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$C_{38}H_{54}N_3O_9P$, a New Compound in Diazadihydrophosphinine Chemistry

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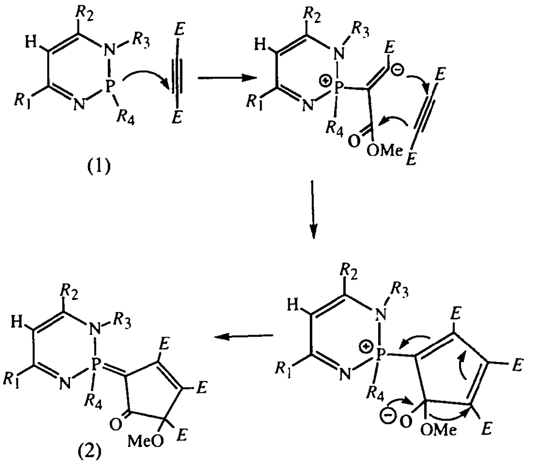
Abstract

Another compound of the diazadihydrophosphinine family has been isolated and structurally characterized. This new compound in diazadihydrophosphinine chemistry was identified as trimethyl 5-[4-*tert*-butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-1,2-dihydro-1,3,2-diazaphosphin-2-ylidene]-3-methoxy-4-oxo-1-cyclopentene-1,2,3-tricarboxylate, $C_{38}H_{54}N_3O_9P$. The parent dihydrodiazaphosphin structure is still present in the new compound and the P atom is linked by a double bond to a five-membered ring. The P(1)—C(31) bond distance is 1.731 (8) Å. The five-membered ring is planar [maximum deviation from the least-squares plane of 0.011 (9) Å for C(35)] and the ylidic charge at Cα to the P atom is stabilized by the electron-attracting groups in the ring.

Comment

Recently we reported on the reactivity of diazadihydrophosphinines, (1), towards one equivalent of dimethylacetylenedicarboxilate (DMAD) (Barluenga, Tomás, Bieger, García-Granda & Santiago-García, 1996). The reaction afforded a bicyclo[3,2,1]phospha-2,8-diaza-1,3,6-octatriene that showed an unexpected reactivity towards electrophiles, leading to polycyclic products in high yields. As DMAD can also be seen as an electrophile, we made a one-pot attempt to gain insight into its reactivity. At high concentrations of DMAD, the major product, (2), was afforded according to ^{31}P-NMR; this was isolated by chromatography and finally obtained in the form of yellow crystals. It was characterized by spectroscopic methods but the structure could not be established without ambiguities. Single crystals were grown from ether/hexane and a diffraction study was performed on one of them. It showed that in the final product, the parent dihydrodiazaphosphin structure was still present. The P atom was linked by a P=C double bond to a five-membered ring system resulting from the interaction with two molecules of DMAD. The mechanism of the reaction is shown in the scheme below.



R_1 = ^{t}Bu R_3 = cHex E = CO_2Me
R_2 = 4-$C_6H_4OCH_3$ R_4 = N^{i}Pr$_2$

The compound was identified as 4-^{t}butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-2-[4-methoxy-2,3,4-tris(methoxycarbonyl)-5-oxo-2-cyclopentenyliden]-1,2-dihydro-1,3,2-diazaphosphinine, (2). The structure resembles a molecule obtained by Tebby and co-workers (Waite, Tebby, Ward & Williams, 1969) by the reaction of DMAD with triphenylphosphine, but in that case no structural data were reported. In the structure itself, most bond parameters are in the expected ranges but the P—N single bonds are shortened, probably as the result of to p–σ^* interactions (Gilheany, 1994). These interactions should also be responsible for the flattening of the N atoms indicated by the sums of the corresponding bond angles [359.2 (18) and 357.8 (16)°, respectively, in the two tricoordinated cases].

The six-membered ring [P(1),N(2),C(3),C(4),C(5),-N(6)] has a skew-boat conformation approaching the $^1S_2$ form in the notation of Boeyens (1978). The Cremer & Pople (1975) ring-puckering parameters are q_2 = 0.445 (7), q_3 = 0.165 (7), Q = 0.474 (6) Å, φ = 22 (1), θ = 70 (1)°. In the six-membered ring, mesomeric stabilization can be observed; this provokes a slight shortening of the single and a widening of the double bonds.

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The five-membered ring is planar to within standard deviation [sum of the angles 539.8 (35)°, maximum deviation from the least-squares plane 0.011 (9) Å fot C(35)]. The ylidic charge at Cα to the P atom is stabilized by the electron-attracting groups in the subsystem, resulting in a lengthening of the C═O distance of the endocyclic carbonyl group to 1.232 (8) Å. The C—C bond to the γ ester group is slightly shortened [1.453 (11) Å] while the C═O distance is lengthened [1.201 (9) Å]. The ester in β could seemingly occupy two possible positions when crystallizing resulting in a disordered structure at this position. Although the methyl C atom could be found in two positions, the O atom had to be refined at the average site. The occupancy factors for the disordered atoms C(37*A*) and C(37*B*) are 0.45 (2) and 0.55 (2), respectively.

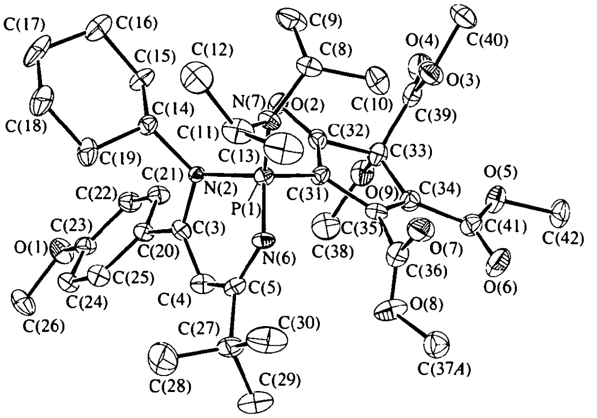

Fig. 1. *EUCLID* (Spek, 1982) plot showing 20% probability displacement ellipsoids and the atomic numbering scheme. H atoms are omitted for clarity.

Experimental

0.57 g (1.3 mmol) diazadihydrophosphinine were dissolved under nitrogen in 10 ml of CH_2Cl_2. A solution of 0.84 g (6 mmol) DMAD in 5 ml CH_2Cl_2 was added to the well stirred mixture at 253 K. After it had been allowed to warm slowly to room temperature, the solvent was removed under reduced pressure and the residue purified by chromatography on SiO_2, eluding first with CH_2Cl_2 then with CH_2Cl_2 and ether. Yield: 0.55 g, ~60%, m.p. 513 K (dec.).

Crystal data

$C_{38}H_{54}N_3O_9P$
$M_r = 727.81$
Monoclinic
$P2_1/c$
$a = 9.846\ (9)$ Å
$b = 38.204\ (9)$ Å
$c = 11.421\ (9)$ Å
$\beta = 113.18\ (7)°$
$V = 3949.2\ (48)$ Å^3
$Z = 4$
$D_x = 1.224$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–$10°$
$\mu = 0.125$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.23 × 0.20 × 0.17 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (*XABS*2: Parkin, Moezzi & Hope, 1995)
$T_{\min} = 0.972$, $T_{\max} = 1.000$
6056 measured reflections
5469 independent reflections
1742 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.083$
$\theta_{\max} = 23.00°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 42$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 200 reflections
frequency: 60 min
intensity decay: 4.24%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0580$
$wR(F^2) = 0.1269$
$S = 0.992$
5454 reflections
461 parameters
H atoms riding, with isotropic common U
$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.270$ e Å^{-3}
$\Delta\rho_{\min} = -0.304$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P(1)	0.0303 (2)	0.12128 (6)	0.2081 (2)	0.0427 (6)
N(2)	0.0280 (6)	0.16476 (14)	0.2197 (5)	0.0333 (15)
C(3)	0.1184 (8)	0.1818 (2)	0.1669 (7)	0.042 (2)
C(4)	0.1437 (9)	0.1665 (2)	0.0686 (8)	0.058 (2)
C(5)	0.0669 (9)	0.1352 (2)	0.0048 (8)	0.049 (2)
N(6)	0.0118 (7)	0.1134 (2)	0.0601 (5)	0.044 (2)
N(7)	−0.1140 (7)	0.1033 (2)	0.2222 (6)	0.045 (2)
C(8)	−0.1122 (11)	0.0823 (2)	0.3307 (9)	0.069 (3)
C(9)	−0.0846 (12)	0.1018 (2)	0.4491 (8)	0.090 (4)
C(10)	−0.0355 (11)	0.0473 (2)	0.3459 (9)	0.093 (4)
C(11)	−0.2575 (10)	0.1036 (3)	0.1047 (9)	0.078 (3)
C(12)	−0.3870 (11)	0.1176 (3)	0.1321 (10)	0.114 (4)
C(13)	−0.2864 (11)	0.0685 (3)	0.0423 (9)	0.111 (4)
C(14)	−0.0884 (8)	0.1850 (2)	0.2475 (7)	0.047 (2)
C(15)	−0.0350 (9)	0.1999 (2)	0.3810 (8)	0.062 (3)
C(16)	−0.1697 (10)	0.2150 (3)	0.4005 (9)	0.079 (3)
C(17)	−0.2492 (12)	0.2423 (3)	0.3056 (12)	0.100 (4)
C(18)	−0.2942 (11)	0.2289 (3)	0.1700 (11)	0.102 (4)
C(19)	−0.1656 (10)	0.2116 (2)	0.1463 (8)	0.074 (3)
C(20)	0.1910 (8)	0.2153 (2)	0.2179 (7)	0.042 (2)
C(21)	0.2688 (8)	0.2197 (2)	0.3484 (7)	0.046 (2)
C(22)	0.3539 (9)	0.2491 (2)	0.3972 (8)	0.053 (2)
C(23)	0.3626 (9)	0.2751 (2)	0.3169 (8)	0.045 (2)
C(24)	0.2817 (9)	0.2720 (2)	0.1855 (7)	0.050 (2)
C(25)	0.1997 (9)	0.2420 (2)	0.1386 (8)	0.053 (2)
C(26)	0.4879 (9)	0.3269 (2)	0.2927 (8)	0.072 (3)
C(27)	0.0413 (11)	0.1295 (2)	−0.1360 (8)	0.063 (3)
C(28)	−0.0398 (12)	0.0955 (3)	−0.1830 (8)	0.113 (4)
C(29)	−0.0458 (13)	0.1601 (3)	−0.2119 (9)	0.128 (5)
C(30)	0.1894 (11)	0.1281 (3)	−0.1488 (9)	0.102 (4)
C(31)	0.1991 (8)	0.1074 (2)	0.3196 (7)	0.043 (2)
C(32)	0.2718 (8)	0.1221 (2)	0.4445 (7)	0.044 (2)
C(33)	0.4234 (10)	0.1024 (2)	0.5113 (8)	0.051 (2)
C(34)	0.4220 (10)	0.0772 (2)	0.4090 (8)	0.050 (2)
C(35)	0.2967 (9)	0.0812 (2)	0.3035 (7)	0.047 (2)
C(36)	0.2625 (12)	0.0593 (3)	0.1869 (9)	0.064 (3)
C(37*A*)†	0.315 (2)	0.0332 (5)	0.0315 (19)	0.078 (9)

C(37*B*)‡	0.159 (3)	0.0121 (6)	0.069 (2)	0.135 (11)
C(38)	0.5579 (10)	0.1475 (3)	0.4615 (10)	0.089 (3)
C(39)	0.4214 (11)	0.0847 (2)	0.6292 (10)	0.058 (3)
C(40)	0.2982 (12)	0.0418 (2)	0.6987 (9)	0.095 (4)
C(41)	0.5331 (10)	0.0504 (3)	0.4272 (10)	0.058 (3)
C(42)	0.7396 (9)	0.0219 (2)	0.5823 (9)	0.076 (3)
O(1)	0.4543 (6)	0.30249 (15)	0.3731 (5)	0.064 (2)
O(2)	0.2340 (6)	0.14577 (14)	0.4986 (5)	0.053 (2)
O(3)	0.3158 (8)	0.0602 (2)	0.5968 (6)	0.072 (2)
O(4)	0.4993 (8)	0.0916 (2)	0.7361 (6)	0.088 (2)
O(5)	0.6337 (7)	0.05010 (14)	0.5474 (6)	0.066 (2)
O(6)	0.5385 (7)	0.0303 (2)	0.3482 (6)	0.090 (2)
O(7)	0.1720 (8)	0.0343 (2)	0.1731 (6)	0.081 (2)
O(8)	0.3209 (7)	0.0666 (2)	0.1123 (7)	0.087 (2)
O(9)	0.5421 (6)	0.1264 (2)	0.5572 (6)	0.065 (2)

† Occupancy 0.453 (15). ‡ Occupancy 0.547 (15).

Table 2. *Selected geometric parameters (Å, °)*

P(1)—N(7)	1.643 (6)	C(32)—C(33)	1.575 (10)
P(1)—N(6)	1.655 (6)	C(33)—O(9)	1.415 (9)
P(1)—N(2)	1.667 (6)	C(33)—C(34)	1.509 (10)
P(1)—C(31)	1.731 (8)	C(33)—C(39)	1.514 (11)
N(2)—C(3)	1.415 (9)	C(34)—C(35)	1.351 (10)
N(2)—C(14)	1.516 (9)	C(34)—C(41)	1.453 (11)
C(3)—C(4)	1.371 (10)	C(35)—C(36)	1.494 (11)
C(3)—C(20)	1.471 (10)	C(36)—O(8)	1.233 (11)
C(4)—C(5)	1.448 (10)	C(36)—O(7)	1.272 (11)
C(4)—H(4*A*)	0.93	C(37*A*)—O(8)	1.56 (2)
C(5)—N(6)	1.288 (9)	C(37*B*)—O(7)	1.43 (2)
C(5)—C(27)	1.542 (10)	C(41)—O(6)	1.201 (9)
C(31)—C(32)	1.435 (10)	C(41)—O(5)	1.340 (10)
C(31)—C(35)	1.450 (10)	C(42)—O(5)	1.443 (9)
C(32)—O(2)	1.232 (8)		
N(7)—P(1)—N(6)	105.8 (3)	O(9)—C(33)—C(34)	117.1 (7)
N(7)—P(1)—N(2)	111.7 (3)	O(9)—C(33)—C(39)	104.9 (7)
N(6)—P(1)—N(2)	105.2 (3)	C(34)—C(33)—C(39)	113.9 (7)
C(3)—N(2)—C(14)	120.7 (6)	O(9)—C(33)—C(32)	110.9 (6)
C(3)—N(2)—P(1)	113.1 (5)	C(34)—C(33)—C(32)	102.2 (7)
C(14)—N(2)—P(1)	124.0 (5)	C(39)—C(33)—C(32)	107.6 (7)
C(4)—C(3)—N(2)	120.1 (7)	C(35)—C(34)—C(41)	125.3 (8)
C(4)—C(3)—C(20)	118.6 (7)	C(35)—C(34)—C(33)	110.2 (7)
N(2)—C(3)—C(20)	121.3 (7)	C(41)—C(34)—C(33)	124.2 (8)
C(3)—C(4)—C(5)	122.4 (8)	C(34)—C(35)—C(31)	112.5 (7)
C(3)—C(4)—H(4*A*)	118.8 (5)	C(34)—C(35)—C(36)	122.6 (8)
C(5)—C(4)—H(4*A*)	118.8 (5)	C(31)—C(35)—C(36)	124.9 (8)
N(6)—C(5)—C(4)	121.6 (7)	O(8)—C(36)—O(7)	125.3 (9)
N(6)—C(5)—C(27)	119.5 (8)	O(8)—C(36)—C(35)	119.1 (10)
C(4)—C(5)—C(27)	118.7 (8)	O(7)—C(36)—C(35)	115.6 (10)
C(5)—N(6)—P(1)	119.0 (6)	O(6)—C(41)—O(5)	122.1 (9)
C(32)—C(31)—C(35)	107.4 (7)	O(6)—C(41)—C(34)	126.6 (9)
C(32)—C(31)—P(1)	124.8 (6)	O(5)—C(41)—C(34)	111.3 (8)
C(35)—C(31)—P(1)	127.6 (6)	C(41)—O(5)—C(42)	116.9 (7)
O(2)—C(32)—C(31)	130.8 (7)	C(36)—O(7)—C(37*B*)	112.1 (12)
O(2)—C(32)—C(33)	121.6 (7)	C(36)—O(8)—C(37*A*)	107.8 (10)
C(31)—C(32)—C(33)	107.5 (7)		
N(2)—P(1)—N(6)—C(5)	32.5 (8)	N(2)—C(3)—C(4)—C(5)	8 (1)
N(6)—P(1)—N(2)—C(3)	−45.6 (7)	C(3)—C(4)—C(5)—N(6)	−25 (1)
P(1)—N(2)—C(3)—C(4)	29 (1)	C(4)—C(5)—N(6)—P(1)	0 (1)

Data were collected by profile analysis over all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978). The structure was solved by Patterson methods and the automatic phase expansion procedure using *DIRDIF* (Beurskens *et al.*, 1992). The structure was refined anisotropically by least-squares methods using *SHELXL*93 (Sheldrick, 1993). Geometrical calculations were made using *PARST* (Nardelli, 1983). All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group VAX computers.

Data collection: *Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *CRYSDA* (Beurskens *et al.*, 1992). Data reduction: *REFLEX* (local program). Program(s) used to solve structure: *DIRDIF*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, spectroscopy data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl Triphenylphosphoranylideneacetate: a Redetermination

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Abstract

The structure of the title compound, $C_{21}H_{19}O_2P$, has been redetermined to provide a more precise molecular geometry. Close C—H···O contacts, not remarked upon in the original paper, are discussed briefly.

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