Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55862 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE1001]

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Structure of (2,4-Pentanedionato-*O*,*O*′)-bis(phenyl 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl phosphite-*P*)rhodium

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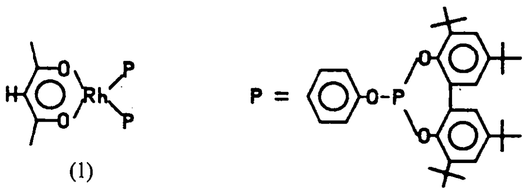
Abstract

The crystal structure of the title compound has been determined. The square-planar coordination of the complex is tetrahedrally distorted. The two phosphite ligands of the Rh complex are deformed as a result of steric interactions.

Comment

The hydroformylation of otherwise unreactive internal and branched alkenes can be achieved by using bulky phosphite-modified Rh catalysts (van Leeuwen & Roobeek, 1983; Tokitoh & Yoshimura, 1987, 1989; Billig, Abatjoglou, Bryant, Murray & Maher, 1988; Polo, Real, Claver, Castillon & Bayon, 1990; Treçiak & Ziolkowski, 1988). The title compound (1) is a precursor of one of these catalysts, and therefore the steric conformation of this bisphosphite Rh complex is of use in the study of the catalytic cycle of these catalysts. The triphenylphosphite analogue (2) of the title compound has been crystallized by Leipoldt, Lamprecht & van Zyl (1985). Other bulky phosphites, *i.e.* tri(2-*tert*-butylphenyl) phosphite (3) (Jongsma, Challa & van Leeuwen, 1991), tri(2,4,6-trimethylphenyl) phosphite (4) (J. Jongsma, G. Challa & P. W. N. M. van Leeuwen, unpublished results) and bi(2-*tert*-butyl-6-methylphenyl) phenyl phosphite (5) (Jongsma, Kimkes, Challa & van Leeuwen, 1992), exclusively yielded the monophosphite Rh complex Rh(acac)(CO)*P* (acac = 2,4-pentanedionato, CO = carbonyl and *P* = phosphite ligand).



(1)

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 1. Each asymmetric unit contains one complete molecule of the title compound with no atom sitting at a special position and two half molecules of disordered toluene solvent molecules. The triclinic unit cell contains two discrete molecules of the title compound and two toluene molecules separated by normal van der Waals distances (Bondi, 1964). Both toluene molecules possess a crystallographically imposed centre of inversion. The square-planar structure of the complex (1) is tetrahedrally distorted [distances of atoms from root-mean-square (r.m.s.) plane of P1-P2-O2-O1: P1 −0.096 (7), P2 0.096 (6), O1 0.108 (7), O2 −0.110 (6) Å]. The central Rh atom is in the plane [distance from r.m.s. plane: Rh 0.004 (6) Å]. Steric hindrance of the two phosphite groups is demonstrated by the large P1—Rh—P2 angle of 99.87 (3)°, *versus* 94.8 (2)° for the triphenyl phosphite Rh complex (2) (Leipoldt, Lamprecht & van Zyl, 1985). The O1—Rh—O2 angle [89.41 (2)°] is only slightly larger than that of the triphenyl phosphite analogue (2) [88.8 (2)°]. The

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steric hindrance has led to distortions within the phosphite ligands. The different P—O—C angles within the ligands [P1—O3—C6 = 126.4 (2) *versus* P1—O4—C20 = 120.1 (2)° and P2—O6—C40 = 118.7 (2) *versus* P2—O7—C54 = 128.0 (2)°] are examples of this distortion. The angles between the two bridged phenyl groups of the phosphite ligands are 49.7 (2) and 51.5 (2)°, respectively. The cone angle (Tolman, 1977) for the 2,2′-bis(4,6-di-*tert*-butylphenyl) phenyl phosphite calculated from this X-ray structure is 164°. The high π-acidity of aryl phosphites leads to the formation of strong π-coordination bonds, which might explain the formation of the bisphosphite complex (1), even though the cone angle of the ligand is too large to expect the formation of bisphosphite Rh complexes. [Triphenylphosphine, cone angle 145°, exclusively yields monophosphine complexes when reacted with Rh(acac)(CO)$_2$, even when a large excess of phosphine is used (Bonati & Wilkinson, 1964).]

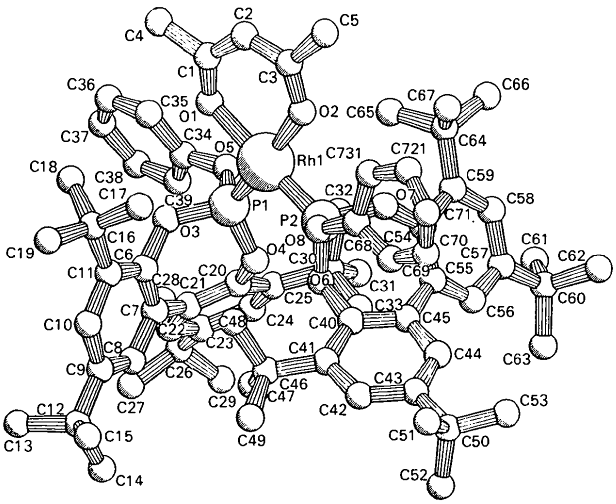

Fig. 1. *PLUTO* drawing of the molecule of the title compound illustrating the puckering and the adopted numbering scheme. H atoms have been omitted to improve clarity.

Experimental

Crystal data

[Rh(C$_5$H$_7$O$_2$)(C$_{34}$H$_{45}$O$_3$P)$_2$].-C$_7$H$_8$
M_r = 1359.56
Triclinic
$P\bar{1}$
a = 11.624 (1) Å
b = 17.244 (2) Å
c = 18.877 (1) Å
α = 79.884 (8)°
β = 84.812 (6)°
γ = 75.398 (9)°
V = 3600.4 (6) Å^3
Z = 2
D_x = 1.254 Mg m^{-3}

Mo $K\bar{\alpha}$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 14.84–18.83°
μ = 0.328 mm^{-1}
T = 130 K
Parallelepiped
0.40 × 0.33 × 0.15 mm
Yellow
Crystal source: by synthesis, details are published elsewhere (Jongsma, Fossen, Challa & van Leeuwen, 1992)

Data collection

Enraf-Nonius CAD-4F single-crystal diffractometer
$\omega/2\theta$ scans
Absorption correction: none
14851 measured reflections
14111 independent reflections

10706 observed reflections [$I > 2.5\sigma(I)$]
$R_{\rm int}$ = 0.022
$\theta_{\rm max}$ = 26.00°
h = 0 → 14
k = −20 → 21
l = −23 → 23
3 standard reflections
frequency: 180 min
intensity variation: 0.3%

Refinement

Refinement on F
Final R = 0.042
wR = 0.046
S = 1.842
10706 reflections
1136 parameters
Calculated weights $w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\rm max}$ = 0.77
$\Delta\rho_{\rm max}$ = 0.99 e Å^{-3}
$\Delta\rho_{\rm min}$ = 0.92 e Å^{-3}

Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.63 (9) × 10^{-4}
Atomic scattering factors from Cromer & Mann (1968) [anomalous-dispersion factors from Cromer & Liberman (1970)]

Data collection: *CAD*-4, version 5.0 (Enraf-Nonius, 1988). Cell refinement: *CAD*-4, version 5.0; *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *EUCLID* (Spek, 1982). Reduced-cell calculations: *LEPAGE* (Spek, 1988). Extra metric symmetry-element calculations: *MISSYM* (Le Page, 1987, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *Xtal CRYLSQ* (Olthof-Hazekamp, 1990). Program(s) used for geometric calculations: *Xtal* (Hall & Stewart, 1990); *PLATON* (Spek, 1990). Molecular graphics: *PLUTO*92 (Meetsma, 1992; Motherwell & Clegg, 1978). Software used to prepare material for publication: *PLATON*92 (Spek, 1992). All calculations were performed on a CDC-Cyber 962-31 computer at the University of Groningen.

The positional and anisotropic thermal displacement parameters for the non-H atoms were refined with block-diagonal least-squares procedures (*CRYLSQ*; Olthof-Hazekamp, 1990) minimizing the function $Q = \Sigma_h[w(|F_o| - |F_c|)^2]$. Subsequent Fourier summations showed density which could be correlated to the disordered phenyl group (C68–C73) and the two solvent molecules of toluene. Both toluene molecules were disordered over a crystallographic inversion centre, each in a different way. The disorder in the phenyl group is described by two positions with occupancy of 0.5 for C72 and C73. Following the inclusion of the positional parameters and appropriate occupancies of 1.0 and 0.5, respectively, of the toluene residues, the remainder of the structure refined smoothly. High thermal displacement motion was found for the disordered fragments. The overall geometry of the toluene molecules appeared rather distorted, suggesting some degree of disorder. The H atoms of the non-disordered fragments were located in subsequent $\Delta\rho$ maps. The H atoms of the disordered fragments were included in the final refinement riding on their carrier atoms with their positions calculated by using sp^2 or sp^3 hybridization at the C atom as appropriate with a fixed C—H distance of 0.96 Å. A final $\Delta\rho$ map was essentially featureless with the highest peaks in the vicinity of the disordered fragments.

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

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh1	0.24589 (2)	0.25048 (2)	0.25092 (1)	0.0167 (1)
P1	0.33686 (7)	0.29811 (5)	0.32160 (4)	0.0160 (2)
P2	0.39402 (7)	0.20136 (5)	0.18155 (4)	0.0181 (2)
O1	0.09006 (19)	0.30273 (14)	0.30461 (12)	0.0270 (8)
O2	0.1490 (2)	0.19744 (14)	0.19480 (12)	0.0284 (8)
O3	0.30218 (17)	0.39500 (12)	0.32417 (10)	0.0169 (6)
O4	0.48010 (17)	0.27538 (12)	0.31838 (10)	0.0167 (6)
O5	0.30010 (19)	0.26871 (12)	0.40434 (10)	0.0206 (7)
O6	0.52260 (18)	0.21956 (12)	0.18494 (10)	0.0173 (6)
O7	0.42558 (19)	0.10493 (12)	0.17982 (11)	0.0213 (7)
O8	0.3615 (2)	0.23240 (13)	0.09835 (11)	0.0235 (7)
C1	−0.0135 (3)	0.2967 (2)	0.29351 (18)	0.0308 (11)
C2	−0.0410 (3)	0.2478 (2)	0.2497 (2)	0.0330 (11)
C3	0.0390 (3)	0.2009 (2)	0.20515 (19)	0.0318 (12)
C4	−0.1145 (4)	0.3488 (3)	0.3326 (2)	0.0504 (18)
C5	−0.0098 (5)	0.1508 (3)	0.1629 (3)	0.0577 (19)
C6	0.3679 (3)	0.45048 (18)	0.29268 (15)	0.0161 (8)
C7	0.4822 (3)	0.44022 (17)	0.31606 (15)	0.0160 (9)
C8	0.5480 (3)	0.49647 (18)	0.28499 (15)	0.0170 (9)
C9	0.5037 (3)	0.56079 (18)	0.23294 (15)	0.0176 (9)
C10	0.3852 (3)	0.57138 (19)	0.21464 (16)	0.0190 (9)
C11	0.3143 (3)	0.51840 (18)	0.24363 (15)	0.0171 (9)
C12	0.5770 (3)	0.62082 (19)	0.19592 (16)	0.0207 (10)
C13	0.5271 (3)	0.7034 (2)	0.22064 (19)	0.0257 (11)
C14	0.7079 (3)	0.5915 (2)	0.2139 (2)	0.0275 (11)
C15	0.5697 (4)	0.6315 (2)	0.11402 (18)	0.0295 (11)
C16	0.1840 (3)	0.53467 (19)	0.22311 (16)	0.0205 (9)
C17	0.1698 (3)	0.4712 (2)	0.1796 (2)	0.0286 (12)
C18	0.1000 (3)	0.5355 (2)	0.2909 (2)	0.0304 (11)
C19	0.1432 (3)	0.6181 (2)	0.1759 (2)	0.0296 (11)
C20	0.5413 (2)	0.29299 (18)	0.37240 (15)	0.0166 (9)
C21	0.5373 (2)	0.37358 (18)	0.37321 (15)	0.0155 (8)
C22	0.5945 (3)	0.39233 (18)	0.42765 (15)	0.0148 (8)
C23	0.6558 (3)	0.33225 (18)	0.47912 (15)	0.0164 (9)
C24	0.6624 (3)	0.25153 (18)	0.47299 (16)	0.0180 (9)
C25	0.6078 (3)	0.22856 (18)	0.41997 (15)	0.0174 (9)
C26	0.7113 (3)	0.35231 (18)	0.54281 (16)	0.0183 (9)
C27	0.7300 (4)	0.4384 (2)	0.5276 (2)	0.0290 (11)
C28	0.6248 (4)	0.3462 (2)	0.60861 (19)	0.0313 (11)
C29	0.8299 (3)	0.2931 (2)	0.5603 (2)	0.0307 (12)
C30	0.6298 (3)	0.13875 (18)	0.41099 (17)	0.0234 (10)
C31	0.6996 (3)	0.0827 (2)	0.4726 (2)	0.0281 (11)
C32	0.5149 (4)	0.1118 (2)	0.4088 (3)	0.0427 (14)
C33	0.7048 (4)	0.1274 (2)	0.3410 (2)	0.0384 (14)
C34	0.2576 (3)	0.31423 (18)	0.45992 (16)	0.0184 (9)
C35	0.1380 (3)	0.3527 (2)	0.46415 (18)	0.0265 (11)
C36	0.0943 (3)	0.3924 (2)	0.52235 (19)	0.0283 (11)
C37	0.1674 (3)	0.3943 (2)	0.57478 (18)	0.0282 (11)
C38	0.2867 (3)	0.3559 (2)	0.56916 (17)	0.0286 (11)
C39	0.3327 (3)	0.3160 (2)	0.51139 (16)	0.0212 (10)
C40	0.6094 (3)	0.20035 (18)	0.12925 (15)	0.0174 (9)
C41	0.6422 (3)	0.26343 (18)	0.08031 (15)	0.0177 (9)
C42	0.7188 (3)	0.23897 (19)	0.02319 (16)	0.0204 (9)
C43	0.7634 (3)	0.15786 (19)	0.01381 (16)	0.0210 (9)
C44	0.7377 (3)	0.09886 (19)	0.06779 (16)	0.0199 (9)
C45	0.6601 (3)	0.11885 (18)	0.12697 (15)	0.0190 (9)
C46	0.6045 (3)	0.35297 (18)	0.09087 (16)	0.0198 (9)
C47	0.6574 (3)	0.3594 (2)	0.16075 (18)	0.0272 (11)
C48	0.4693 (3)	0.3868 (2)	0.0957 (2)	0.0277 (11)
C49	0.6540 (3)	0.4070 (2)	0.02873 (19)	0.0273 (11)
C50	0.8371 (3)	0.1391 (2)	−0.05558 (17)	0.0248 (10)
C51	0.7661 (4)	0.1858 (2)	−0.12076 (18)	0.0311 (11)
C52	0.9526 (3)	0.1657 (3)	−0.0566 (2)	0.0351 (14)
C53	0.8643 (4)	0.0484 (2)	−0.0611 (2)	0.0337 (11)
C54	0.5229 (3)	0.04575 (18)	0.20837 (16)	0.0197 (9)
C55	0.6368 (3)	0.05231 (18)	0.18369 (15)	0.0188 (9)
C56	0.7342 (3)	−0.00838 (19)	0.21093 (16)	0.0199 (9)
C57	0.7195 (3)	−0.07524 (19)	0.26058 (16)	0.0227 (10)
C58	0.6019 (3)	−0.0811 (2)	0.27983 (17)	0.0247 (10)
C59	0.5018 (3)	−0.02250 (19)	0.25557 (16)	0.0223 (10)
C60	0.8243 (3)	−0.1420 (2)	0.29257 (18)	0.0288 (11)
C61	0.8060 (4)	−0.1581 (2)	0.3749 (2)	0.0354 (12)
C62	0.8298 (4)	−0.2204 (2)	0.2626 (2)	0.0413 (14)
C63	0.9423 (4)	−0.1188 (2)	0.2741 (2)	0.0369 (12)
C64	0.3760 (3)	−0.0334 (2)	0.27887 (17)	0.0258 (11)
C65	0.3126 (4)	0.0299 (2)	0.3264 (2)	0.0304 (12)
C66	0.3786 (4)	−0.1176 (2)	0.3219 (2)	0.0397 (16)
C67	0.3033 (4)	−0.0247 (3)	0.2126 (2)	0.0402 (14)
C68	0.3578 (3)	0.1891 (2)	0.04307 (16)	0.0223 (10)
C69	0.4510 (4)	0.1582 (5)	0.0050 (3)	0.135 (4)
C70	0.4449 (6)	0.1207 (4)	−0.0521 (3)	0.110 (3)
C71	0.3488 (5)	0.1135 (3)	−0.0715 (2)	0.073 (2)
C721 †	0.2671 (6)	0.1159 (5)	−0.0222 (4)	0.034 (3)
C722 †	0.2385 (8)	0.1922 (6)	−0.0537 (4)	0.055 (4)
C731 †	0.2645 (6)	0.1578 (4)	0.0353 (4)	0.027 (2)
C732 †	0.2528 (7)	0.2226 (6)	0.0080 (4)	0.044 (3)
C78	0.9090 (5)	0.5265 (4)	0.0303 (3)	0.068 (2)
C79	0.8838 (11)	0.5992 (7)	−0.0078 (6)	0.077 (5)
C80	0.9811 (7)	0.6133 (4)	−0.0667 (3)	0.090 (3)
C81 †	0.9320 (8)	0.4532 (7)	0.0693 (5)	0.051 (4)
C82 †	0.9945 (10)	0.4624 (7)	0.0273 (5)	0.054 (4)
C74	0.0236 (4)	0.0708 (4)	0.4655 (4)	0.090 (3)
C75	0.0049 (4)	0.0594 (5)	0.5396 (4)	0.100 (3)
C76	0.0192 (4)	0.0092 (5)	0.4277 (4)	0.100 (3)
C77 †	0.0516 (9)	0.1373 (5)	0.4359 (5)	0.056 (3)

† Occupancy 0.5.

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

Rh1—P1	2.1566 (9)	O5—C34	1.400 (4)
Rh1—P2	2.1549 (9)	O6—C40	1.412 (4)
Rh1—O1	2.070 (2)	O7—C54	1.395 (4)
Rh1—O2	2.074 (2)	O8—C68	1.395 (4)
P1—O3	1.625 (2)	C1—C2	1.388 (5)
P1—O4	1.610 (2)	C1—C4	1.508 (6)
P1—O5	1.609 (2)	C2—C3	1.394 (5)
P2—O6	1.612 (2)	C3—C5	1.508 (7)
P2—O7	1.616 (2)	C6—C7	1.397 (5)
P2—O8	1.614 (2)	C7—C21	1.488 (4)
O1—C1	1.273 (4)	C40—C45	1.387 (4)
O2—C3	1.264 (4)	C45—C55	1.486 (4)
O3—C6	1.392 (4)	C54—C55	1.389 (5)
O4—C20	1.410 (3)		
P1—Rh1—P2	99.87 (3)	O3—C6—C11	119.5 (3)
P1—Rh1—O1	86.43 (7)	C7—C6—C11	122.0 (3)
P1—Rh1—O2	172.67 (7)	C6—C7—C8	118.4 (3)
P2—Rh1—O1	171.94 (7)	C6—C7—C21	123.6 (3)
P2—Rh1—O2	84.83 (7)	C8—C7—C21	118.0 (3)
O1—Rh1—O2	89.41 (9)	C7—C8—C9	122.2 (3)
Rh1—P1—O3	119.52 (8)	C8—C9—C10	117.1 (3)
Rh1—P1—O4	119.18 (8)	C8—C9—C12	122.7 (3)
Rh1—P1—O5	110.17 (9)	C10—C9—C12	120.1 (3)
O3—P1—O4	103.25 (11)	C9—C10—C11	123.7 (3)
O3—P1—O5	97.30 (11)	C6—C11—C10	116.2 (3)
O4—P1—O5	104.37 (11)	C6—C11—C16	122.5 (3)
Rh1—P2—O6	121.07 (8)	C10—C11—C16	121.3 (3)
Rh1—P2—O7	117.76 (9)	C9—C12—C13	109.6 (3)
Rh1—P2—O8	109.76 (9)	C9—C12—C14	111.9 (3)
O6—P2—O7	103.23 (12)	C9—C12—C15	109.8 (3)
O6—P2—O8	103.80 (12)	C13—C12—C14	108.3 (3)
O7—P2—O8	98.04 (12)	C13—C12—C15	108.9 (3)
Rh1—O1—C1	125.2 (2)	C14—C12—C15	108.2 (3)
Rh1—O2—C3	125.3 (2)	C11—C16—C17	110.4 (3)
P1—O3—C6	126.46 (19)	C11—C16—C18	110.6 (3)
P1—O4—C20	120.07 (17)	C11—C16—C19	111.8 (3)
P1—O5—C34	129.79 (19)	C17—C16—C18	110.7 (3)
P2—O6—C40	118.72 (19)	C17—C16—C19	106.8 (3)
P2—O7—C54	128.0 (2)	C18—C16—C19	106.4 (3)
P2—O8—C68	130.8 (2)	O4—C20—C21	117.4 (2)
O1—C1—C2	126.6 (3)	O4—C20—C25	119.1 (3)
O1—C1—C4	115.2 (3)	C21—C20—C25	123.4 (3)
C2—C1—C4	118.2 (3)	C7—C21—C20	122.9 (3)
C1—C2—C3	126.3 (3)	C7—C21—C22	118.8 (3)
O2—C3—C2	126.6 (3)	C40—C45—C44	117.8 (3)
O2—C3—C5	115.9 (3)	C44—C45—C55	118.8 (3)
C2—C3—C5	117.5 (4)	C45—C55—C54	123.0 (3)
O3—C6—C7	118.3 (3)	C45—C55—C56	118.3 (3)

P2—Rh1—P1—O3	117.84 (9)	Rh1—P2—O7—C54	−108.5 (2)
P2—Rh1—P1—O4	−10.32 (10)	O6—P2—O7—C54	27.8 (3)
P2—Rh1—P1—O5	−130.85 (9)	O8—P2—O7—C54	134.1 (2)
O1—Rh1—P1—O3	−57.10 (11)	Rh1—P2—O8—C68	−121.4 (3)
O1—Rh1—P1—O4	174.74 (11)	O6—P2—O8—C68	107.9 (3)
O1—Rh1—P1—O5	54.21 (11)	O7—P2—O8—C68	2.0 (3)
P1—Rh1—P2—O6	−9.44 (10)	Rh1—O1—C1—C2	7.4 (5)
P1—Rh1—P2—O7	118.81 (10)	Rh1—O1—C1—C4	−172.6 (2)
P1—Rh1—P2—O8	−130.27 (10)	Rh1—O2—C3—C2	7.8 (5)
O2—Rh1—P2—O6	176.23 (11)	Rh1—O2—C3—C5	−174.2 (3)
O2—Rh1—P2—O7	−55.52 (12)	P1—O3—C6—C11	123.6 (3)
O2—Rh1—P2—O8	55.40 (11)	P1—O3—C6—C7	−62.1 (3)
P1—Rh1—O1—C1	−176.5 (3)	P1—O4—C20—C21	−70.8 (3)
O2—Rh1—O1—C1	−2.5 (3)	P1—O4—C20—C25	112.4 (3)
P2—Rh1—O2—C3	−179.0 (3)	P1—O5—C34—C39	−102.4 (3)
O1—Rh1—O2—C3	−4.6 (3)	P1—O5—C34—C35	81.5 (4)
Rh1—P1—O3—C6	−104.0 (2)	P2—O6—C40—C45	−71.2 (3)
O4—P1—O3—C6	31.2 (2)	P2—O6—C40—C41	110.2 (3)
O5—P1—O3—C6	137.8 (2)	P2—O7—C54—C59	126.7 (3)
Rh1—P1—O4—C20	−168.32 (17)	P2—O7—C54—C55	−59.7 (4)
O3—P1—O4—C20	56.3 (2)	P2—O8—C68—C731	80.5 (5)
O5—P1—O4—C20	−44.9 (2)	P2—O8—C68—C732	132.8 (4)
Rh1—P1—O5—C34	−127.9 (3)	P2—O8—C68—C69	−82.6 (5)
O3—P1—O5—C34	−2.7 (3)	O1—C1—C2—C3	−5.4 (6)
O4—P1—O5—C34	103.0 (3)	C44—C45—C55—C54	−129.3 (3)
Rh1—P2—O6—C40	−167.26 (17)	C40—C45—C55—C54	50.9 (5)
O7—P2—O6—C40	58.3 (2)	C40—C45—C55—C56	−132.1 (3)
O8—P2—O6—C40	−43.6 (2)	C44—C45—C55—C56	47.7 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry, as well as a molecular packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55972 (97 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1032]

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Structures of two Cobalt(III) Sepulchrate Complexes*

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Abstract

The complex (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-icosane)cobalt(III) perchlorate thiosulfate, $[Co(C_{12}H_{30}N_8)](ClO_4)(S_2O_3)$, crystallizes in the hexagonal space group $P6_322$. Cations and anions occupy special-site positions with the anions disordered as a result of symmetry requirements. $Co(sep)^{3+}$ (sep = $C_{12}H_{30}N_8$) adopts the optically active D_3 crystallographic geometry. The packing consists of layers of interacting $Co(sep)^{3+}$ and $S_2O_3^{2-}$ ions, intercalated by isolated ClO_4^- anions. The second complex, *rac*-(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)cobalt trichloride monohydrate, *rac*-$Co(C_{12}H_{30}N_8)]Cl_3\cdot H_2O$, crystallizes in the

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