Heteroatom Chemistry
Volume 3, Number 2, 1992

Lewis Acid Properties of Phosphenium and Arsenium Cations: Study of their Adducts with Pyridine

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Received 2 May 1991.

ABSTRACT

In the growing field of dicoordinated Group 15 cations, the quantitative study of the Lewis acid properties of phosphenium or arsenium cations has not yet been undertaken. Moreover, there are only a few described examples of syntheses of arsenium cations. The aim of this work is to enhance this series and to develop a quantitative comparative study of their complexation with Lewis bases such as pyridine. The observation of the ^{13}C *NMR C-4 variation in the pyridine ring is a good probe to obtain the apparent equilibrium constant* K_c *and thus a Lewis acidity scale. Phosphenium cations are more acidic than arsenium cations.*

INTRODUCTION

Phosphenium and arsenium cations (R_2P^+ and R_2As^+) are six valence electron moeties with one vacant orbital and a lone pair. They can thus behave as both Lewis acids and bases, and their amphoteric character has been investigated [1]. Their acidic character was first described by Schultz and Parry [2a] by the formation of phosphenium adducts where phosphanes act as Lewis bases. According to another point of view, diphosphonium ions may also belong to this class of products [2b]. Other examples were recently described [3] and studied by ^{31}P NMR. They are essentially characterized by a large shift between the free and complexed form of the phosphenium ion and by the great value of the $^1J_{PP}$ coupling constant (350–450 Hz).

To our knowledge, no arsenium adduct has been described. Burford et al. [4] recently provided evidence for the formation of a dithiaarsenium dimer by coordination of a sulfur atom on arsenic. Moreover, we were not able to find in the literature a quantitative description of the Lewis acid character of dicoordinated phosphorus or arsenic cations. Therefore, we tried to study the Lewis acidity of these compounds toward bases such as pyridine, triethylamine, or triphenyl- and tributylphosphane.

This article presents the synthesis of new phosphenium and arsenium cations and the quantitative study of the complexation of phosphenium and arsenium cations with pyridine.

RESULTS AND DISCUSSION

Synthesis and Characterization of the New Phosphenium and Arsenium Salts

We used the well-known synthetic routes [5] common to phosphorus or arsenic (amino groups are cyclic or acyclic).

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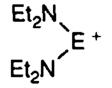
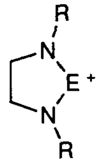
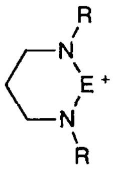
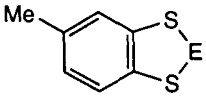
$$(R_2N)_2ECl + AlCl_3 \xrightarrow[R.T.]{CH_2Cl_2} (R_2N)_2E^{+}\ AlCl_4^{-} \qquad E = As, P$$

$$(R_2N)_2ECl + CF_3SO_3X \xrightarrow[R.T.]{CH_2Cl_2} (R_2N)_2E^{+}\ CF_3SO_3^{-} + XCl \qquad X = SiMe_3 \text{ or } Ag$$

About one hundred phosphenium cations are encountered in the literature, whereas only fifteen arsenical homologues are known. We recently described the synthesis and characterization of cyclic and noncyclic arsenium cations with the –N–As$^+$–N– moiety [6].

Table 1 presents, on the one hand, the newly synthesized arsenium cations (compounds **2b**, **2d**, **2e**) and, on the other hand, compounds **1b**, **1c**, **2c**, which are especially designed for the study of their adducts with pyridine. Only salts with $CF_3SO_3^-$ (triflate) counterion were used but tetrachloroaluminates were also synthesized and information about them will be published later.

TABLE 1 Phosphenium and Arsenium Triflates and the Apparent Complexation Constants K_c (mole^{-1}•l) of Their Pyridine Adducts. A: Method of Shapior *et al.* B: Method of Chuche *et at.*

	No.	E	R	K_c	Method
	**1a**[a]	P		385	A
	2a[b]	As		102	A
	**1b**	P	Et	98	A
	2b[a]	As	Et	106	A
	2d[c]	As	Me		
	**2e**	As	Me		
	2f	As	Me		
	**1c**[d]	P		4742	B
	2c[e]	As		1724	B

[a] [6].
[b] [19].
[c] Previously described with $GaCl_4^-$ counterion [4].
[d] Ibid $AlCl_4^-$ [17].
[e] Ibid $AlCl_4^-$ [20].

The cations are identified by their spectroscopic parameters: ^1H, ^{13}C, ^{19}F, and particularly ^{31}P NMR in the case of phosphenium. Owing to the dicoordinated structure and the positive charge, their δ_p values range between 360 and 220. For the arsenium ions, IR spectroscopy was used to check the absence of νAs–Cl (~275 cm^{-1}) and the presence of the characteristic bands of the counterion. The trifluoromethanesulfonate presents two strong bands at 1031 and 1163 cm^{-1} for the SO_3 group and one large band at 1250 cm^{-1} for CF_3. The presence of the counterion is also assessed by NMR spectroscopy. In ^{19}F NMR, $CF_3SO_3^-$ gives a sharp singlet at −3 (upfield of external CF_3COOH). By ^{13}C NMR, the presence of $CF_3SO_3^-$ is well characterized by a quadruplet for CF_3 (δ_c = 120–121; $^1J_{C-F}$ = 320 Hz).

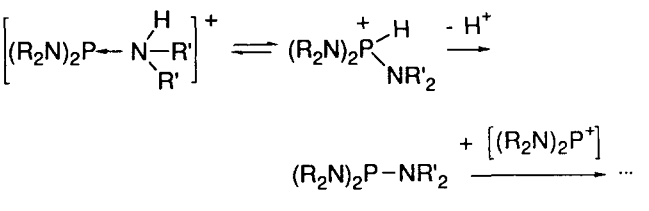
Lewis Base Addition

The Lewis base addition to the phosphenium and arsenium salts gives rise to two kinds of difficulties. The former is related to the nature of the counterion, the latter to the Lewis base itself. In the $AlCl_4^-$ anion, the base B can displace a chloride ion to give back the corresponding tricoordinated chlorophosphane [7] or arsane.

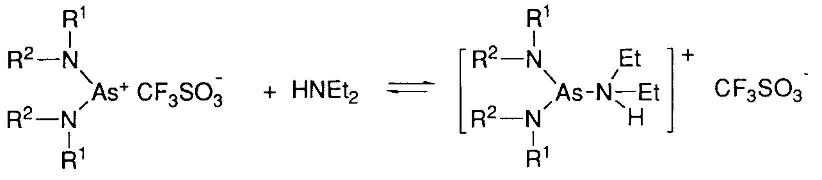
$$B + (R_2N)_2E^{+}\ AlCl_4^{-} \rightarrow (R_2N)_2ECl + [B \rightarrow AlCl_3] \qquad E = P, As$$

This reaction was followed by ^{27}Al NMR spectroscopy, and the formation of the adduct [B → $AlCl_3$] was assessed for different bases such as pyridine, dimethylaminopyridine, and triethylamine. Thus, for this article, we only studied cations with $CF_3SO_3^-$ counterions.

The other difficulty, related to the nature of the Lewis base (i.e., primary and secondary amines) is the decomposition of the adduct via a phosphonium salt, as in the following scheme [8].



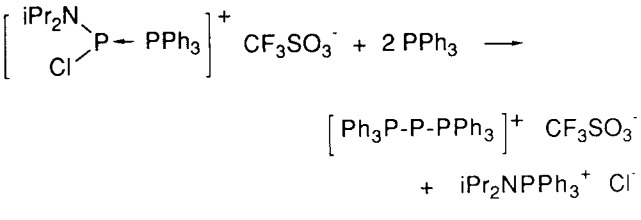
In fact, we did not observe such a reaction with arsenium salts. In the studied examples, IR spectra displayed only $>N^+$—H absorption bands without νAs–H expected in the 2100–2120 cm^{-1} area), but the products decomposed after a few days.



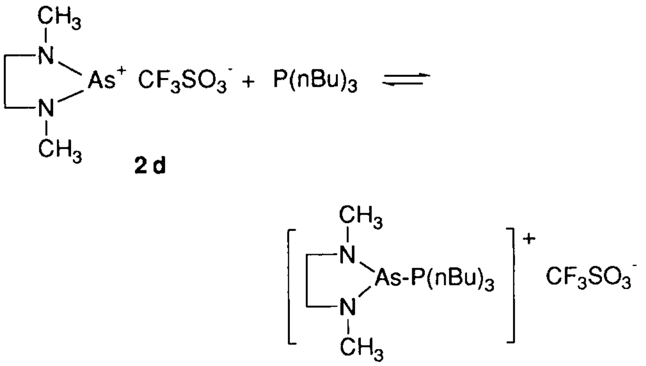
R¹ = R² = Et

R¹ = Me, R² = CH₂— (**2d**)

In the case of tertiary phosphanes, the reactions are more complicated. In a first step with phosphenium salts, the formation of the adduct is observed by ^{31}P NMR spectroscopy [3b]. However, with progressive addition of increasing amounts of phosphane, secondary reactions occurred. A typical case is exemplified for the adduct between the diisopropylaminochlorophosphenium cation and triphenylphosphane [9].

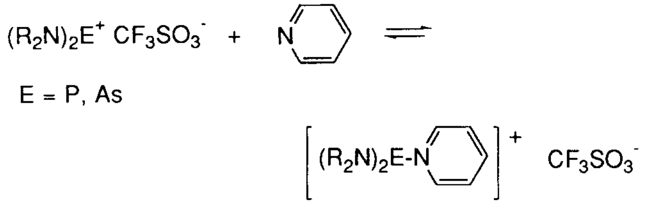


The study of the same reaction with arsenium homologues is currently in progress. The addition of tributylphosphane to the arsenium salt **2d** results in an equilibrium, which can be followed by ^{31}P NMR spectroscopy. For a stoichiometric amount of arsenium salt and phosphane, the resulting shift, δ_P, is 12.9, whereas it is −30 for the phosphane alone. Moreover, in ^{1}H NMR spectroscopy we observed a deshielding for the signals of the phosphane and a shielding for the arsenium cations. These findings are in accordance with the balanced formation of an adduct. With an excess of tributylphosphane, the ^{31}P chemical shift observed varied between +12.9 and −30 (slightly enlarged signal), thus revealing the presence of a rapid equilibrium. Other experiments (i.e. DNMR) were performed to confirm this fact.



2d

Owing to those observations, the choice of pyridine as the Lewis base seemed to us the best; with both phosphenium and arsenium cations the same reaction took place:



The formation of adducts of pyridine with Lewis acids is well documented, especially in borane chemistry [10]. In this field Contreras et al. [11] determined an acidity scale for a series of boranes by ^{13}C NMR spectroscopy. They found that the chemical shift variation of the C-4 carbon of the pyridine ring was highly sensitive to the strength of the dative B ← N bond in the adduct. Starting from this concept, it appears that the $\delta_{C\text{-}4}$ measurement should permit a quantitative evaluation of this equilibrium.

^{13}C NMR Study of the Complexation Equilibrium of Arsenium and Phosphenium Salts

In our case, we observed a rapid equilibrium relative to the NMR scale. The measured chemical shift of the C-4 carbon of the pyridine thus corresponded to the balanced value between the chemical shifts of C-4 for the free and for the complexed pyridine. Numerous mathematical treatments of experimental values allowed for extraction of K_c, the apparent equilibrium constant, and δSR, the theoretical chemical shift of the pure substrate–pyridine complex

For this study, we used two different methods that seemed reliable according to the expected equilibrium constants. The first one (method A) is the two-step method introduced by Shapiro and Johnson [12]. It employs an analysis of shifts and equilibria without approximatives. δSR and K_c are extracted by a fitting procedure from experimental $\Delta\delta_i$ results obtained by the following procedure. Increasing amounts of ligand (L = pyridine) were added to a substrate solution of known concentration (S_0 = initial concentration of arsenium or phosphenium salt). Each time, $\Delta\delta_i$(^{13}C induced shift of C-4 of the pyridine, $\Delta\delta_i = \delta_{\text{observed}} - \delta_{\text{free L}}$) was measured. The fitting procedure correlates experimental and calculated curves $\Delta\delta_i = f\left(\frac{S_0}{\text{L}}\right)$ with a minimal reliability factor (computer program RMNSTAB developed in one of our laboratories by M. Perry). Phosphenium cations **1a**, **1b** and arsenium cations **2a**, **2b** were studied by this method.

For a critical evaluation of the accuracy of the principal methods described in the literature, see Raber and Hardee [13].

The other method (B) was developed by Chuche and Bouquant [14]. This method is reliable only in the case of a 1:1 stoichiometric complex. As the Shapiro method permitted us to assume that complexes with pyridine are stoichiometric, we used this latter method in two cases, for phosphenium **1c** and arsenium **2c** cations, especially because **1c** is totally soluble only after addition of a stoichiometric amount of pyridine. The method was also used for **2c** for comparative purposes [15]. One can establish the following equation:

$$\Delta\delta_i = \delta\text{SR} - \sqrt{\frac{\delta\text{SR}}{K_c}}\sqrt{\frac{\Delta\delta_i}{S_0}}$$

where $\Delta\delta_i$, δSR, K_c, and S_0 are defined as before.

Making $\text{L}_0 = \text{S}_0$ constant, the initial solution is diluted with the solvent and associated $\Delta\delta_i$ is measured. The function $\Delta\delta_i = f\left(\sqrt{\frac{\Delta\delta_i}{S_0}}\right)$ must be a straight line with δSR as intercept and with a slope of $f\left(\sqrt{\frac{\Delta\delta_i}{K_c}}\right)$ giving K_c.

Table 1 summarizes the K_c determined for each cation. Figure 1 presents the variations for cations **1b** and **2b** of the ^{13}C shifts of the C-2 and C-4 pyridine ring carbons as a function of the pyridine/cation ratio. The positive charge delocalization on the pyridine ring induces a large deshielding effect on C-4 (the same trend is observed for C-3 but with a slightly reduced deshielding) and a shielding on C-2 coherent with the formation of a pyridinium salt [16]. The various values of K_c in Table 1 are to be discussed in Lewis acidity terms. In the phosphorus series, K_c increases in the order **1b** < **1a** < **1c**, ranging from 100 to 4,700. The maximum acidity is observed for the dithiaphosphenium cation **1c**. This fact can be related to the greater electron donating effect of $-\text{NR}_2$ ligands relative to –S– and to the π-bonding within the 2-hetero benzo–dithia system, as proposed by Burford et al. [17] for **1c**.

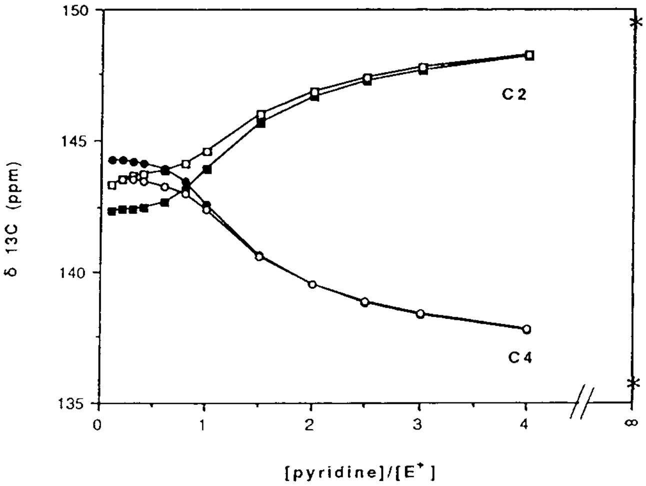


FIGURE 1 ^{13}C shift variation of the C-2 (■: **1b**; □: **2b**) and C-4 (●: **1b**, ○: **2b**) carbons of the pyridine in the adducts as a function of the ratio [pyridine]/[E$^+$] (*: free pyridine).

There is a significant difference between K_c values for **1a** (385) and **1b** (98). The conformational rigidity introduced by the cyclic strain induces a greater overlap of the nitrogen lone pairs toward the dicoordinated phosphorus. Moreover, two R_2N groups at the same center cannot be coplanar; thus, they interact less with the vacant orbital at this center than in the cyclic case.

For the arsenium cations, the range of K_c variation (100 to 1,700) is less than that observed for the phosphenium cations with a similar acidity order of **2b** ≃ **2a** < **2c**. Like **1c**, the dithiaarsenium cation **2c** presents the greatest Lewis acidity but with lower K_c (1724) than for the phosphorus analog **1c**. This fact is consistent with a greater overlap of the sulfur lone pairs with As (**2c**) than with P (**1c**).

In the case of bis(dialkylamino)arsenium ions, **2a** and **2b**, we obtained almost the same K_c (~100). Owing to the large difference observed between the K_c ratio for the **1a–2a** or **1c–2c** cations, it seems that the **2b** value is higher than expected. In this case, the back donation effect of the nitrogen lone pair, which diminishes the vacant orbital availability, should be counterbalanced by the increase in size of the heteroatom.

In conclusion, the quantitative ^{13}C study of the complexation of the dicoordinated cations, phosphenium and arsenium, by pyridine clearly indicates the Lewis acidic character of these salts. Thus the $\delta_{\text{C-4}}$ variation of the pyridine is an appropriate probe to determine their acid–base equilibrium constant. This equilibrium is sensitive to the nature of the elements directly bounded to P or As. Moreover, phosphenium cations are more acidic than arsenium cations [18].

Other complexation studies with various pyridines and phosphanes are in progress.

EXPERIMENTAL

All syntheses were carried out under an argon atmosphere. The solvents were distilled and dried before use.

Synthesis of Chlorinated Precursors

1,3-Dimethyl-2-chloro-2-arsa-1,3-diazacyclopentane (**D**). This product was previously synthesized by a direct method [21]: 70.9 mL (113.4 mmol) of a hexane solution of butyllithium were added dropwise to a solution of 1,2-bis(*N,N'*-dimethylamino)ethane (5.8 g; 56.7 mmol) in 300 mL of dry ether. The mixture was stirred at 0°C for 0.5 h. A solution of $AsCl_3$ (10.26 g; 56.7 mmol) in ether was then added dropwise. The precipitate of LiCl that had formed was filtered off, and the etherate solution was evaporated. The yellow liquid obtained was distilled (68°C; 2 mm Hg). The pale yellow oily liquid distillate turned to a solid at low temperature. Yield 45%. ^{1}H NMR (CD_2Cl_2), δ_H = 2.84 (s, 6H), 3.31 (s, 4H); ^{13}C NMR (50.3 MHz, CD_2Cl_2), δ_c = 36.18, 57.29; IR (polyethylene plates), νAs–Cl 279 cm^{-1}; Anal. Calcd. for $C_4H_{10}N_2AsCl$: C, 24.45; H, 5.13; N, 14.26. Found: C, 25.63; H, 5.38; N, 14.45.

1,3-Dimethyl-2-chloro-2-arsa-1,3 diazacyclohexane (**E**). Pale yellow liquid (87.5 C; 1.75 mmHg); yield 62%. ^{1}H NMR (CD_2Cl_2), δ_H = 1.18 (t, 6H), 1.95 (m, 2H), 2.95 (q, 4H), 3.01 (t, 4H). ^{13}C NMR (50.3 MHz, CD_2Cl_2), δ_C = 14.12, 28.08, 46.54, 48.29; IR (polyethylene plates), νAs–Cl 268 cm^{-1}(s); Anal. Calcd. for $C_7H_{16}N_2AsCl$: C, 35.24; H, 6.76; N, 11.74. Found: C, 36.03; H, 6.99; N, 12.12.

1,3-Dimethyl-2-chloro-2-arsa-1,3-diazacyclohexane (**F**). White crystals, mp 48°C; yield 70%. Anal. Calcd. for $C_5H_{12}N_2AsCl$: C, 28.52; H, 5.75; N, 13.31. Found: C, 28.32; H, 5.89; N, 13.19.

Synthesis of Arsenium and Phosphenium Triflates

1,3-Dimethyl-1,3-diaza-2-arseniumcyclopentane Triflate (**2d**). Trimethylsilyl triflate (0.66 g; 3.3 mmol) was dropwise added at room temperature to a CH_2Cl_2 solution of **D** (0.53 g; 2.7 mmol). The immediate formation of a precipitate was observed. After a few minutes of stirring, the supernatant yellow solution was discarded with the aid of a transfer needle. This solution contained the solvent, the trimethylsilyl triflate excess, and the Me_3SiCl formed. The pale yellow precipitate was then dried. Yield 87%. ^{1}H NMR (CD_3CN), δ_H = 3.15 (s, 6H), 3.73 (s, 4H); ^{13}C NMR (50.3 MHz, CD_3CN), δ_C = 37.44, 57.19; IR (KBr), νSO_3 1032, 1163, νCF_3 1252 cm^{-1}; ^{19}F NMR (CD_3CN), δ_F = −0.56; Anal. Calcd. for $C_5H_{10}N_2AsF_3SO_3$: C, 19.36; H, 3.25; N, 9.03. Found C, 19.00; H. 3.42; N, 8.87.

1,3-Diethyl-1,3-diaza-2-arseniumcyclohexane Triflate (**2e**). Trimethylsilyl triflate (0.51 g; 2.3 mmol) was added dropwise to a CH_2Cl_2 solution of **E** (0.51 g; 2.1 mmol). An orange color appeared. After a few minutes of stirring, the solvent, excess of trimethylsilyl triflate, and Me_3SiCl were evaporated to give an orange-brown solid. ^{1}H NMR (CD_2Cl_2), δ_H = 1.33 (t, 6H), 2.32 (m, 2H), 3.47 (q, 4H), 3.39 (t, 4H); ^{13}C NMR (CD_2Cl_2), δ_C = 14.94, 26.54, 48.47, 50.13, 120.89 (q, J_{C-F} = 320.16 Hz); ^{19}F NMR ($CDCl_3$), δ_F = −3.2; IR (KBr), νCF_3 1250, νSO_3 1162, 1031 cm^{-1}; Anal. Calcd. for $C_8H_{16}N_2AsF_3SO_3$: C, 27.28; H, 4.58; N, 7.95. Found: C, 27.12; H, 4.82; N, 7.79.

1,3-Dimethyl-1,3-diaza-2-arseniumcyclohexane Triflate (**2f**). Trimethylsilyl triflate (0.52 g; 2.3 mmol) was slowly added at room temperature to a 10-mL CH_2Cl_2 solution of **F** (0.44 g; 2.1 mmol). We observed the appearance of an orange color. Solvent, excess of trimethylsilyl triflate, and Me_3SiCl were discarded. An orange solid was obtained. ^{1}H NMR (CD_2Cl_2), δ_H = 1.98 (m, 2H), 3.15 (s, 6H), 3.31 (t, 4H); ^{13}C NMR (CD_2Cl_2), δ_C = 26.44, 41.20, 50.37, 120.87 (q, J_{C-F} = 320.04 Hz); ^{19}F NMR (CD_2Cl_2), δ_F − 3.05; IR (KBr), νCF_3 1260, νSO_3 1031, 1165 cm^{-1}; Anal. Calcd. for $C_6H_{12}N_2AsF_3SO_3$: C, 22.23; H, 3.73; N, 8.64. Found: C, 21.65; H, 3.78; N, 8.42.

5-Methyl-1,3,2-benzodithiarsolium Triflate (**2c**). 2-Chloro-5-methyl-1,3,2-benzodithiarsole (0.22 g; 0.82 mmol) in a 4-mL solution of CH_2Cl_2 was added to a suspension of silver triflate (0.21 g; 0.82 mmol) in 1 mL of CH_2Cl_2. A bright orange color immediately appeared, and the silver chloride precipitate was filtered off. The solvent was removed at reduced pressure and a garnet-red solid was obtained. ^{1}H NMR ($CDCl_3$), δ_H = 2.39 (s, 3H), 7.13 (m, 1H), 7.48 (m, 1H), 7.55 (m, 1H); ^{13}C NMR ($CDCl_3$), δ_C = 20.81, 118.51 (q, J_{C-F} = 318.9 Hz), 126.50, 127.15, 128.30, 137.24, 137.74, 140.75.

5-Methyl-1,3,2-benzodithiaphospholium Triflate (**1c**). Oily orange liquid. ^{1}H NMR ($CDCl_3$), δ_H = 2.42 (s, 3H), 7.19 (m, 1H), 7.56 (m, 1H), 7.71 (m, 1H); ^{13}C NMR ($CDCl_3$), δ_C = 20.93, 118.27 (q, J_{C-F} = 319.49 Hz), 125.13, 125.21, 125.91, 125.99, 128.51, 133.98, 137.55, 137.95; ^{31}P NMR ($CDCl_3$), δ_P = 196.5.

1,3-Diethyl-1,3-diaza-2-phospheniumcyclopentane Triflate (**1b**). Trimethylsilyl triflate (0.12 g; 0.55 mmol) was added dropwise to a 2-mL CH_2Cl_2 solution of 1,3-diethyl-2-chloro-2-phospha-1,3-diazacyclopentane. The solution became light yellow colored. After 5 minutes of stirring, the solvent was evaporated to give a yellow oil. ^{31}P NMR ($CDCl_3$), δ = 264.15; ^{1}H NMR ($CDCl_3$), δ_H = 1.35 (t, $^3J_{H-H}$ = 7.1 Hz; $^4J_{H-P}$ = 1.8 Hz; 6H, CH_3–CH_2), 3.42 (qd, $^3J_{H-H}$ = 7.1 Hz; $^3J_{H-P}$ = 10.4 Hz; 4H, CH_3–CH_2), 3.82 (s, $^3J_{P-H}$ = 5.2 Hz, 4H cyclic CH_2); ^{13}C NMR

($CDCl_3$), δ_C = 14.20 (d, $^3J_{C-P}$ = 9.9 Hz, CH_3–CH_2), 43.24 (d, $^2J_{C-P}$ = 17.9 Hz, CH_3–CH_2), 52.08 (d, $^2J_{C-P}$ = 9.0 Hz, cyclic CH_2), 120.31 (q, $^1J_{C-F}$ = 319.9 Hz, CF_3SO_3).

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