

METALLOPHOSPHORANES: CARBONYL SUBSTITUTION REACTIONS AND THE X-RAY CRYSTAL STRUCTURE OF *cis*-Cat₂PMn(CO)₄P(OPh)₃ (Cat = benzodioxyl)

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Summary

Cat₂PMn(CO)₅ (1, cat = ) is found to undergo carbonyl substitution reactions with phosphorus donors to give the isolable products cat₂PMn(CO)₄L, where L = *cis*-PPh₃ (2); *trans*-PPh₃ (3); *cis*-P(OMe)₃ (4); and *cis*-P(OPh)₃ (5). No evidence for CO insertion into the pentacoordinate P–Mn bond is observed. The X-ray crystal structure of 5 shows that the crystals are monoclinic, space group *P*2₁/*n*. The unit cell parameters are: *a* 10.523(2), *b* 25.765(5), *c* 13.344(2) Å, β 99.11(2)°, and *Z* = 4. Full matrix least squares refinement reached *R* = 0.054 for 3099 observed reflections. The pentacoordinate phosphorus adopts a distorted trigonal bipyramid geometry with the Mn in an equatorial position. Noteworthy is the small equatorial O–P–O angle of 110.1(2)°.

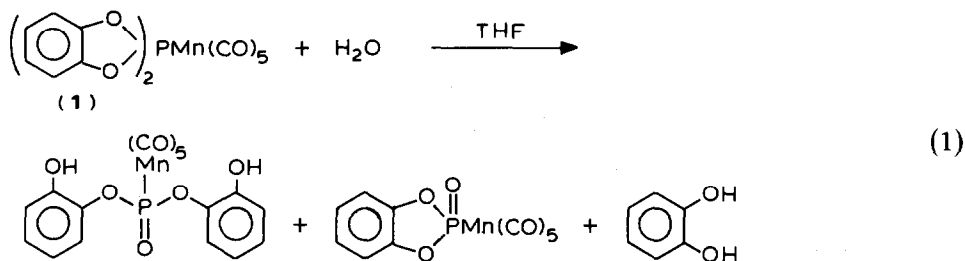
Introduction

Recently, examples of pentacoordinate Group VA molecules with bonds to transition metals have appeared in the literature [1–4]. Methods of syntheses have included proton abstraction from a nitrogen in a polycyclic species with phosphine- and amine-metal bonds [2], oxidative addition to metallo-substituted trivalent P and Sb molecules [3,4], and nucleophilic substitution at pentacoordinate phosphorus by transition-metal carbonyl anions [1]. In the cases where structures have been obtained [1c,2,4], the transition metal is found to occupy the equatorial position of a distorted trigonal bipyramid (tbp) about the Group VA atom.

Our interests lie not only in the synthesis and structure of these species, but also

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in their reactivity, both at the "hypervalent" center and at the transition metal. We have reported [1b,5] the novel hydrolysis reaction of $\text{cat}_2\text{PMn}(\text{CO})_5$ (**1**) (reaction 1), where the symmetrically cleaved P–Mn product is an intermediate which subsequently rearranges to $\text{catP}(\text{O})\text{Mn}(\text{CO})_5$ and catechol.



We herein report some thermal carbonyl substitution reactions of **1** and the X-ray crystal structure of *cis*- $\text{cat}_2\text{PMn}(\text{CO})_4\text{P}(\text{OPh})_3$ (Ph = phenyl).

Results and discussion

Reactions

1 is found readily to undergo carbonyl substitution at moderate temperatures (27–55°C) according to eq. 2 to give isolable products where L = *cis*-PPh₃ (**2**),

$$\mathbf{1} + \text{L} \rightarrow \text{cat}_2\text{PMn}(\text{CO})_4\text{L} + \text{CO} \quad (2)$$

trans-PPh₃ (**3**), *cis*-P(OMe)₃ (**4**, Me = methyl), and *cis*-P(OPh)₃ (**5**). The initial species formed appear to be the *cis*-substituted molecules which undergo further reaction, usually leading to multiple products which cannot be separated. In order to isolate the above *cis*-compounds, the reactions are monitored (by IR and NMR spectroscopy) and stopped prior to formation of any further products. Separation of the starting materials from the *cis*-products is relatively straightforward. The initial *cis*-substitution is consistent with the dissociative substitution mechanism of $\text{L}'\text{Mn}(\text{CO})_5$ complexes [6].

Isolation of a further reaction product was only possible with L = PPh₃ since **3** precipitates from the reaction solvent (toluene). That **2** does indeed rearrange to **3** was clearly demonstrated by taking an isolated sample of **2**, dissolving it in THF, and following the spectral changes at ambient temperature. The rearrangement is ca. 95% complete after 9 days. The appearance of free PPh₃ in the ³¹P spectra during this reaction suggests a dissociative path for the rearrangement (no free PPh₃ is observed when **2** is initially dissolved).

Part of the problem in the identification and isolation of the other *trans* isomers is the fact that multiple products form, as mentioned above. For example, prolonged heating of **1** with P(OPh)₃ yields a mixture of products, one of which gives two relatively sharp resonances in the ³¹P spectrum: a doublet at δ 162 ppm, ²J(P–P) 125 Hz, and a triplet (or pseudotriplet) at δ 82 ppm, ²J(P–P) 125 Hz, indicating the disubstituted product, $\text{cat}_2\text{PMn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$. This is the only case where we observe P–P coupling since all of the other compounds give unresolvable broad resonances. The formation of disubstituted products, even when the starting materials are mixed in a 1/1 molar ratio, has been observed before in reactions of the type

TABLE 1
SPECTROSCOPIC DATA FOR $\text{Cat}_2\text{PMn}(\text{CO})_4\text{L}$

L	$^{31}\text{P}(\text{ppm})^a$	$^{13}\text{C}(\text{ppm})^a$		$\nu(\text{CO}) (\text{cm}^{-1})^b$
		Cat group	Other	
CO, 1 ^c	67	110.6, 3J 7 Hz 121.4 147.0, 2J 4 Hz	206(br)	2040(vs) 2131(m)
<i>cis</i> - PPh_3 , 2	49 73	110.5, 3J 3 Hz 120.6 148.0, 2J 9 Hz	129.4, 3J 9 Hz 131.5 134.1, 2J 10 Hz (135) ^d	1935(w) 1984(s) 2002(vs) 2085(s)
<i>trans</i> - PPh_3 , 3	59 79	110.4, 3J 7 Hz 120.9 148.0, 2J 4 Hz	130.1, 3J 10 Hz 132.0 133.8, 2J 10 Hz 135.0, 1J 44 Hz	1994(vs) 2040(w) 2092(vw)
<i>cis</i> - $\text{P}(\text{OMe})_3$, 4 ^e	75 (very br) 160 (very br)	110.3, 3J 4 Hz 120.7 147.9, 2J 6 Hz	54.2, 2J 8 Hz	1992(sh) 2010(vs) 2023(sh) 2095(m)
<i>cis</i> - $\text{P}(\text{OPh})_3$, 5	72 153	110.4 120.8 147.8	121.8 126.4 130.6 152.1, 2J 8 Hz 209, 213 (br)	1997(s) 2012(vs) 2093(m)

^a NMR data in THF solution. All ^{31}P peaks are broad. All coupling constants are $J(\text{P}-\text{C})$. ^b Data in CH_2Cl_2 solution. ^c NMR data from reference **1a**. ^d Approximate value, overlapping. ^e ^1H data for **4** (CDCl_3): δ 3.68 ppm (d, br, 9H), $^3J(\text{P}-\text{H})$ 10.8 Hz; and δ 6.76 ppm (br, 8H).

$\text{XMn}(\text{CO})_5 + \text{L}$ ($\text{X} = \text{halogen}$) [7]. It has been suggested [7b,8] that loss of CO is facile from both $\text{XMn}(\text{CO})_5$ and $\text{XMn}(\text{CO})_4\text{L}$ and that both species can react with free L to yield products during the course of the reaction.

The carbonyl stretching frequencies decrease upon CO substitution by the phosphorus donors, the usual trend in metal carbonyls, while the ^{31}P chemical shift of the phosphorane phosphorus moves slightly downfield (see Table 1). The assignments of the peaks for **4** and **5** are straightforward due to the large difference in chemical shifts; thus, the 160 and 153 ppm peaks are assigned to the trivalent phosphorus and the 75 and 72 ppm peaks to the pentavalent phosphorus. The most probable assignments for **2** and **3** are the 73 and 79 ppm peaks to the pentavalent phosphorus since similar chemical shifts would be expected for all the high-coordinate phosphorus atoms.

In summary, $\text{cat}_2\text{PMn}(\text{CO})_5$ appears to undergo normal substitution reactions with phosphorus donors and no evidence for CO insertion is observed.

Structure of *cis*- $\text{cat}_2\text{PMn}(\text{CO})_4\text{P}(\text{OPh})_3$ (**5**)

The structure of **5**, determined by X-ray diffraction, is illustrated in Fig. 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. There are four molecules of **5** and two molecules of cyclohexane (solvent of crystallization) per unit cell. The cyclohexane molecules lie around centers of symmetry.

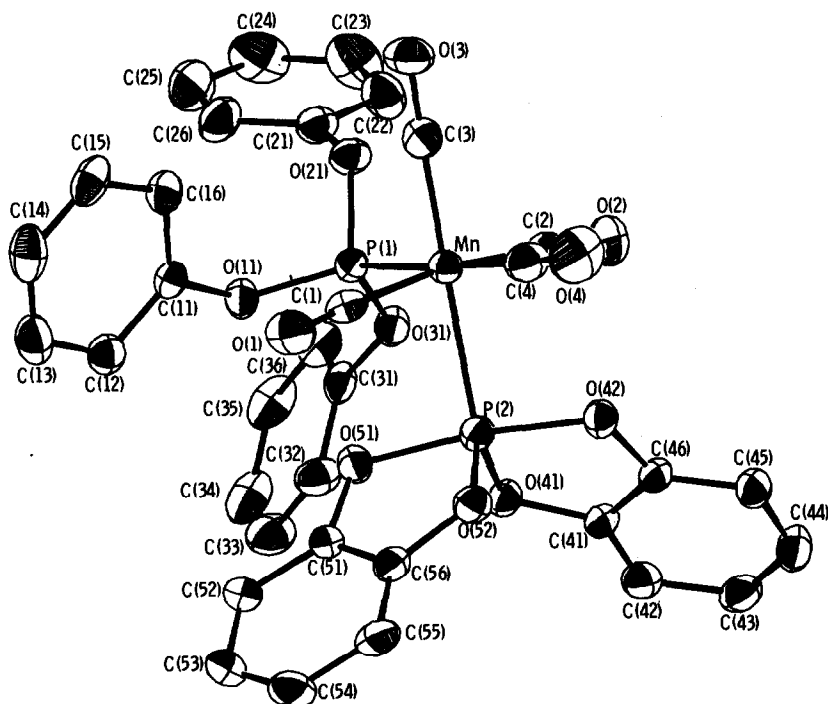


Fig. 1. Drawing of *cis-cat*₂PMn(CO)₄P(OPh)₃ (**5**).

The structure shows that the phosphorus atoms are arranged in a *cis* configuration. The Mn adopts a distorted octahedral geometry while the tetracoordinate phosphorus, P(1), is a distorted tetrahedron. The geometry about the pentacoordinate phosphorus, P(2), is a distorted tbp with O(42) and O(51) the axial substituents and Mn, O(41), and O(52) the equatorial substituents. The nine angles around P(2) are close to the ideal tbp angles with the largest deviations found in the equatorial plane. Although the sum of the equatorial angles about P(2) is 360.0(4)°, one of the atoms, O(41), appears to be out of its "normal" position as is evident from the Mn–P(2)–O(41) and O(41)–P(2)–O(52) angles of 128.6(1) and 110.1(2)°, respectively. We find the intra- and inter-molecular nonbonded distances between O(41) and its nearest neighbors to be similar to the nonbonded distances between the other equatorial oxygen, O(52), and its nearest neighbors. To maintain these distances O(41) appears to be pushed out of its expected position by the P(OPh)₃ group. The cat₂P and Mn(CO)₄P(OPh)₃ moieties are "staggered"; that is, the P(2)–O bonds approximately bisect the P(1)–Mn–C and C–Mn–C angles when viewed down the Mn–P(2) bond. Such an arrangement minimizes the steric interaction.

The axial P–O bonds are ca. 0.12 Å longer than the equatorial P–O bonds, as expected in tbp geometries [9]. The solid-state structure of **5** indicating a tbp and the fact that only three resonances are found for the cat₂P carbons in the ¹³C NMR spectrum imply Berry pseudorotation [10] for **5**. Such an exchange process is, most likely, responsible for the observation of only three ¹³C resonances for the cat₂P carbons in **1–4** as well.

Both P–Mn bonds are within the normal range of known P–Mn bond lengths.

TABLE 2

SELECTED BOND LENGTHS FOR *cis*-Cat₂PMn(CO)₄P(OPh)₃ (**5**) (ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

Atoms	Distance (Å)
Mn–C(1)	1.878(6)
Mn–C(2)	1.850(5)
Mn–C(3)	1.825(5)
Mn–C(4)	1.838(7)
Mn–P(1)	2.266(2)
Mn–P(2)	2.350(2)
C(1)–O(1)	1.122(7)
C(2)–O(2)	1.141(7)
C(3)–O(3)	1.147(7)
C(4)–O(4)	1.141(9)
P(1)–O(11)	1.598(3)
P(1)–O(21)	1.600(4)
P(1)–O(31)	1.588(4)
P(2)–O(41)	1.650(3)
P(2)–O(42)	1.768(3)
P(2)–O(51)	1.784(3)
P(2)–O(52)	1.660(4)
O(41)–C(41)	1.389(6)
O(42)–C(46)	1.358(6)
C(41)–C(42)	1.365(8)
C(41)–C(46)	1.382(7)
C(42)–C(43)	1.388(8)
C(43)–C(44)	1.364(9)
C(44)–C(45)	1.386(9)
C(45)–C(46)	1.373(8)
O(51)–C(51)	1.353(6)
O(52)–C(56)	1.382(6)
C(51)–C(52)	1.383(8)
C(51)–C(56)	1.382(7)
C(52)–C(53)	1.382(9)
C(53)–C(54)	1.380(10)
C(54)–C(55)	1.395(9)
C(55)–C(56)	1.371(8)

Previous data [11] have shown that in complexes containing both phosphonate, (RO)₂P(O), and phosphite ligands, the P^V–metal bond is ca. 0.05 to 0.09 Å longer than the P^{III}–metal bond. In the present case, the P^V–metal bond in **5** is 0.084(4) Å longer than the P^{III}–metal bond. A smaller difference (ca. 0.025 Å) was found between the two types of P–Co bonds in *trans*-cat₂PCo(CO)₃PPh₃ [1c].

Experimental

All reactions were performed in an atmosphere of prepurified nitrogen. Solvents were rigorously dried over appropriate drying agents and distilled and deoxygenated prior to use. **1** was prepared as described previously [1a]. IR spectra were recorded on a Perkin–Elmer 283 infrared spectrophotometer. ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on an IBM WP200SY multinuclear NMR spectrometer

TABLE 3

SELECTED BOND ANGLES FOR *cis*-Cat₂PMn(CO)₄P(OPh)₃ (**5**) (ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

Atoms	Angle (°)	Atoms	Angle (°)
C(1)–Mn–C(2)	171.0(2)	Mn–P(2)–O(52)	121.3(1)
C(1)–Mn–C(3)	95.0(2)	O(41)–P(2)–O(42)	89.6(2)
C(1)–Mn–C(4)	89.0(3)	O(41)–P(2)–O(51)	86.1(2)
C(1)–Mn–P(1)	95.0(2)	O(41)–P(2)–O(52)	110.1(2)
C(1)–Mn–P(2)	83.7(2)	O(42)–P(2)–O(51)	172.9(2)
C(2)–Mn–C(3)	94.0(2)	O(42)–P(2)–O(52)	87.0(2)
C(2)–Mn–C(4)	91.2(3)	O(51)–P(2)–O(52)	89.2(2)
C(2)–Mn–P(1)	85.0(2)	P(2)–O(41)–C(41)	114.3(3)
C(2)–Mn–P(2)	87.4(2)	P(2)–O(42)–C(46)	111.3(3)
C(3)–Mn–C(4)	89.0(3)	O(41)–C(41)–C(42)	125.5(5)
C(3)–Mn–P(1)	89.0(2)	O(41)–C(41)–C(46)	111.7(4)
C(3)–Mn–P(2)	177.0(2)	C(42)–C(41)–C(46)	122.8(5)
C(4)–Mn–P(1)	175.6(2)	C(41)–C(42)–C(43)	116.7(5)
C(4)–Mn–P(2)	88.3(2)	C(42)–C(43)–C(44)	120.9(6)
P(1)–Mn–P(2)	93.7(1)	C(43)–C(44)–C(45)	122.2(6)
Mn–C(1)–O(1)	175.8(5)	C(44)–C(45)–C(46)	117.1(5)
Mn–C(2)–O(2)	177.6(5)	O(42)–C(46)–C(41)	112.2(4)
Mn–C(3)–O(3)	179.0(5)	O(42)–C(46)–C(45)	127.5(5)
Mn–C(4)–O(4)	177.2(6)	C(41)–C(46)–C(45)	120.3(5)
Mn–P(1)–O(11)	125.1(1)	P(2)–O(51)–C(51)	110.5(3)
Mn–P(1)–O(21)	106.5(2)	P(2)–O(52)–C(56)	113.5(3)
Mn–P(1)–O(31)	115.3(2)	O(51)–C(51)–C(52)	126.9(5)
O(11)–P(1)–O(21)	104.4(2)	O(51)–C(51)–C(56)	112.3(4)
O(11)–P(1)–O(31)	99.3(2)	C(52)–C(51)–C(56)	120.8(5)
O(21)–P(1)–O(31)	104.3(2)	C(51)–C(52)–C(53)	117.5(5)
P(1)–O(11)–C(11)	126.5(3)	C(52)–C(53)–C(54)	121.1(6)
P(1)–O(21)–C(21)	126.0(3)	C(53)–C(54)–C(55)	121.6(6)
P(1)–O(31)–C(31)	128.6(3)	C(54)–C(55)–C(56)	116.5(5)
Mn–P(2)–O(41)	128.6(1)	O(52)–C(56)–C(51)	112.4(4)
Mn–P(2)–O(42)	93.2(1)	O(52)–C(56)–C(55)	125.2(5)
Mn–P(2)–O(51)	93.9(1)	C(51)–C(56)–C(55)	122.4(5)

resonating at 50.327 and 81.026 MHz, respectively. Spectra were run in 8 mm NMR tubes containing the sample inserted into 10 mm NMR tubes containing D₂O as a lock. ¹³C spectra were calibrated relative to solvent peaks referenced to TMS. ³¹P spectra were referenced to external H₃PO₄. ¹H NMR spectra were recorded on a Perkin–Elmer R32 90 MHz NMR spectrometer. Elemental analyses were done by Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada, and Galbraith Laboratories, Inc., Knoxville, TN, U.S.A.

cis-cat₂PMn(CO)₄PPh₃ (**2**). A mixture of **1** (0.74 g, 1.7 mmol) and PPh₃ (0.44 g, 1.7 mmol) in 20 ml of toluene was stirred at ambient temperature for 4 d. The volatiles were then removed and the residue washed with hexane (to remove starting materials), dissolved in toluene and precipitated with hexane, yielding a colorless solid, **2** (0.25 g, 22%). Anal. Found: C, 60.03; H, 3.44; P, 9.54. C₃₄H₂₃MnO₈P₂ calcd.: C, 60.37; H, 3.43; P, 9.16%.

trans-cat₂PMn(CO)₄PPh₃ (**3**). A mixture of **1** (1.54 g, 3.48 mmol) and PPh₃ (0.915 g, 3.49 mmol) in 15 ml of toluene was stirred at 50–55°C for 16 h. The white

TABLE 4

CRYSTALLOGRAPHIC DATA FOR *cis-cat*₂PMn(CO)₄P(OPh)₃ (**5**)

Formula	C ₃₄ H ₂₃ O ₁₁ P ₂ Mn · 1/2C ₆ H ₁₂
Formula weight	766.52
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i>	10.523(2) Å
<i>b</i>	25.765(5) Å
<i>c</i>	13.344(2) Å
β	99.11(2)°
<i>U</i>	3572.3(1.2) Å ³
<i>Z</i>	4
ρ (calc)	1.425 g cm ⁻³
μ (Mo- <i>K</i> α)	5.00 cm ⁻¹
λ (Mo- <i>K</i> α)	0.71069 Å
Crystal size	0.27 × 0.24 × 0.14 mm
Total number of independent reflections with $2\theta < 45^\circ$	4681
Number of observed reflections [$I \geq 2\sigma(I)$]	3099
<i>R</i>	0.054
<i>R</i> _w	0.052

solid which precipitated was filtered off and washed with toluene, yielding **3** (1.79 g, 76%). Anal. Found: C, 59.69; H, 3.56; P, 9.40. C₃₄H₂₃MnO₈P₂ calcd.: C, 60.37; H, 3.43, P, 9.16%.

*cis-cat*₂PMn(CO)₄P(OMe)₃ (**4**). A solution of **1** (0.59 g, 1.3 mmol) and P(OMe)₃ (0.16 ml, 1.3 mmol) in 5 ml of CH₂Cl₂ was refluxed for 24 h. The volatiles were removed and the residue redissolved in CH₂Cl₂ and precipitated with hexane, yielding a light yellow solid, **4** (0.27 g, 39%). Anal. Found: C, 41.95; H, 2.92; P, 11.91. C₁₉H₁₇MnO₁₁P₂ calcd.: C, 42.40; H, 3.19; P, 11.51%.

*cis-cat*₂PMn(CO)₄P(OPh)₃ (**5**). A solution of **1** (0.30 g, 0.68 mmol) and P(OPh)₃ (0.18 ml, 0.68 mmol) in 8 ml of THF was heated at 40–50°C for 12 h. The volatiles were removed and the residue washed with hexane, dissolved in toluene, filtered and dried yielding an oily product. Addition and evaporation of hexane yielded a solid, slightly yellow product, **5** (0.18 g, 37%).

X-Ray structure determination

5 was recrystallized from cyclohexane yielding colorless, transparent crystals. A suitable single crystal was coated with epoxy cement prior to mounting on a Syntex P2₁ computer controlled diffractometer. The data were collected in the $\theta/2\theta$ scan mode. There were 4681 independent reflections collected; of these, 3099 were considered observed with $I \geq 2\sigma(I)$ and used in the solution and refinement of the structure.

Data were corrected for Lorentz and polarization effects. The position of the manganese atom was deduced from a Patterson map. Successive difference Fourier maps and full matrix-least squares refinement allowed location of all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the subsequent refinement. Near the

TABLE 5

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS (ESTIMATED STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

Atom	x	y	z
Mn	4320(1)	1222(0)	5467(1)
C(1)	4887(6)	1792(2)	4780(4)
O(1)	5250(4)	2146(2)	4425(3)
C(2)	3622(5)	736(2)	6244(4)
O(2)	3161(4)	449(2)	6730(3)
C(3)	5184(5)	739(2)	4834(4)
O(3)	5741(4)	435(2)	4449(3)
C(4)	5750(6)	1291(3)	6445(5)
O(4)	6666(4)	1323(2)	7027(4)
P(1)	2546(1)	1073(1)	4300(1)
O(11)	2088(3)	1424(1)	3322(2)
C(11)	2881(5)	1653(2)	2692(4)
C(12)	2525(6)	2145(2)	2345(4)
C(13)	3272(8)	2387(3)	1708(5)
C(14)	4335(7)	2141(3)	1453(5)
C(15)	4653(6)	1656(3)	1789(4)
C(16)	3920(5)	1393(2)	2422(4)
O(21)	2716(3)	506(1)	3851(3)
C(21)	1747(6)	212(2)	3251(5)
C(22)	1251(7)	-208(2)	3684(5)
C(23)	333(7)	-512(3)	3123(7)
C(24)	-87(8)	-394(3)	2140(7)
C(25)	408(8)	22(3)	1693(5)
C(26)	1365(7)	336(3)	2252(5)
O(31)	1230(3)	1042(1)	4738(3)
C(31)	-4(5)	1227(3)	4298(4)
C(32)	-301(6)	1739(3)	4434(4)
C(33)	-1518(6)	1920(3)	4048(5)
C(34)	-2413(6)	1584(4)	3543(5)
C(35)	-2093(6)	1072(3)	3411(5)
C(36)	-888(6)	883(3)	3799(4)
P(2)	3311(1)	1862(1)	6319(1)
O(41)	1857(3)	1855(1)	6634(2)
O(42)	3943(3)	1614(1)	7531(2)
C(41)	1833(5)	1742(2)	7649(4)
C(42)	768(6)	1755(2)	8114(4)
C(43)	944(7)	1627(2)	9137(4)
C(44)	2130(7)	1494(3)	9640(5)
C(45)	3209(6)	1482(2)	9165(4)
C(46)	3040(5)	1611(2)	8154(4)
O(51)	2581(3)	2173(1)	5177(2)
O(52)	4050(3)	2415(1)	6689(3)
C(51)	2717(5)	2694(2)	5260(4)
C(52)	2127(6)	3064(2)	4592(4)
C(53)	2442(7)	3578(3)	4799(5)
C(54)	3301(7)	3716(2)	5649(5)
C(55)	3892(6)	3345(2)	6329(5)
C(56)	3581(5)	2837(2)	6105(4)
C(61)	1027(10)	4860(4)	5797(6) ^a
C(62)	1346(8)	5057(3)	4793(7) ^a
C(63)	238(10)	4921(4)	3961(6) ^a

^a C(61), C(62), and C(63) are the carbon atoms in the cyclohexane molecule.

end of the refinement, two distances in the cyclohexane molecule of 1.45 Å, C(61)–C(62), and 1.56 Å, C(62)–C(63), were constrained to 1.52 Å. The atoms were then allowed to refine normally. The weighting scheme used was $w = 1/[\sigma^2(F_o) + kF_o^2]$, where $k = 5.92 \times 10^{-4}$. The final R -factors were $R = 0.054$ and $R_w = 0.052$. The final difference Fourier map showed no peaks higher than $0.39 \text{ e}^-/\text{\AA}^3$. Pertinent crystallographic data and fractional atomic coordinates are listed in Tables 4 and 5, respectively. (Complete lists of bond lengths, bond angles, fractional atomic coordinates for the hydrogen atoms, anisotropic temperature factors, and structure factors are available upon request from the authors.)

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