2,4-Dimethoxycarbonyl-1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete

Ekkehard Fluck*

Gmelin-Institut für Anorganische Chemie und Grenzgebiete der Max-Planck-Gesellschaft, Varrentrappstr. 40/42, D-6000 Frankfurt am Main 90, Germany

Manfred Spahn and Gernot Heckmann

Institut für Anorganische Chemie der Universität, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany

Horst Borrmann and Axel Obermeyer

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, Germany

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ABSTRACT

1,1,3,3 - Tetrakis(dimethylamino) - 1λ^5,3λ^5 - diphosphete, 1, reacts with cyanoformic acid methyl ester to form two isomers of the title compound 2. Properties, NMR, mass, and IR spectra of 2, as well as the molecular and crystal structure of the E isomer of 2, are described and discussed.

INTRODUCTION

In earlier investigations we have shown that the four-membered ring of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete 1 [1] is split by protonactive nitriles [2], whereas nonprotonactive nitriles are inserted into the ring to form 1,2λ^5,4λ^5-azadiphosphorines [3]. In this connection, it is interesting that mono- and disubstituted acetylenes are generally inserted into the ring [4–6]. Thus far, we have observed the preservation of the four-membered ring system and substitution at the endocyclic carbon atom only in the reaction of 1 with bis(trimethylsilyl)-acetylene [7]. It was therefore of

particular interest to study the interaction of 1 with an ester of cyanoformic acid.

The Reaction of 1 with Cyanoformic Acid Methyl Ester

1,1,3,3 - tetrakis(dimethylamino) - 1λ^5,3λ^5 - diphosphete 1 readily reacts at −70°C with cyanoformic acid methyl ester. If the reaction is carried out in 1,2-dimethoxyethane, light-yellow and air-sensitive crystals precipitate. The NMR spectra together with the elemental analysis are identifying the title compound 2.

One can assume that the first reaction step is the reaction of the carbanionic carbon atom of 1 with the carboxyl carbon atom of the ester; the formation of a carbon–carbon bond is followed by split-off of HCN (see Equation (1)). Two isomers, 2a and 2b, of the title compound are formed.

The NMR Spectra of 2a and 2b

The NMR spectra of the title compound are compiled in Table 1. The temperature dependencies of the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra show that the rotation of the methoxycarbonyl groups about the C^1C^2 axis (the numbering of the atoms is given in Table 1) is hindered at room temperature, and two isomers 2a(Z) and 2b(E) exist at 220 K in a 1:1 molar ratio (see Figures 1 and 2). In the $^{31}P\{^1H\}$ NMR spectrum of 2a(Z) one observes an AB system

$$1 + CH_3OC(O)CN$$

2a(Z)   **2b(E)**
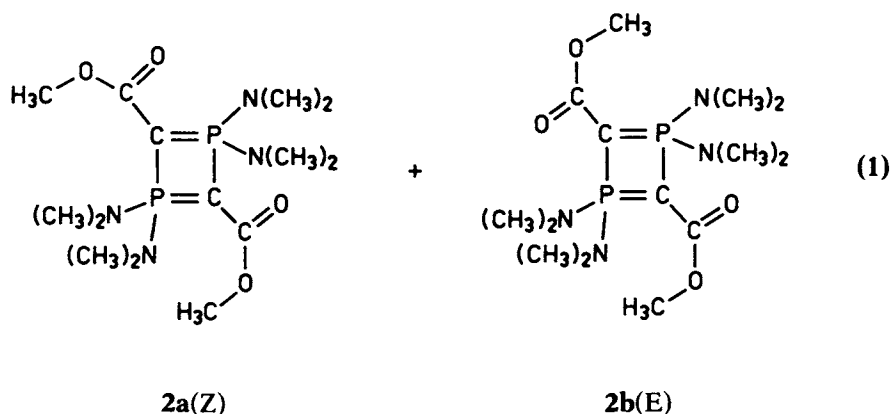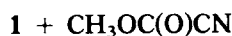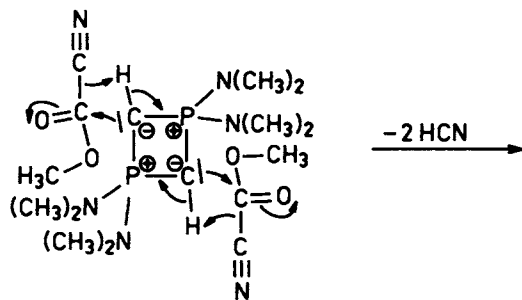
with $J_{AB}/\delta\nu_0 = 0.535$ at 220 K; in the $^{13}C\{^1H\}$ NMR spectrum of this isomer, the X part of an ABX system can be found at this temperature for the two quaternary carbon atoms C^1 and C^2 detected with DEPT pulse sequences (see Figure 2). The chemical shift $\delta(H^a)$ of the two isomers differs by 0.007 at

220 K. The shape of the NMR spectra of **2b**(E) agrees at 220 and 380 K on symmetrical grounds.

The free activation energy $\Delta G\ddagger$ for the rotation around the C^1C^2 axis can be estimated with the following equation [14], $\Delta G\ddagger = 1.914 \times 10^{-2} T_c$ [$9.972 + \log(T_c/\sqrt{\delta\nu^2 + 6J_{AB}^2})$], $T_c = 317$ K, and the

TABLE 1 NMR Parameters of **2a**(Z) and **2b**(E) (See Equation (1)) in Toluene-d_8 at 220 K; Concentration 10% (by weight). Coupling Constants J in Hz.

$$R = C^2OOC^3H_3^a$$

	2a(Z)	**2b**(E)		**2a**(Z)	**2b**(E)
$\delta(^{31}P)$:	42.28	40.10	$^1J(P,C^1)$	111.5	115.1
	37.80			118.6	
$\delta(^{13}C)$: C^1	44.74	44.76	$^2J(P,P)$	194.0	
C^2	165.19	165.17	$^2J(P,C^2)^d$	5.7	3.6
C^3	50.0^a	50.0^a		1.5	
C_4	(37.4–37.6)^b	37.52			
$\delta(^1H)^c$: H^b	(2.56–2.62)^b	2.592			

^{a} Structured line at 300 K, line width 5 Hz: $^4J(P,C^3) = 2.0$ Hz.
^{b} Area in which individual δ-values are located; $\delta(C^4)$ and $\delta(H^b)$, respectively, of **2b**(E) follow from the X-part (3 lines) of the AA'X system of the atoms PPC^4 and PPH^b, respectively.
^{c} H^a gives a singlet for both isomers ($\delta = 3.481$ and 3.474).
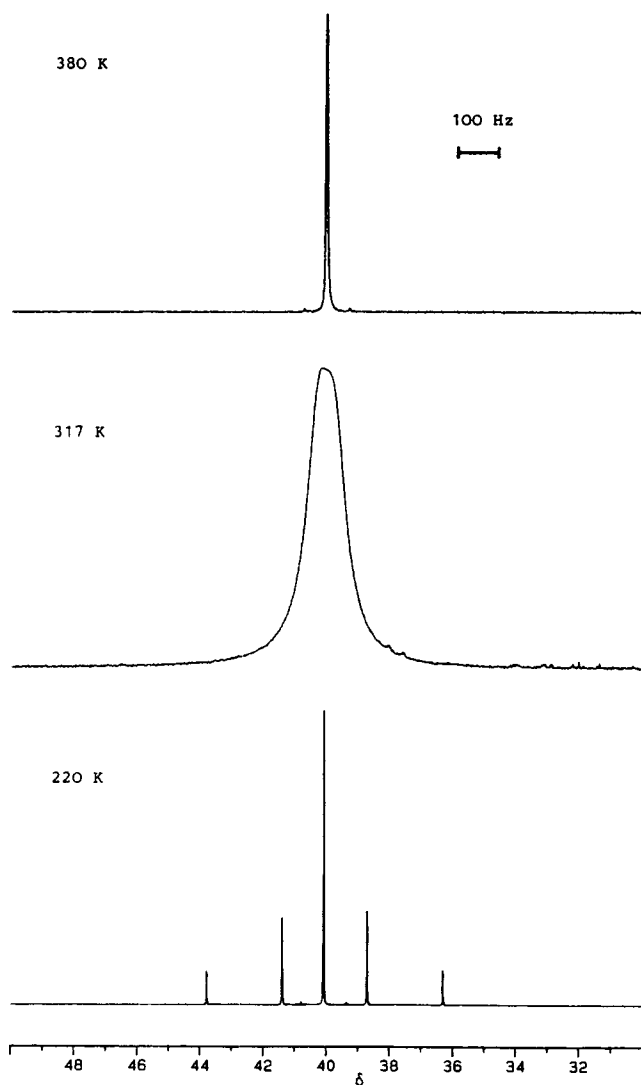^{d} At 300 K: $^2J(P,C^2) = 3.5$ Hz.

FIGURE 1 81.015 MHz ^{31}P{^{1}H} NMR spectrum of **2** in toluene-d_8 at different temperatures. The coalescence temperature was determined to 317 K (center, see text). The frequency marking (above) holds for the other two spectra, too.

FIGURE 2 50.324 MHz ^{13}C{1H} NMR spectrum of the endocyclic C^1 atoms of **2** in toluene-d_8 at 220 K (below, for the numbering of the atoms see Table 1) and 320 K. The frequency marking (above) holds for both spectra. The marking of 2 Hz (below) belongs to the individual, split lines, which in each case show the expanded signals at δ = 46.9 and 42.4, respectively. The splitting amounts in both cases to 0.6 Hz (see text; digital resolution 0.1 Hz). The lines denoted with "0" form the X portion of the ABX spectrum of the PC^{1}P triad of **2a**(Z).

^{31}P shift difference $\delta\nu$ of the two phosphorus atoms at 220 K to be 59 kJ mol^{-1}.

δ(^{31}P) and ^1J(PC) of **2** are in the range of the λ^5-1,3-diphosphetes with dimethylamino groups attached to P (see Table 2). The large shift of the endocyclic carbon atoms C^1 toward lower field strengths by about 36 is noticeable in the ^{13}C{^{1}H} NMR spectra of **2** compared to those of **1**. A comparable downfield shift was observed for the lines of the ring carbon atoms of the phenyl-substituted diphosphete **3** (see Table 2) [9]. This shift toward lower field strengths is caused by a decrease of the electron density at the ylidic C^1 carbon atom. Moreover, the distance between C^1 and C^2 atoms of the methoxycarbonyl groups of **2b**(E) clearly shows the
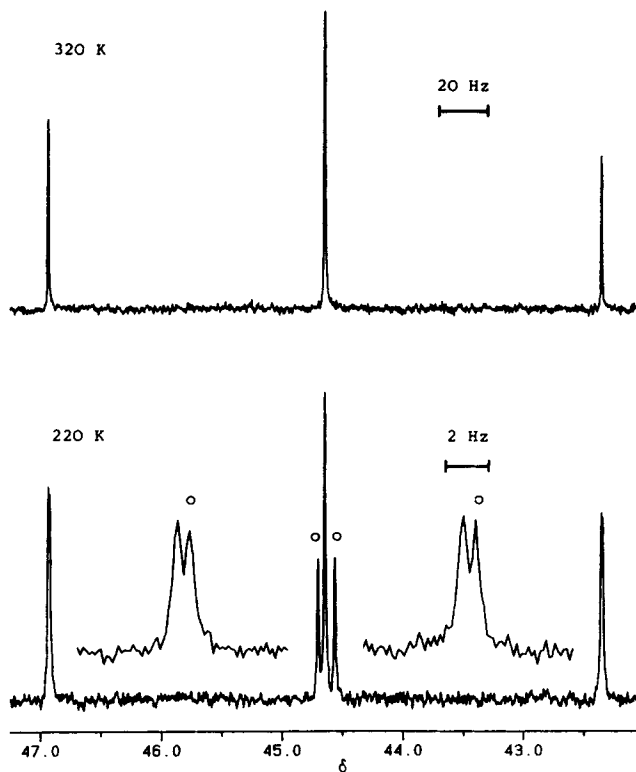
partial double bond character of these bonds (see Table 3). These observations indicate a noticeable statistical weight of the limiting mesomeric formula **2b'**. The same can be assumed for **2a**(Z).

The first ^2J(PP) coupling constant of λ^5-diphosphetes could be determined for the **2a**(Z) isomer; its numerical value of 194.0 Hz is surprisingly large.
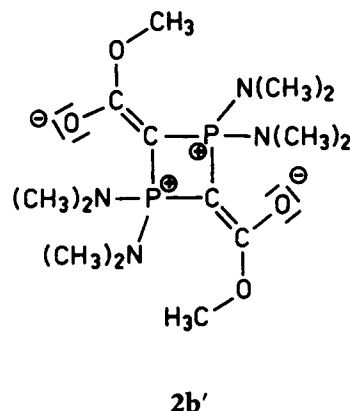

2b'

TABLE 2 ^{31}P and ^{13}C NMR Parameters of the Ring Atoms of λ^5-1,3-Diphosphetes

Compound[a]	$\delta(^{31}P)$	$\delta(^{13}C)$	$^1J(P,C)/Hz$	Ref.
[HCP(NMe$_2$)$_2$]$_2$ **1**	48.9	8.2	97.3	[1]
[MeCOOCCP(NMe$_2$)$_2$]$_2$ **2**[c]	41.2	46.0	115.0	[d]
[HCP(NEt$_2$)$_2$]$_2$	43.4	19.8	97.1	[8]
[MeCP(NMe$_2$)$_2$]$_2$	44.9	12.2	109.3	[9]
[MeCP(NEt$_2$)$_2$]$_2$	42.6	16.7	113.5	[8]
[Pe^{n}CP(NEt$_2$)$_2$]$_2$	44.8	34.3	106.5	[21]
[PhCP(NEt$_2$)$_2$]$_2$ **3**	34.6	50.8	114.9	[9]
[PhCP(CH$_2$Ph)NEt$_2$]$_2$	20.6	47.3	99.0	[11]
[SiMe$_3$CP(NMe$_2$)$_2$]$_2$	47.5	21.5	73.5	[7]
[(Pr^{irb_2}N)$_2$P(O)CPPh$_2$]$_2$	21.2[b] 20.8			[10]
[Ph$_2$P(O)CPPh$_2$]$_2$	31.6[b] 19.3			[10]
[(Pr$^i_2$N)$_2$P(O)CP(OMe)Ph]$_2$	39.8[b] 24.3			[10]
[Ph$_3$PCPPh$_2$]$_2$Cl$_2$	33.64[b] 14.4	18.29	111.69	[12]
[(Me$_2$N)$_3$PCP(NMe$_2$)$_2$]$_2$Cl$_2$	42.59[b] 37.89			[13]

[a] Me: CH$_3$, Et: CH$_2$CH$_3$, Pr^i: (CH$_3$)$_2$CH, Ph: C$_6$H$_5$, Pe^n: n-C$_5$H$_{11}$.
[b] Not assigned.
[c] At 360 K.
[d] This work.

TABLE 3   Selected Bond Distances [pm] and Angles [°] for molecule **2b**(E). Standard deviations in parentheses.

P1–C1	174.3(2)	P1–N1	165.5(3)
P1–N2	164.5(2)	O1–C2	122.5(3)
P1–C1'	174.3(3)	O2–C3	144.3(3)
O2–C2	137.6(3)	C1–C2	141.6(3)
N1–C12	145.9(4)	N1–C12	144.9(3)
N2–C22	146.6(3)	N2–C21	145.7(3)
C1–P1–N1	121.8(1)	C1–P1–N2	113.1(1)
N1–P1–N2	101.2(1)	C1–P1–C1'	87.4(1)
N1–P1–C1'	111.9(1)	N2–P1–C1'	122.9(1)
C2–O2–C3	114.2(2)	P1–C1–C2	131.1(2)
P1–C1–P1'	92.6(1)	C2–C1–P1'	136.3(2)
O1–C2–O2	121.3(2)	O1–C2–C1	126.5(2)
O2–C2–C1	112.2(2)	O2–C3–H31	108.0(18)
O2–C3–H32	107.3(23)	O2–C3–H33	111.1(19)
P1–N1–C11	120.8(2)	P1–N1–C12	121.5(2)
C11–N1–C12	112.2(2)	P1–N2–C21	122.8(2)
P1–N2–C22	120.3(1)	C21–N2–C22	113.8(2)

Similarly large values were found for a 6-aza-2λ^5,4λ^5-diphosphafulvene [16] and for monosubstituted 1λ^5, 3λ^5-diphosphabenzenes [4], while the values for di-substituted 1λ^5,3λ^5-diphosphabenzenes are smaller by about $\frac{1}{3}$ [5, 6].

Molecular Structure

The single-crystal structure determination proves that the examined crystal consisted entirely of the conformational isomer **2b**(E). There is only one molecule in the triclinic unit cell, which therefore lies on a crystallographic inversion center. A projection onto the four-membered ring is shown in Figure 3. Table 3 shows that the P–C distances in the exactly planar ring are very close to the value given for P–C bonds with aromatic character (173 pm) [17] and are in good agreement with those values previously found in similar compounds (Table 4). The angle at the P atoms is by 2.6° smaller than 90°, and that at the C atoms is 2.6° larger than 90°. A closer examination of the molecule **2b** reveals that the ester groups are coplanar to the central ring. The C^1–C^2 distance is unusually short (see [18]
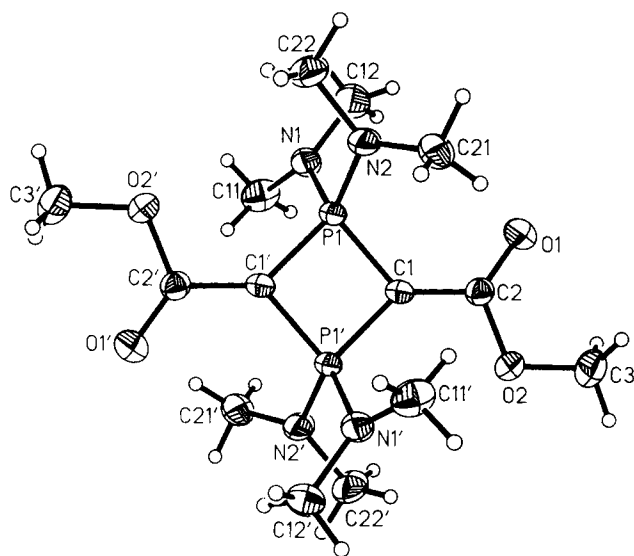
FIGURE 3 Molecular structure of **2b**(E) projected onto the plane of the four-membered ring. The thermal ellipsoids are drawn on the 70% probability level. The size of the H atoms is arbitrary.

for comparison) and its value is only slightly larger than that found in benzene [19]. This can be attributed to the conjugation between the ester group and the ring as a result of the overlap between the respective π-systems, which is optimal for both being coplanar. In addition, and probably more important, there seems to be a considerable contribution from a polar form shown as **2b'**. This has also been discussed for the similar compound [(Pr$_2^i$N)$_2$P(O)CP(C$_6$H$_5$)$_2$]$_2$, Pr^i: (CH$_3$)$_2$CH (see Table 4, [10]).

EXPERIMENTAL

The NMR spectra were taken with a temperature-controlled AM 200-NMR spectrometer of Bruker Analytische Messtechnik GmbH, Rheinstetten (^{1}H: 200.133 MHz; ^{13}C: 50.324 MHz using tetramethylsilane as a reference; ^{31}P: 81.015 MHz using an 85% aqueous orthophosphoric acid standard). The digital spectral resolution was <0.12 Hz in each case.

As usual, shifts toward lower field strengths are taken to be positive. The spectra of the ABX systems were simulated on a Bruker-Aspect 3000 computer using the PANIC program (Bruker software). The IR spectra were taken with a Perkin-Elmer IR spectrometer and a CDS data station. The mass spectra were registered with a Varian Type MAT 711 spectrometer.

All operations were performed under an argon blanket. A high vacuum system was provided to evacuate the equipment to 10^{-3} torr and back fill with dry high-purity argon. The solvents were dried and flushed with argon using known procedures.

X-ray Analysis

At about $-10°C$ a selected crystal of compound **2b**(E) was transferred in a dry argon atmosphere directly from the solution into a glass capillary, which was immediately sealed with a small flame. The capillary was subsequently mounted on an upgraded Syntex P2$_1$ diffractometer, equipped with a low-temperature device, AgKα radiation and a graphite monochromator. Crystal parameters and information relating to data collection and structure refinement are summarized in Table 5 [22]. Final atomic coordinates and isotropic thermal parameters are shown in Table 6.

2,4-Di(methoxycarbonyl)-1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete 2

To a solution of 2.71 g (10 mmol) 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete **1** [1] in 10 mL 1,2-dimethoxyethane, a solution of 0.92 g (10 mmol) CH$_3$OOC—CN in 10 mL 1,2-dimethoxyethane was added dropwise with stirring. The mixture was stirred for 0.5 h at $-20°C$ and then gradually warmed to room temperature. The yellow precipitate that had formed was collected on a glass frit, washed with 1 mL of 1,2-dimethoxyethane, and recrystallized at $-10°C$ from tetrahydrofuran. The bright-yellow crystals of **2** melted at 153–154°C with decomposition; yield 0.90 g (23%). Anal. Calcd. for C$_{14}$H$_{30}$N$_4$O$_4$P$_2$ (380.37): C, 44.21; H, 7.95; N, 14.73. Found: C, 44.58; H, 8.21; N, 14.87.

TABLE 4 Bond Lengths [pm] and Bond Angles [°] of λ^5-1,3-Diphosphetes[a]

Compound		P1–C1	P1–C1'	P1–C1–P1'	C1–P1–C1'	Ref.
[HCP(NMe$_2$)$_2$]$_2$	**1**[b]	172.5(1)	172.5(1)	88.6(1)	91.4(1)	[1]
[PhCP(NEt$_2$)$_2$]$_2$	**3**[b]	174.6(2)	174.1(2)	90.5(1)	89.5(1)	[9]
[MeO(O)CCP(NMe$_2$)$_2$]$_2$	**2**[c]	174.3(2)	174.3(3)	92.6(1)	87.4(1)	
[Pr$_2^i$N)$_2$P(O)CPPh$_2$]$_2$[d]		175.1(3)	174.7(3)	89.5(2)	90.5(2)	[10]
[Ph$_3$PCPPh$_2$]$_2$[NO$_3$]$_2$·H$_2$O[d]		170.0(5)	176.5(3)	91.7(2)	88.3(2)	[12]

[a] To date all structurally characterized λ^5-1,3-diphosphetes are molecules with C$_i$ symmetry.
[b] At ca. 140 K.
[c] At ca. 123 K.
[d] Data collection at room temperature.

TABLE 5 Details of Data Collection and Crystal Structure Refinement [20] of **2b**(E).

Formula, wt.	$C_{14}H_{30}N_4O_4P_2$, 380.37 amu
Lattice constants	a = 694.8(5), b = 869.1(7), c = 911.5(7) pm
	α = 64.78(5), β = 74.30(6), γ = 77.75(6)°
Space group	$P\bar{1}$ (no. 2)
Volume, Z	476.4(6) × 10^6 pm³; 1
D_c	1.326 g/cm³
Crystal size	0.91 × 0.50 × 0.22 mm
μ(AgKα), λ	2.46 cm^{-1}; 56.087 pm
Diffractometer	Syntex-P2₁, graphite monochromator, scintillation counter
2Θ range	4.5 to 46.0°, ω-2Θ scan
Scan speed	Variable, 1.25 to 19.53°/min. in ω
Temperature (K)	123 ± 2
Data collected	2694
unique, observed	2694, 2288 ($F > 3 \times \sigma(F)$)
Absorption correction	ψ-scans, 11 hkl, $\Delta\psi$ = 10°
Structure solution	Direct Methods in P1
Refinement method	Full-Matrix Least-Squares, 157 parameters
Weighting scheme	$w = 1/(\sigma^2(F) + GF F^*)$; G = 0.0001
R(aniso)	0.053, 0.065 for all data
wR	0.058, 0.058 for all data
Goodness-of-fit	1.73

TABLE 6 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters [pm²][a] for Compound **2b**(E)[b]

	x	y	z	$U(eq)$
P1	4759(1)	9395(1)	4036(1)	149(2)
O1	2771(3)	6242(2)	7386(2)	238(6)
O2	3153(3)	7493(2)	9008(2)	238(6)
C1	4211(3)	8845(2)	6168(2)	160(6)
C2	3326(3)	7430(2)	7495(2)	167(6)
C3	2373(4)	6023(3)	10406(3)	301(9)
N1	2964(3)	9974(2)	2962(2)	201(6)
N2	6103(3)	7847(2)	3497(2)	227(7)
C11	1713(3)	11592(3)	2707(3)	254(8)
C12	1952(5)	8709(3)	2886(3)	317(9)
C21	7126(4)	6347(3)	4627(3)	232(7)
C22	6895(4)	8154(3)	1745(3)	290(9)

[a] U_{eq} is defined as $\frac{1}{3}$ of the trace of the orthogonalized U_{ij}-tensor.
[b] The hydrogen atoms in the methyl groups were finally refined with a common C–H distance and a common temperature factor.

TABLE 7 Results of El Mass Spectrum of **2** [15]

	Rel. Int.		Rel. Int.		
m/e	20 eV	330 K	70 eV	330 K	Fragment
381	17.56			7.96	M⁺(^{13}C)
380	96.27			48.31	M⁺
349	11.92			12.30	(M–OMe)⁺
337	48.28			27.81	(M–NMe₂ + H)⁺
336	2.12			4.38	(M–NMe₂)⁺
294	26.81			21.50	(M–2NMe₂ + 2H)⁺
293	100.00			100.00	(M–2NMe₂ + H)⁺
119	4.89			14.75	(P(NMe₂)₂)⁺
76	—			15.89	(HPNMe₂)⁺
44	—			15.96	(NMe₂)⁺
42	—			8.76	(NMe₂–2H)⁺

Mass spectral data are given in Table 7. High-resolution mass determination: M⁺, calcd. 380.1742 (found 380.1744); [M − N(CH₃)₂ + H]⁺ 337.1320 (337.1320); [M − 2N(CH₃)₂ + H]⁺ 293.0820 (293.01816) [15]. IR spectrum: Rubbing in nujol between CsBr discs (in cm^{-1}): 3000 m; 2930 s; 2890 s; 2850 s; 2810 s; 1660 m, sh; 1635 s; 1455 m; 1435 s; 1410 m; 1375 s; 1308 vs, b; 1287 s, b; 1180 m, b; 1095 m; 1068 w; 1028 m; 983 s; 925 w; 768 m; 735 w; 723 vw; 665 m; 533 m; 488 w; 458 w; 385 w (vs = very strong, s = strong, m = middle, w = weak, vw = very weak, b = broad, sh = shoulder).

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