by an aminolithiated derivative and a base-induced dehydrohalogenation reaction (Scheme 2).

Firstly, the addition of one equivalent of *n*BuLi to a diethyl ether solution of *N*-isopropyl-2-(isopropylamino)troponimine [9] (*i*Pr₂ATI)H **1** at 0 °C afforded the transient lithiated compound which in turn reacted with PCl₃ (Scheme 2a). The ³¹P NMR analysis of the reaction mixture indicated two products which displayed resonances at 134.47 ppm and 160.95 ppm. Secondly, in sharp contrast, the reaction of PCl₃ with a mixture of triethylamine and (*i*Pr₂ATI)H in toluene at room temperature for 3 h yielded selectively the compound which exhibited a signal at 134.47 ppm (Scheme 2b). Single crystals suitable for X-ray crystallographic analysis were grown from a dichloromethane solution at –30 °C. The molecular representation (Fig. 1) shows unambiguously the formation of the *N,N'*-chelated chlorophosphonium cation **2a**. The ³¹P chemical shift of δ 134.47 ppm is lower than the values (200–260 ppm) typically found for other *N*-heterocyclic phosphonium cations [10] presumably because of the delocalization of the positive charge on the ligand backbone. Analogously, the ¹H NMR spectrum of **2a** exhibits resonances for the ring protons that are significantly shifted downfield (Δδ: 2.00 ppm) compared to those of the starting ligand **1**. A similar effect (increased conjugation of π-electrons in the newly formed metallacycles), but less pronounced, has been already observed in the case of the isovalent germanium(II) aminotroponimine complex (*i*Pr₂ATI)GeCl [11].

Concerning the second product **2b**, the ³¹P NMR resonance (δ 160.95) is in the typical region for aminodichlorophosphine [12]. The simultaneous formation of both dissociated and non-dissociated

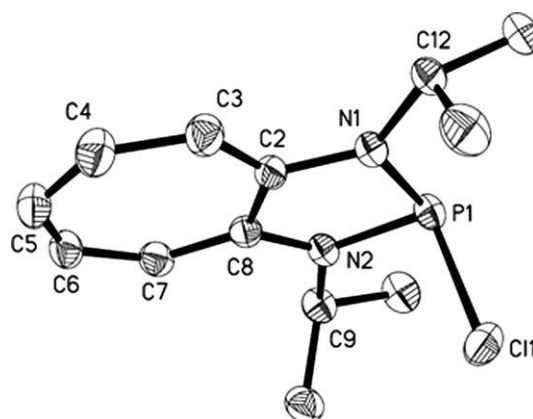
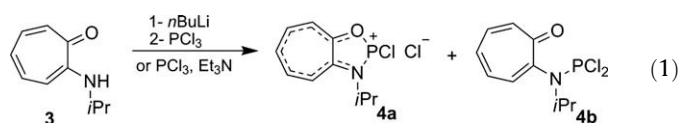


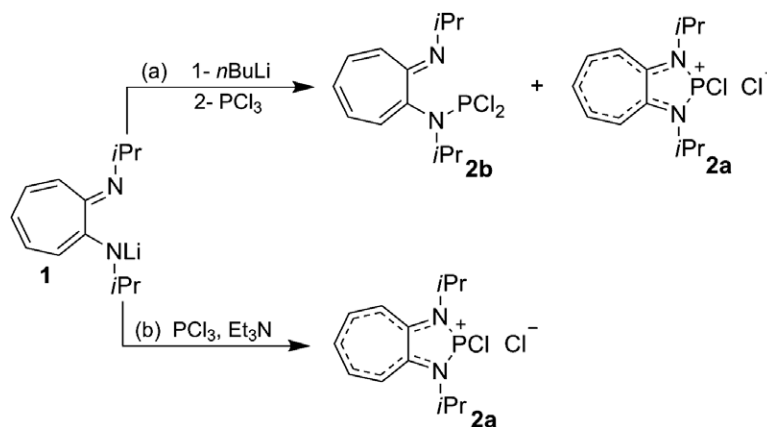
Fig. 1. Molecular structure of the cationic part of **2a** (50% probability level for the thermal ellipsoids). All H atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] are: P(1)–N(1) 1.6969(13), P(1)–N(2) 1.7075(13), P(1)–Cl(1) 2.1543(6), C(7)–C(8) 1.396(2), C(2)–C(3) 1.392(2), C(3)–C(4) 1.390(2), C(4)–C(5) 1.390(3), C(5)–C(6) 1.387(3), C(6)–C(7) 1.385(2); N(2)–P(1)–N(1) 88.88(6), N(1)–P(1)–Cl(1) 101.70(5), N(2)–P(1)–Cl(1) 100.41(5), C(2)–N(1)–P(1) 114.94(10), C(8)–N(2)–P(1) 114.84(10).

ated forms has been already reported but not clearly evidenced with *N,N,N'*-trimethylethylenediamine [13] as substituent. An equilibrium between covalent and ionic compounds has been suggested with displacement to covalent species upon heating [13a]. In our case, the cationic form **2a** seems to be more stable than **2b** probably due to the presence of a conjugated backbone.

For comparison, we tested the coordinating properties of 2-(isopropylamino)troponone ((*i*PrAT)H **3** toward the phosphorous atom. Regardless of the procedure used (Eq. (1)), a mixture of two compounds **4a** and **4b** (³¹P NMR: δ 155.70 ppm and 171.01 ppm, respectively) was always obtained with ratios varying from 1:1 to 2:1.



Yellow crystals were isolated by slow crystallization from dichloromethane in the case of the dehydrohalide coupling reaction, and structurally identified as the cationic form **4a**. However, it was more unstable than the *N,N'*-chelated analogue **2a**, particularly in solution with formation of ligand **3**. Moreover, compared to



Scheme 2.

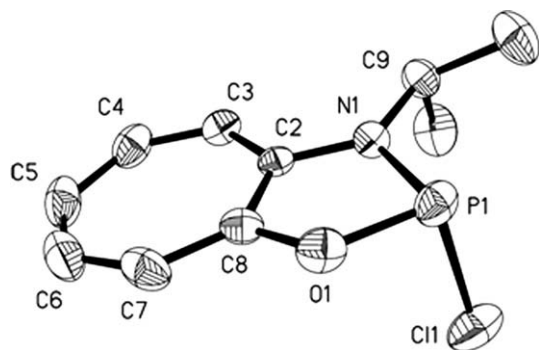


Fig. 2. Molecular structure of cationic part of **4a** (50% probability level for the thermal ellipsoids). All H atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] are: P(1)—O(1) 1.646(2), P(1)—N(1) 1.732(2), P(1)—Cl(1) 2.1262(12), C(2)—C(3) 1.406(4), C(2)—C(8) 1.423(4), C(7)—C(8) 1.364(4), C(6)—C(7) 1.394(4), C(5)—C(6) 1.364(4), C(4)—C(5) 1.397(5); O(1)—P(1)—N(1) 89.95(11), O(1)—P(1)—Cl(1) 97.88(9), N(1)—P(1)—Cl(1) 97.63(9), C(2)—N(1)—P(1) 112.82(18), C(2)—O(1)—P(1) 114.83(18).

2a, the ^{31}P chemical shift (δ 155.70 ppm) is slightly shifted to high fields, probably due to less effective charge dispersion, although a similar downfield shift of the ring protons was observed in the ^1H NMR spectrum. Compound **4b** has a signal at 171.01 ppm in the expected region for such a dichlorophosphine [12].

The molecular structures of **2a** and **4a** (including selected bonds and angles) are shown in Figs. 1 and 2. Both compounds show the same general features in the solid state – both consist of separated ion-pairs with chlorine as anion. Nearest distances between the ions are $\text{Cl}\cdots\text{H}(\text{cation})$ distances 2.54 Å (**2a**) and 2.64 Å (**4a**), and shortest distances between the anions and the phosphorus atoms are 5.36 Å and 3.05 Å for **2a** and **4a**, respectively. The cationic parts are formed by PCI units, which are stabilized by the chelating ligand systems. The three-coordinated phosphorus atoms adopt pyramidal geometries (the sum of the angles are 291.0° (**2a**) and 285.5° (**4a**)), with the bonded chlorine atoms in approximately orthogonal positions towards the heterobicyclic planes. In the case of **2a**, the P—N distances, 1.697(1) and 1.708(1) Å, are in good agreement with the values observed by Cowley et al. in cyclic phosphonium cations [4,14]. In the asymmetric compound **4a**, the P—O bond (1.646(2) Å) is in between a typical P—O single bond (1.71 Å) and a P=O double bond (1.40 Å) [15], which confirms the very strong covalent bond character of this formally donor bond. Consequently, the C—O bond (1.365 Å) is about 10 pm longer than in the neutral corresponding tropone (1.245 Å) [16]. The P—N distance is slightly longer (1.732(2) Å) compared to those of **2a**. These strong interactions between the formally P^+ centers and the chelating systems are also reflected by the C—C bonds in the carbon backbones. Such small differences between the C—C bond distances combined with the nearly perfect planarity of both the two cyclic systems and the geometries around the nitrogen atoms are strong evidence for a high degree of delocalization of the electrons in the systems, which means delocalization of the positive charge.

In order to gain more insight about the electronic state of these cations, Density Functional Theory (DFT) calculations were done on

phosphonium cations **2a** and **4a** using the Amsterdam Density Functional package, ADF 2005 [17]. The input parameters for the geometry optimization were generated from the X-ray crystallographic data of **2a** and **4a**. The HOMO are localized into the bicyclic systems and the heteroatoms (N, O, Cl), whereas the LUMO are more localized on the seven-membered cycle and less on the heterocycle. The phosphorous lone-pair resides in HOMO-1 orbitals that are at 0.79 and 0.76 eV below their corresponding HOMO.

The NICS (Nucleus-Independent Chemical Shifts) values [18] calculated at the centre of the rings (NICS(0)) and 1.0 Å above and below the ring (NICS(1)) for the two systems (**2a**, **4a**) are given in Table 1. NICS(0) are influenced by the sigma bonds so the NICS(1) values are considered as better indicators of π -electron delocalization. These data show that the electron delocalization in the seven-membered ring is similar in **2a** and **4a**; however, the five-membered ring exhibits slight differences, displaying somewhat lower NICS(1) values for **4a** than in **2a**. Thus, the π -electrons in the five-membered ring of **4a** are less delocalized, in accordance with the bond lengths in this ring and the chemical shifts in the ^{31}P NMR. The out-of-plane component of the NICS(1) value, NICS(1)_{zz} might be considered as another indicator of the electron delocalization [19]. Again, the five-membered ring of **4a** exhibit lower values for NICS(1)_{zz} in accordance with less efficient π -electron delocalization.

These computational studies and the X-ray structural data indicate an extensive delocalization of the positive charge over the seven-membered ring cycle suggesting that these species could be formally better described as chlorophosphines bearing a cationic substituent.

3. Conclusion

An easy and direct route to the first phosphonium cations supported by N,N' or N,O-chelation derived from a tropolone scaffold was achieved. The presence of a π -unsaturated backbone in the aminotroponimate and aminotroponate ligands not only prevents the competitive γ -carbon substitution previously observed for diketiminate ligand but also allows a complete positive charge delocalization on the seven-membered cycles. This result was confirmed by the X-ray structural data and DFT calculations. The expected Lewis amphoterism which is illustrated on the one hand, by the high-lying phosphorus lone-pair orbital (HOMO-1), and on the other hand, by the delocalized positive charge opens up new perspectives for the involvement of these ambiphilic species as valuable ligands for new catalysts.

4. Experimental

4.1. General methods

All reactions were done under Argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. NMR spectra were recorded with Bruker Avance II 300 spectrometers with different frequencies: ^1H (300.13 MHz), ^{13}C (75.47 MHz), ^{31}P (121.49 MHz).

Table 1
B3LYP/6-31G(d,p) calculated NICS and NICS_{zz} values for **2a** and **4a**.

Distance from the center (Å)	2a		4a		2a		4a	
	Seven-membered ring		Five-membered ring		Seven-membered ring		Five-membered ring	
1	NICS	NICS _{zz}	NICS	NICS _{zz}	NICS	NICS _{zz}	NICS	NICS _{zz}
0	-7.49	-17.07	-4.04	-11.17	-7.64	-17.90	-3.28	-11.25
1 ^a	-5.40	-6.21	-6.81	-26.21	-5.49	-6.37	-6.36	-26.17
	-7.56	-16.84	-6.47	-10.75	-7.75	-17.12	-5.07	-8.47

^a Face opposite to the PCI bond.

Mass spectra were measured with a Hewlett-Packard HP 5989A in the electron impact mode (70 eV). Melting points were measured on a Leitz microscope or Electrothermal apparatus (capillary). Elemental analyses were done by the Centre de Microanalyse de l'École Nationale Supérieure des Ingénieurs en Arts Chimiques Et Technologiques.

4.2. Synthesis of **2a**

To a mixture of (*i*Pr₂-ATI)H **1** (0.52 g, 2.5 mmol) and Et₃N (0.26 g, 2.5 mmol) in toluene (15 mL) was added PCl₃ (0.35 g, 2.5 mmol) in toluene (5 mL). The mixture was stirred for 3 h. After filtration, volatiles were removed under vacuo and the residue was dissolved in CH₂Cl₂. The saturated solution was placed in a freezer at –30 °C for 7 days to yield yellow crystals of **2a** (0.40 g, 52%). Mp: 230 °C. ³¹P {¹H} (121 MHz, CDCl₃): δ 134.47 ppm. ¹H NMR (300 MHz, CDCl₃): δ 1.61 (d, d, ³J = 6.6 Hz, ⁴J_{HP} = 1.7 Hz, 12H, CH–CH₃); 4.77 (sept, d, ³J = 6.6 Hz, ³J_{HP} = 10.9 Hz, 2H, CH–CH₃); 7.88 (t, d, ³J = 9.6 Hz, ⁶J_{HP} = 3.4 Hz, 1H, H₅); 8.43 (t, ³J = 9.7 Hz, 2H, H_{4,6}); 8.55 (d, d, ³J = 11.0 Hz, ⁴J_{HP} = 2.5 Hz, 2H, H_{3,7}). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 21.89 (d, ³J_{CP} = 12.6 Hz, CH–CH₃); 50.91 (d, ²J_{CP} = 12.6 Hz, CH–CH₃); 127.83 (d, ³J_{CP} = 5.7 Hz, C_{3,7}); 136.99 (d, ⁵J_{CP} = 5.0 Hz, C₅); 144.56 (d, ⁴J_{CP} = 5.7 Hz, C_{4,6}); 155.57 (d, ²J_{CP} = 12.7 Hz, C_{2,8}). EI-MS: *m/z* 270 [M⁺–Cl+H, 16%], 235 [M⁺–2Cl, 42%]. Anal. C₁₄H₂₁Cl₄N₂P (390.11): Calc.: C, 43.10; H, 5.43; N, 7.18. Found: C, 43.29; H, 6.08; N, 7.45.

4.3. Reaction of (*i*Pr₂ATI)Li with PCl₃

A 1.6 M solution of *n*BuLi in hexanes (2.0 mmol) was slowly added to a cooled (0 °C) solution of **1** (0.34 g, 1.6 mmol) in diethyl ether (30 mL). The suspension was warmed to room temperature and stirred for 30 min, and it was slowly added to a cooled (–75 °C) solution of PCl₃ (0.22 g, 1.6 mmol) in diethyl ether (20 mL). The mixture was allowed to reach room temperature and stirred for 3 h. After filtration, the remaining solid was washed with diethyl ether and dried under vacuo, leading to a yellow powder. The ¹H spectrum of the crude product indicated the presence of **2a** (20%) and **2b** (80%). **2b**: NMR ³¹P {¹H} (121 MHz, CDCl₃): δ 160.95. ¹H NMR (300 MHz, CDCl₃): δ 1.51 (d, ³J = 6.3 Hz, 6H, CH–CH₃); 1.54 (d, ³J = 6.3 Hz, 6H, CH–CH₃); 3.98 (sept, ³J = 6.8 Hz, 1H, CH–CH₃); 4.02 (sept, ³J = 6.8 Hz, 1H, CH–CH₃); 6.80–6.87 (m, 2H, C₇H₅); 7.35–7.44 (m, 1H, C₇H₅); 7.89 (t, ³J = 9.0 Hz, 1H, C₇H₅); 8.30–8.41 (m, 1H, C₇H₅). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 21.20 and 21.35 (CH–CH₃); 48.02 and 49.03 (CH–CH₃); 115.80 (C_{3,7}); 125.09 (C₅); 140.50 (C_{4,6}); 150.64 and 151.47 (C_{2,8}). EI-MS: *m/z* 304 [M⁺, 16%], 289 [M⁺–CH₃, 21%], 269 [M⁺–Cl, 7%].

4.4. Synthesis of **4a**

Using the same procedure described for **2a**, **3** (0.40 g, 2.5 mmol), Et₃N (0.26 g, 2.5 mmol) and PCl₃ (0.34 g, 2.5 mmol) in toluene (15 mL) gave a mixture of **4a** (45%) and **4b** (55%) (% determined from the ¹H NMR spectrum). A slow crystallization from dichloromethane at –30 °C gave **4a** as yellow crystals (0.31 g, 48%). NMR ³¹P {¹H} (121 MHz, CDCl₃): δ 155.70 ppm. ¹H NMR (300 MHz, CDCl₃): δ 1.71 (d, d, ³J = 6.6 Hz, ⁴J_{PH} = 2.2 Hz, 6H, CH–CH₃); 4.69 (sept, ³J = 6.9 Hz, 1H, CH–CH₃); 8.13–8.15 (m, 1H, H₅); 8.28–8.35 (m, 2H, H_{4,6}); 8.65 (d, l, ³J = 5.5 Hz, 2H, H_{3,7}). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 21.18 (d, ³J_{CP} = 11.3 Hz, CH–CH₃); 51.12 (d, ²J_{CP} = 8.3 Hz, CH–CH₃); 128.62 (d, ³J_{CP} = 3.1 Hz, C₇); 130.34 (d, ³J_{CP} = 2.9 Hz, C₃); 138.79 (d, ⁵J_{CP} = 2.0 Hz, C₅); 143.55 (d, ⁴J_{CP} = 2.6 Hz, C₆); 147.57 (d, ⁴J_{CP} = 2.1 Hz, C₄); 156.39 (d, ²J_{CP} = 4.6 Hz, C₂); 166.41 (d, ²J_{CP} = 15.5 Hz, C₈). **4a** is very sensitive to hydrolysis and oxidation. Reproducible analyses could not be obtained.

4.5. Reaction of (*i*PrAT)Li with PCl₃

Using the same procedure described for **2b**, (2.0 mmol) of *n*BuLi (1.6 M) in hexanes, **3** (0.30 g, 1.8 mmol), and PCl₃ (0.28 g, 2.0 mmol) in diethyl ether (15 mL) gave a mixture of **4a** (65%) and **4b** (35%) identified by ¹H NMR analyses. **4b**: ³¹P {¹H} (121 MHz, CDCl₃): δ 171.01 ppm. ¹H NMR (300 MHz, CDCl₃): δ 1.36 (d, ³J = 6.4 Hz, 6H, CH–CH₃); 3.98–4.08 (m, 1H, CH–CH₃); 7.30 (t, ³J = 12.0 Hz, 1H, H₅); 7.31 (d, ³J = 9.4 Hz, 1H, H₃); 7.62 (t, d, ³J = 10.3 Hz, ⁵J = 1.0 Hz, 1H, H₄); 7.80 (d, d, ³J = 9.3 Hz, ³J = 10.0 Hz, 1H, H₆); 8.48 (d, ³J = 10.6 Hz, 1H, H₇). ¹³C {¹H} NMR (75 MHz, CDCl₃): δ 21.79 (CH–CH₃); 45.81 (CH–CH₃); 120.46, 125.95, 130.85 (C_{3,5,7}); 140.90, 142.56 (C_{4,6}); 155.33 (C₂); 163.25 (C₈).

4.6. X-ray structural determination

Structural data were collected at low temperature (173 K) using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods [20] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F² [21]. **2a**: C₁₄H₂₁Cl₄N₂P, M = 390.00, triclinic P $\bar{1}$, a = 9.2570(6) Å, b = 9.6340(7) Å, c = 12.4169(9) Å, α = 87.538(1)°, β = 70.060(1)°, γ = 62.132(1)°, V = 911.17(11) Å³, Z = 2, 5306 reflections (3658 independent, R_{int} = 0.0117) were collected. Largest diff. peak and hole: 0.446 and –0.243 eÅ^{–3}, R₁ (for I > 2σ(I)) = 0.0289 and wR₂ = 0.0749 (all data) with R₁ = ∑ ||F_o| – |F_c|| / ∑ |F_o| and wR₂ = (∑ w(F_o² – F_c²)² / ∑ w(F_o²)^{0.5}). **4a**: C₁₁H₁₄Cl₄NOP, M = 349.00, monoclinic P2₁/c, a = 7.0170(7) Å, b = 11.4932(12) Å, c = 19.630(2) Å, β = 92.484(2)°, V = 1581.7(3) Å³, Z = 4, 9066 reflections (3260 independent, R_{int} = 0.0501) were collected. Largest diff. peak and hole: 0.494 and –0.444 eÅ^{–3}, R₁ (for I > 2σ(I)) = 0.0476 and wR₂ (all data) = 0.1009.

4.7. Details on computations

Density functional calculations were made with the Amsterdam Density Functional package, ADF 2005 [22]. Structures were fully optimized via analytical energy gradient techniques employing the local density approximation (LDA) [23] and the generalized gradient approximation (GGA) method using Vosko-Wilk-Nusair local exchange correlations [24] with nonlocal exchange corrections by Becke [25] and nonlocal electronic correlations by Perdew [26]. We used uncontracted type IV basis sets using triple-ζ accuracy sets of Slater-type orbitals [27] (STO) with a single polarization function added for the main group elements (2p on H, 3d on C, N and O and 4d on P). Frozen core approximations [28] were applied to the inner orbitals of the constituent atoms: the C, N, O core up to 1s and P up to 2p.

Acknowledgments

We thank the ECONET Program (n° 18824SD) and “Le comité mixte interuniversitaire franco-marocain” (PHC: n° MA/05/123) for financial support.

Appendix A. Supplementary data

CCDC 705298 and 705299 contain the supplementary crystallographic data for **2a** and **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.01.022.

References

- [1] K. Dimroth, P. Hoffman, *Angew. Chem. Int. Ed. Engl.* 3 (1964) 384.
- [2] (a) N.J. Hardman, M.B. Abrams, M.A. Pribisko, T.M. Gilbert, R.L. Martin, G.J. Kubas, R.T. Baker, *Angew. Chem. Int. Ed. Engl.* 43 (2004) 1955–1958;
(b) H.A. Spinney, G.P.A. Yap, I. Korobkov, G. DiLabio, D.S. Richeson, *Organometallics* 25 (2006) 3541–3543.
- [3] (a) H. Nakazawa, *Adv. Organomet. Chem.* 50 (2004) 108–143;
(b) D. Gudat, *Coord. Chem. Rev.* 163 (1997) 71–106.
- [4] D. Vidovic, Z. Lu, G. Reeske, J.A. Moore, A.H. Cowley, *Chem. Commun.* (2006) 3501–3503.
- [5] (a) R. Menye Biyogo, F. Delpech, A. Castel, P. Rivière, H. Gornitzka, *Angew. Chem. Int. Ed. Engl.* 42 (2003) 5610–5612;
(b) R. Menye-Biyogo, F. Delpech, A. Castel, V. Pimienta, H. Gornitzka, P. Rivière, *Organometallics* 26 (2007) 5091–5101.
- [6] (a) P.W. Roesky, *Chem. Soc. Rev.* 29 (2000) 335–345;
(b) H.V.R. Dias, Z. Wang, W. Jin, *Coord. Chem. Rev.* 176 (1998) 67–86.
- [7] D. Pappalardo, M. Mazzeo, P. Montefusco, C. Tedesco, C. Pellicchia, *Eur. J. Inorg. Chem.* (2004) 1292–1298.
- [8] (a) S. Dehnen, M.R. Bürgstein, P.W. Roesky, *J. Chem. Soc., Dalton Trans.* (1998) 2425–2430;
(b) F.A. Hicks, M. Brookhart, *Organometallics* 20 (2001) 3217–3219;
(c) N. Meyer, K. Löhnwitz, A. Zulus, P.W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* 25 (2006) 3730–3734;
(d) S. Datta, P.W. Roesky, S. Blechert, *Organometallics* 26 (2007) 4392–4394;
(e) N. Meyer, R. Rüttinger, P.W. Roesky, *Eur. J. Inorg. Chem.* (2008) 1830–1833.
- [9] H.V.R. Dias, W. Jin, R.E. Ratcliff, *Inorg. Chem.* 34 (1995) 6100–6105.
- [10] (a) A.H. Cowley, R. Kemp, *Chem. Rev.* 85 (1985) 367–382;
(b) M. Sanchez, M.R. Mazzières, L. Lamandé, R. Wolf, in: M. Regitz, O. Scherer (Eds.), *Phosphorous Chemistry*, Georg Thieme Verlag, Stuttgart, 1990, pp. 129–148.
- [11] H.V.R. Dias, Z. Wang, *J. Am. Chem. Soc.* 119 (1997) 4650–4655.
- [12] R.B. King, N.D. Sadani, *Synth. React. Inorg. Met.-Org. Chem.* 15 (1985) 149–153.
- [13] (a) W. Becker, D. Schomburg, P.G. Jones, R. Schmutzler, *Phosphorus Sulfur Silicon* 49/50 (1990) 109–114;
(b) T. Kaukorat, I. Neda, R. Schmutzler, *Coord. Chem. Rev.* 137 (1994) 53–107;
(c) N. Burford, P.J. Ragona, *J. Chem. Soc., Dalton Trans.* (2002) 4307–4315.
- [14] G. Reeske, C.R. Hoberg, N.J. Hill, A.H. Cowley, *J. Am. Chem. Soc.* 128 (2006) 2800–2801.
- [15] L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.
- [16] P.W. Roesky, M.R. Bürgstein, *Inorg. Chem.* 38 (1999) 5629–5632.
- [17] ADF2006.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <<http://www.scm.com/>>, Methods and results are presented in Supporting Information.
- [18] (a) P.v.R. Schleyer, C. Maerker, A. Dransfeld, H.N.J.R. Jiao, E. Hommes, *J. Am. Chem. Soc.* 118 (1996) 6317–6318;
(b) P.v.R. Schleyer, H. Jiao, v.E. Hommes, V.G. Malkin, O.L. Malkina, *J. Am. Chem. Soc.* 119 (1997) 12669–12670.
- [19] C. Corminboeuf, T. Heine, G. Seifert, P.v.R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* 6 (2004) 273–276.
- [20] G.M. Sheldrick, *Acta Cryst. A* 46 (1990) 467–473.
- [21] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- [22] G. teVelde, E.J. Baerends, *J. Comput. Phys.* 99 (1992) 84–98.
- [23] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133–A1138.
- [24] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200–1211.
- [25] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098–3100.
- [26] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822–8824.
- [27] J.G. Snijders, P. Vernooijs, E.J. Baerends, *At. Nucl. Data Tables* 26 (1982) 483–509.
- [28] E.J. Baerends, D.E. Ellis, P. Ros, *Chem. Phys.* 2 (1973) 41–51.