Crystal Structure of Methyl 4-Hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl- λ^5 -phosphanylidene)-1,3-cyclopentadiene-1-carboxylate

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The crystal structure of methyl 4-hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl- λ^5 -phosphanylidene)-1,3-cyclopentadiene-1-carboxylate was determined by crystallographic methods. The crystal, $C_{31}H_{23}N_2O_7P$, belongs to space group $P2_1/n$ with cell dimensions of $a = 11.0660(6)$, $b = 21.1793(12)$, $c = 11.7339(6)$ Å, $\beta = 100.1860(10)^\circ$, $V = 2706.7(3)$ Å³, $Z = 4$, $D_{\text{cal}} = 1.390$ Mg/m³, $T = 120(2)$ K. The crystal structure was solved by direct methods and refined by full-matrix least squares to final values of $R1 = 0.0559$ and $wR2 = 0.1122$ with 4470 reflections ($I > 2\sigma(I)$). There is an intramolecular-hydrogen bond between the O(2) atom of the nitro group and the hydrogen of the OH group.

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Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activities.¹ The cyclopentadienylides are of interest to us because these compounds may serve as ligands in the synthesis of many inorganic complexes. Furthermore, these compounds are thought to be stable and quite unreactive for a ylide.²

In this paper we report on the crystal structure of a new synthesized compound of cyclopentadienylide derivatives with four different functional groups: methyl 4-hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl- λ^5 -phosphanylidene)-1,3-cyclopentadiene-1-carboxylate.

Methyl 4-hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl- λ^5 -phosphanylidene)-1,3-cyclopentadiene-1-carboxylate was prepared by the following procedure: To a magnetically stirred solution of 0.14 g of dimethyl acetylenedicarboxylate (1 mmol) and 0.19 g of 1-nitro-4-[(*E*)-2-nitro-1-ethenyl]benzene (1 mmol) in 5 mL dry diethyl ether was added drop wise a solution of 0.26 g of triphenylphosphine (1 mmol) in 3 mL dry diethyl ether at room temperature over 10 min. The reaction mixture was stirred for 1 h. The resulting solid was filtered off, washed with dry diethyl ether and dried in a vacuum (0.55 g yield 98%). Yellow powder, d.p. 184–185°C. Anal. Calcd. for $C_{31}H_{23}N_2O_7P$ (566.50): C, 65.73; H, 4.09; N, 4.94%. Found: C, 65.6; H, 4.0; N, 4.8%. Red crystals were obtained from a methanol-acetone mixture solution with slow evaporation at

room temperature. A chemical diagram for the title compound is represented in Fig. 1.

The crystal structure was solved by direct methods and refined by full-matrix least squares. All of the H atoms were calculated geometrically. The crystal and experimental data, and the atomic parameters of non-H atoms are given in Tables 1 and 2, respectively.

An ORTEP drawing of the molecule together with the atomic numbering is shown in Fig. 2. The P atom is coplanar with each of the phenyls, but deviates from the five-ring plane (see Table 3). The *para*-nitrophenyl group and cyclopentadienylidene are not coplanar. The *para*-nitrophenyl group is significantly deviated from the plan of the cyclopentadienylidene. The

Fig. 1 Chemical diagram of PCYCLO.

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Table 1 Crystal and experimental data

Formula: $C_{31}H_{23}N_2O_7P$
Formula weight = 566.48
Crystal system, Space group: monoclinic, $P2_1/n$
Unit cell dimensions:
$a = 11.0660(6)$ Å
$b = 21.1793(12)$ Å $\beta = 100.1890(10)^\circ$
$c = 11.7339(6)$ Å
$V = 2706.7(3)$ Å ³
Z , Calculated density: 4, 1.390 Mg/m ³
Absorption coefficient = 0.155 mm ⁻¹
$F(0\ 0\ 0) = 1176$
Crystal size = 0.43 × 0.25 × 0.25 mm ³
θ range for data collection = 1.92 to 29.00°
Index ranges: $-11 \leq h \leq 15$, $-28 \leq k \leq 20$, $-15 \leq l \leq 14$
Reflections collected = 14736
Completeness to $\theta = 29.00^\circ$, 99.2%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission = 0.962 and 0.906
Refinement method: full-matrix least-squares on F^2
Data/restraints/parameters: 7113/0/372
Goodness-of-fit on $F^2 = 1.071$
Final R indices for 4470 refl. with $[I > 2\sigma(I)]$:
$R1 = 0.0559$, $wR2 = 0.1122$
R indices (all data): $R1 = 0.0917$, $wR2 = 0.1214$
Largest diff. peak and hole: 0.493 and -0.593 eÅ ⁻³

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	$U(\text{eq})$		x	y	z	$U(\text{eq})$
P(1)	7483(1)	1486(1)	2579(1)	18(1)	C(12)	7062(2)	1310(1)	-342(2)	23(1)
O(1)	7433(1)	1(1)	3230(1)	25(1)	C(13)	6731(2)	2419(1)	-437(2)	33(1)
O(2)	7495(2)	-1105(1)	2275(1)	34(1)	C(14)	8032(2)	1275(1)	4072(2)	20(1)
O(3)	7334(2)	-1217(1)	399(1)	37(1)	C(15)	9282(2)	1212(1)	4492(2)	28(1)
O(4)	5609(1)	-726(1)	-5149(1)	35(1)	C(16)	9683(2)	1025(1)	5628(2)	38(1)
O(5)	7525(2)	-994(1)	-4850(1)	36(1)	C(17)	8846(2)	910(1)	6346(2)	34(1)
O(6)	7288(2)	1303(1)	-1313(1)	35(1)	C(18)	7601(2)	976(1)	5941(2)	28(1)
O(7)	6710(1)	1828(1)	166(1)	24(1)	C(19)	7193(2)	1157(1)	4803(2)	24(1)
N(1)	7379(2)	-873(1)	1261(2)	25(1)	C(20)	8668(2)	1952(1)	2100(2)	18(1)
N(2)	6622(2)	-771(1)	-4525(2)	27(1)	C(21)	9573(2)	1628(1)	1639(2)	23(1)
C(1)	7252(2)	806(1)	1719(2)	19(1)	C(22)	10495(2)	1967(1)	1252(2)	30(1)
C(2)	7349(2)	189(1)	2122(2)	20(1)	C(23)	10513(2)	2618(1)	1309(2)	30(1)
C(3)	7316(2)	-221(1)	1156(2)	20(1)	C(24)	9619(2)	2938(1)	1766(2)	31(1)
C(4)	7177(2)	147(1)	120(2)	20(1)	C(25)	8693(2)	2602(1)	2164(2)	25(1)
C(5)	7143(2)	771(1)	456(2)	21(1)	C(26)	6099(2)	1937(1)	2561(2)	20(1)
C(6)	7041(2)	-94(1)	-1084(2)	21(1)	C(27)	6095(2)	2457(1)	3275(2)	25(1)
C(7)	8029(2)	-359(1)	-1500(2)	30(1)	C(28)	5022(2)	2801(1)	3244(2)	28(1)
C(8)	7896(2)	-581(1)	-2623(2)	29(1)	C(29)	3954(2)	2618(1)	2516(2)	29(1)
C(9)	6762(2)	-537(1)	-3331(2)	22(1)	C(30)	3950(2)	2093(1)	1812(2)	30(1)
C(10)	5755(2)	-277(1)	-2950(2)	24(1)	C(31)	5022(2)	1750(1)	1833(2)	24(1)
C(11)	5910(2)	-55(1)	-1829(2)	23(1)

Fig. 2 ORTEP diagram and showing hydrogen bonding in PCYCLO at 50% probability level.

torsion angle of C(3)-C(4)-C(6)-C(11) is $107.8^\circ(2)$. Selected bond lengths, bond angles and torsion angles are given in Table 3.

There is an intramolecular-hydrogen bond between the O(2) atom of the nitro group and the hydrogen atom of the hydroxyl group. The hydrogen-bond parameters are $\text{O}(1)\cdots\text{H}(10) = 0.88$, $\text{H}(10)\cdots\text{O}(2) = 1.85$, $\text{O}(1)\cdots\text{O}(2) = 2.603(2)\text{\AA}$ and $\angle(\text{O}(2)\text{HO}(1)) = 143.0^\circ$. The geometry of the hydrogen-bond is given in Table

Table 3 Selected bond lengths ($\text{\AA}$), bond angles ($^\circ$) and torsion angles ($^\circ$)

Bond lengths ($\text{\AA}$)		Bond lengths ($\text{\AA}$)	
P(1)-C(1)	1.752(2)	C(3)-C(4)	1.429(3)
P(1)-C(14)	1.806(2)	C(4)-C(6)	1.484(3)
C(1)-C(2)	1.388(3)	C(5)-C(12)	1.468(3)
C(1)-C(5)	1.468(3)	C(3)-N(1)	1.358(3)
C(2)-C(3)	1.424(3)	C(2)-O(1)	1.346(2)
Bond angles ($^\circ$)		Bond angles ($^\circ$)	
C(1)-P(1)-C(14)	110.20(10)	O(2)-N(1)-O(3)	121.15(19)
C(1)-C(2)-O(1)	126.52(19)	C(2)-C(3)-C(4)	109.18(18)
C(1)-C(2)-C(3)	108.29(18)	C(3)-C(4)-C(6)	126.92(19)
C(2)-O(1)-H(10)	106.2	C(3)-C(4)-C(5)	106.46(18)
C(2)-C(3)-N(1)	122.88(19)	C(4)-C(5)-C(1)	109.57(18)
Torsion angles ($^\circ$)		Torsion angles ($^\circ$)	
C(1)-P(1)-C(14)-C(19)	-89.37(19)	C(1)-C(2)-C(3)-C(4)	-0.9(2)
P(1)-C(1)-C(2)-O(1)	11.8(3)	P(1)-C(14)-C(19)-C(18)	178.02(17)
C(1)-C(2)-C(3)-N(1)	-179.21(18)	P(1)-C(14)-C(15)-C(16)	-177.4(2)
P(1)-C(1)-C(2)-C(3)	-169.55(14)	P(1)-C(20)-C(25)-C(24)	-179.07(16)
P(1)-C(1)-C(5)-C(4)	169.86(15)	P(1)-C(26)-C(27)-C(28)	179.61(17)

Table 4 Hydrogen bond D-H $\cdots$ A in the crystal of PCYCLO

D-H	D (D-H)	d (H $\cdots$ A)	<DHA	d (D $\cdots$ A)	A
O(1)-H(10)	0.88 \AA	1.85 \AA	143 $^\circ$	2.603 \AA	O(2)

4.

The bond lengths, angles, and other parameters in the $\text{Ph}_3\text{P-C}$ portion of the molecule have values close to those observed in a number of other triphenylphosphonium ylides.³

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 249062 for methyl 4-hydroxy-3-nitro-2-(4-nitrophenyl)-5-(1,1,1-triphenyl- λ^5 -phosphanylidene)-1,3-cyclopentadiene-1-carboxylate.

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