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Reactions of $^{i}Pr_2N-C{\equiv}P$ with Methylating Agents: Formation of the Diamino-2-phosphaallylic Cation $[MePC(N^{i}Pr_2)PC(N^{i}Pr_2)]^{\oplus}$

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ABSTRACT

The reaction of di(isopropyl)aminophosphaethyne **1** *with iodomethane or the methyl ester of trifluormethylsulfonic acid (methyl triflate) yields the ionic $1\lambda^3$, $3\lambda^3$-diphosphetene derivatives $[MePC(N^{i}Pr_2)PC(N^{i}Pr_2)]^{+}\ X^{-}$ (**2a**: X = I; **2b**: X = CF_3SO_3). On the basis of NMR spectroscopic and X-ray diffraction studies, the cation can be described as a combination of an amino-2-phosphaallylic cation and its methylated derivative.*

INTRODUCTION

Phosphaalkynes of the type P≡C–R have been extensively studied during the last 10 years and found to offer a rich potential of chemical reactivity, often with unexpected results [2]. On the other hand, only little is known about the behavior of aminosubstituted analogues [3]. Recent PE spectroscopic results and structural information about some representatives of the C-aminophosphaethynes [1,4–6] suggest an increased nucleophilicity of the phosphorus atom due to $n(N)-\pi(P{\equiv}C)$ conjugation according to the following mesomeric formulas:

$$\ddot{P}{\equiv}C-NR_2 \longleftrightarrow \dot{P}^{\ominus}=C=\overset{\oplus}{N}R_2 \quad (R = \text{Organyl})$$

This led us to investigate the reactions of $^{i}Pr_2NC{\equiv}P$ (**1**) with methylating agents such as MeI or $MeOSO_2CF_3$; here, we report on the results of our studies.

RESULTS AND DISCUSSION

Di(isopropyl)aminophosphaethyne **1** reacted with iodomethane (molar ratio 2:1) within 10 days, at −20°C in acetonitrile solution according to Equation (1) to give the 1,3-diphosphacyclobutene derivative **2a**. The reaction was monitored by NMR measurements. The same compound was obtained when an excess of MeI was used (molar ratio 1:1). After 5 days, a crystalline solid precipitated from the yellow-orange solution. The product **2a** was isolated by removing the supernatant solution with the help of a pipette and by repeated recrystallization of the precipitate from dichloromethane. Since the crystals obtained by this procedure were of limited quality for an X-ray diffraction study (they contain disordered solvent molecules) [7], methyl triflate, $MeOSO_2CF_3$, instead of MeI, was used for the preparation. This reaction proceeded within 12 hours, thus effectively avoiding the decomposition

Dedicated to Prof. Reinhard Schmutzler on the occasion of his sixtieth birthday. Part 39 of the series *Reactive E = C (p–p)π-Systems*, Part 38; see Ref. [1].

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of **1** and producing **2b** in about 82% yield. Furthermore, the presence of the triflate anion led to crystals of **2b** of good quality.

Composition and constitution of **2a** and **2b** have been determined by elemental analysis, NMR spectra (^{31}P, ^{1}H, ^{13}C), and X-ray diffraction studies of single crystals. As expected, the NMR data of the cations of **2a** and **2b** were almost identical. The $^{31}P\{^{1}H\}$ NMR spectra showed two doublets of an AX spin system, a low field signal with δ = 155.3 (**2a**) or 156.2 (**2b**), and a high field resonance at δ = 71.4 (**2a**) or 67.7 (**2b**). The ^{1}H coupled phosphorus spectrum enabled the assignment of the high field signals to the trivalent phosphorus atom of the MeP group [^{2}J(PH) = 3 (**2a**), 3.4 (**2b**) Hz]. The ^{2}J(PP) couplings amounted to 16.4 (**2a**) and 15.4 (**2b**) Hz, respectively, in good agreement with values of 16.2 to 16.9 Hz for 1,3-diphosphacyclobutenes described by Appel et al. [8]. There is a remarkable difference, however, with respect to the ^{2}J(PP) coupling of halogen substituted 1,3-diphosphetenes having typical values of about 90 Hz [9,10].

For the methyl groups of the isopropyl substituents of **2a** and **2b**, four proton resonances showed up in the ^{1}H NMR spectra. Obviously, this is due to a barrier to rotation around the sp^2C–N bond leading to a chemical nonequivalence of the Me groups. This explanation is supported by four ^{13}C-signals observed for the Me groups of **2a** or **2b**. The resonances of the sp^2C-atoms appeared as a doublet of doublets in the olefinic region of the ^{13}C spectrum [δ = 197.0 (**2a**), 196.1 (**2b**)], with $^{1}J(\sigma^2 - PC) \approx 60$ and $^{1}J(\sigma^3 - PC) \approx 9$ Hz.

The most important information about the geometrical and electronic structures of the cations of **2a** and **2b** come from single crystal X-ray diffraction studies. Because of disordered CH_2Cl_2 molecules in the unit cell [7] of **2a**, only the more exactly determined structural data of **2b** will be presented and discussed. In agreement with analytical and NMR-spectroscopic data, the molecular structure of the cation proves that only one of the two P-atoms of the 1,3-diphosphacyclobutadiene ($^{i}Pr_2NCP)_2$ is methylated (Figure 1), thus allowing extensive delocalization in the system.

All atoms of the $(C_2NCP)_2$-skeleton are situated in one plane (average deviation: 0.045 Å). The bond distances P1–C1 and P1–C2 are equal and correspond to typical PC single bonds (1.840 Å). However, the P2–C1 and P2–C2 bonds are significantly shorter (1.776 and 1.782 Å), indicating a bond order larger than one. The trigonal planar arrangement of the substituents on N1 and N2, together with very short C1–N1 and C2–N2 bonds (1.308 and 1.304 Å), points to a strongly delocalized electronic structure. Therefore, the bonding system in the cation can be represented by the mesomeric formulas **A** to **C**.

Of particular interest is the fact that the structural data of the four-membered ring system **2** are nearly identical with those of the 1,3-diphosphabutadiene $(^{i}Pr_2NCP)_2$ coordinated to two $[Ni(CO)_3]$ fragments with only one of the two P-atoms (compound **3**) [11]. Furthermore, there is a strong relationship between **2** and the 2-phosphaallylic cation **4** and its methylated derivative **5** investigated by Day et al. [12].

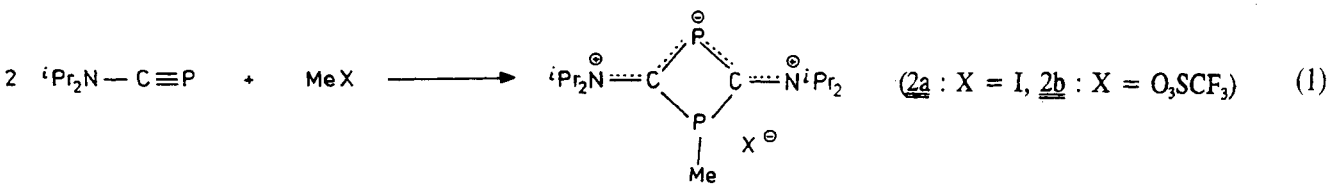
Structural analyses of the crystalline perchlorate of **4** and the diiodide of **5** have led to the conclusion that the electronic structures of **4** and **5** are very close to the description of the formulas **4A** and **5B**, respectively. Comparison of the structural data of **4**, **5**, and **2b** leads to the suggestion that the cation of **2b** includes structural features of both **4A** and **5B**. Consequently, the compounds **2a**, **2b**, and **3** have to be considered as members of the class of 2-phosphaallylic cations [13]. For the formation of **2a** or **2b**, we offer for discussion a pathway according to Equation (2). The reaction is initiated by an electrophilic attack of the methylating agent on the P-atom of **1**, giving the cationic species **6**, which undergoes a quick [2 + 2] cycloaddition reaction with an additional molecule of **1**.

This suggestion is based on the following experimental results.

(a) Cyclodimerization of **1** has not been observed so far in the absence of Lewis acids [3e].

(b) Phosphaalkynes readily react with phosphaalkenes via [2 + 2] cycloaddition to give 1,3-diphosphetenes [9,10,14].

In the special case of the olefinic cation **6**, a particularly high reactivity can be expected compared with neutral phosphaalkenes. In fact, the following reaction of **6** with the aminophosphaethyne **1** proceeded so quickly that even an attempted spectroscopic detection of the intermediate failed.



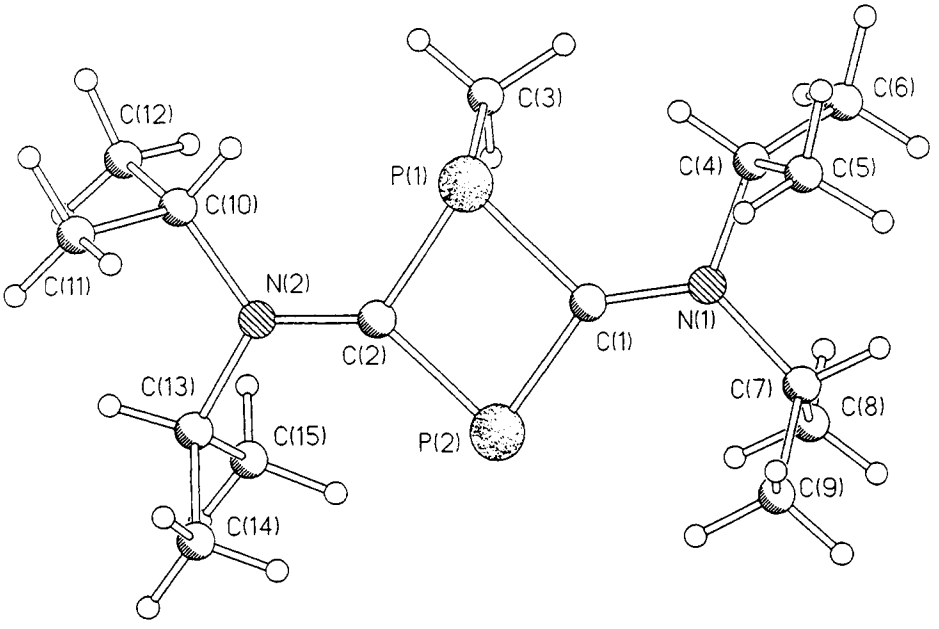
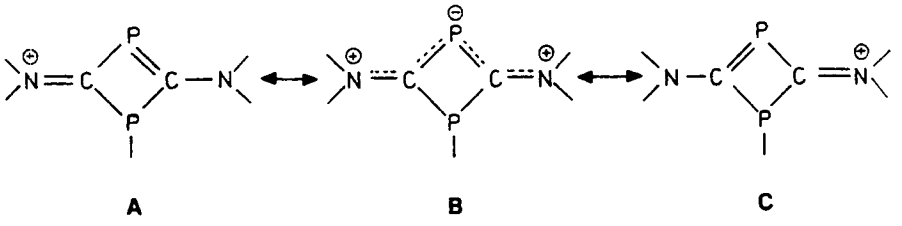
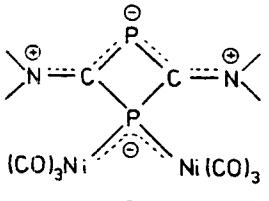


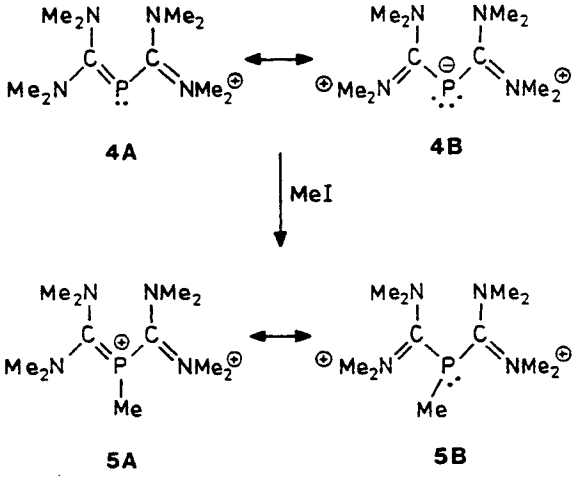
FIGURE 1 Molecular structure of the cation of **2b**.



A **B** **C**



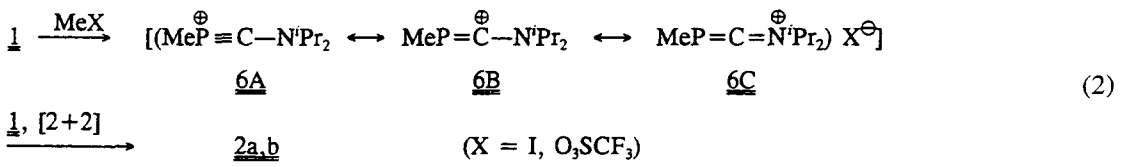
3



4A **4B**

MeI

5A **5B**



(2)

TABLE 1 Selected Bond Lengths (Å) and Bond Angles (°) in the Cation of **2b**

P(1)–C(1)	1.840(3)	C(2)–P(1)–C(3)	99.9(1)
P(1)–C(2)	1.840(3)	C(1)–P(2)–C(2)	81.2(1)
P(1)–C(3)	1.845(3)	P(1)–C(1)–P(2)	100.5(1)
P(2)–C(1)	1.776(3)	P(1)–C(1)–N(1)	125.4(2)
P(2)–C(2)	1.782(3)	P(2)–C(1)–N(1)	134.2(2)
N(1)–C(1)	1.308(4)	P(1)–C(2)–P(2)	100.2(1)
N(1)–C(4)	1.492(3)	P(1)–C(2)–N(2)	125.4(2)
N(1)–C(7)	1.502(3)	P(2)–C(2)–N(2)	134.4(2)
N(2)–C(2)	1.304(3)	C(1)–N(1)–C(4)	120.1(2)
N(2)–C(10)	1.487(3)	C(1)–N(1)–C(7)	122.7(2)
N(2)–C(13)	1.499(3)	C(4)–N(1)–C(7)	117.1(2)
		C(2)–N(2)–C(10)	121.2(2)
C(1)–P(1)–C(2)	78.0(1)	C(2)–N(2)–C(13)	121.7(2)
C(1)–P(1)–C(3)	100.3(1)	C(10)–N(2)–C(13)	117.0(2)

TABLE 2 Crystallographic Data for Compound **2b**

Crystal size (mm)	0.15 × 0.22 × 0.23
Molecular formula	$C_{15}H_{31}N_2P_2 \cdot CF_3SO_3$
Molecular weight	450.4
Space group	$P\bar{1}$
Cell dimensions	
a (Å)	8.442(2)
b (Å)	11.869(3)
c (Å)	12.074(3)
α (°)	108.99(2)
β (°)	91.63(2)
γ (°)	97.77(2)
V (Å^3)	1130.1
Z	2
d_x (g/cm^3)	1.32
T (K)	170
Scan mode, scan range	2θ; $4° < 2\theta < 54°$
Number of measured reflections	4969
Number of observed data with $I > 2\sigma(I)$	3536
Solution	direct methods, SHELXTL PLUS
Refinement	full-matrix least-squares; all nonhydrogen atoms from E-map; H atoms from difference Fourier synthesis, isotropic temperature factors
R	0.0416
R_w	0.0393

TABLE 3 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound **2b**

Atom	*x*	*y*	*z*	U_{eq}
P(1)	0.48733(8)	0.21079(6)	0.29221(6)	0.0200(3)
P(2)	0.78890(8)	0.33923(6)	0.29453(6)	0.0256(3)
S(1)	0.18596(8)	−0.17816(6)	0.25090(6)	0.0237(9)
N(1)	0.5084(2)	0.4405(2)	0.2701(2)	0.0203(9)
N(2)	0.7577(2)	0.0990(2)	0.3002(2)	0.0198(9)
O(1)	0.2474(2)	−0.0556(2)	0.2618(2)	0.0322(9)
O(2)	0.3030(2)	−0.2449(2)	0.2766(2)	0.040(1)
O(3)	0.0338(2)	−0.1941(2)	0.2978(2)	0.039(1)
F(1)	0.0274(2)	−0.1974(2)	0.0542(2)	0.058(1)
F(2)	0.0803(2)	−0.3653(1)	0.0632(2)	0.054(1)
F(3)	0.2670(3)	−0.2389(2)	0.0344(2)	0.069(1)
C(1)	0.5837(3)	0.3550(2)	0.2812(2)	0.021(1)
C(2)	0.7010(3)	0.1948(2)	0.2969(2)	0.020(1)
C(3)	0.4280(4)	0.1259(3)	0.1358(2)	0.027(1)
C(4)	0.3298(3)	0.4264(2)	0.2677(2)	0.026(1)
C(5)	0.2774(4)	0.5198(3)	0.3741(3)	0.034(2)
C(6)	0.2556(4)	0.4284(3)	0.1525(3)	0.038(2)
C(7)	0.5944(3)	0.5558(2)	0.2601(2)	0.025(1)
C(8)	0.6833(4)	0.5312(3)	0.1501(3)	0.037(2)
C(9)	0.7018(4)	0.6264(3)	0.3707(3)	0.035(1)
C(10)	0.6497(3)	−0.0088(2)	0.3054(2)	0.023(1)
C(11)	0.6876(4)	−0.0318(3)	0.4196(3)	0.031(1)
C(12)	0.6583(4)	−0.1177(3)	0.1977(3)	0.033(1)
C(13)	0.9332(3)	0.0910(2)	0.2954(2)	0.023(1)
C(14)	1.0294(4)	0.1825(3)	0.4023(3)	0.033(1)
C(15)	0.9901(4)	0.0984(3)	0.1799(3)	0.033(2)
C(16)	0.1371(4)	−0.2493(3)	0.0932(3)	0.035(1)

EXPERIMENTAL

The methylating reactions of di(isopropyl)-aminophosphaethyne [3e] were carried out in closed reaction vessels using standard high vacuum techniques. Solvents were thoroughly dried and degassed. MS: Model CH 5 MAT Finnigan; electron energy: 70 eV; NMR: 200.13 (^{1}H), 188.31 (^{19}F), 81.02 (^{31}P), and 50.32 (^{13}C)MHz; AC 200 spectrometer (Bruker); external standard: TMS (^{1}H, ^{13}C), CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P).

Preparation of the 1λ^3, 3λ^3-Diphosphetene Derivatives **2a** *and* **2b**

A 140 mg (1 mmol) amount of di(isopropyl)-aminophosphaethene **1**, 142 mg (1 mmol) of MeI [or 164.1 mg (1 mmol) of $MeOSO_2CF_3$], and ca. 1 mL of CD_3CN were transferred into an ampoule equipped with a break seal and an NMR tube by vacuum condensation. After having been sealed off

and melted, the reaction mixture was kept at −20°C for 10 days (**2a**) or 12 hours (**2b**). To purify the resulting crude solid product, the mixture was covered with a dry argon atmosphere and the supernatant solution removed from the precipitate by means of a pipette. The solid residue was then dissolved in dichloromethane and recrystallized by cooling at −20°C. **2a** and **2b** were deposited in the form of light yellow crystals. After repeated crystallization, 212 mg (49.5%) of **2a** and 369.2 mg (82%) of **2b** were obtained. Side-products of the reaction were phosphorus-rich compounds resulting from the slow decomposition of **1**.

2a: NMR (CD_3CN): δ = 1.33 (d, ^3J(HH) = 6.5 Hz, 6H, CH_3), 1.35 (d, ^3J(HH) = 6.5 Hz, 6H, CH_3), 1.48 (d, ^3J(HH) = 6.9 Hz, 6H, CH_3), 1.50 (d, ^3J(HH) = 6.9 Hz, 6H, CH_3), 1.81 (d, ^2J(PH) = 3 Hz, 3H, PCH_3), 3.86 (dsept, ^3J(HH), ^4J(PH) = 6.5 Hz, 2H, CH), 4.26 (dsept, ^3J(HH) = 6.9, ^3J(PH) = 2.5 Hz, 2H, CH); $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 71.4 (d, ^2J(PP) = 16.4 Hz, PCH_3), 155.3 (d, ^2J(PP) = 16.4 Hz); $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 18.9 (s, $\underline{C}H_3$), 19.2 (d, ^4J(PC) = 11.5 Hz, $\underline{C}H_3$), 19.7 (s, $\underline{C}H_3$), 20 (s, $\underline{C}H_3$), 21.1 (d, ^1J(PC) = 13.1 Hz, $P\underline{C}H_3$), 53.6 (s, $\underline{C}H$), 62.1 (d, ^3J(PC) = 18.9 Hz, $\underline{C}H$), 197 (dd, ^1J(PC) = 60.1 and 9.3 Hz, $\underline{C}$ = P); mass spectrum, principal ion fragments: *m/z*: 428 (M^+, 1%), 413 (M^+−Me, 10%), 286 (M^+−MeI, 83%), 174 ($M^+-C_8H_{17}NI$, 100%). Anal. calcd for $C_{15}H_{31}N_2P_2I$: C, 42.07; H, 7.30; N, 6.54. Found: C, 41.75; H, 7.15; N, 6.18.

2b: ^1H NMR (CD_3CN): δ = 1.38 (d, ^3J(HH) = 6.5, 6H, CH_3), 1.40 (d, ^3J(HH) = 6.5 Hz, 6H, CH_3), 1.52 (d, ^3J(HH) = 6.9 Hz, 6H, CH_3), 1.55 (d, ^3J(HH) = 6.9 Hz, 6H, CH_3), 1.84 (d, ^2J(PH) = 3.4 Hz, 3H, PCH_3), 3.88 (dsept, ^3J(HH), ^4J(PH) = 6.4 Hz, 2H, CH), 4.18 (dsept, ^3J(HH) = 6.9, ^4J(PH) = 2.5 Hz, 2H, CH); ^{19}F NMR: δ = −77.2 (s); $^{31}P\{^1H\}$ NMR (CD_3CN): 67.8 (d, ^2J(PP) = 15.4 Hz, PCH_3), 156.2 (d, ^2J(PP) = 15.4 Hz); $^{13}C\{^1H\}$ NMR (CD_3CN): 18.9 (s, $\underline{C}H_3$), 19.2 (s, $\underline{C}H_3$), 19.7 (s, $\underline{C}H_3$), 20 (s, $\underline{C}H_3$), 20.9 (d, ^1J(PC) = 12.7 Hz, $P\underline{C}H_3$), 53.1 (s, $\underline{C}H$), 61.2 (d, ^3J(PC) = 19.5 Hz, $\underline{C}H$), 121 (q, ^1J(FC) = 320.9, $\underline{C}F_3$), 196.1 (dd, ^1J(PC) = 61.1 and 9.3 Hz, $\underline{C}$ = P). Anal. calcd for $C_{16}H_{31}F_3N_2O_3P_2S$: C, 42.62; H, 6.88; N, 6.22. Found: C, 42.51; H, 6.97; N, 6.29.

X-ray Diffraction Study [15] of **2b**

The data were collected on a Siemens P3 Four-Circle-Diffractometer using Mo K_α radiation. The structure was solved by direct methods (SHELXTL-plus). Details of the structure determination are given in Table 2. Atomic coordinates and selected bond lengths and angles in the cation of **2b** are presented in Tables 1 and 3.

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