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Bis[μ -3,3',5,5'-tetra-*tert*-butylbiphenyl-2,2'-diyl phosphonato(1-)]bis[(acetonitrile)carbonylrhodium(I)] dichloromethane sesquisolvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
Disorder in main residue
R factor = 0.043
wR factor = 0.098
Data-to-parameter ratio = 17.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[μ -3,3',5,5'-tetra-*tert*-butylbiphenyl-2,2'-diyl phosphonato(1-)]bis[(acetonitrile)carbonylrhodium(I)] dichloromethane sesquisolvate

The title compound, $[\text{Rh}_2(\text{C}_{28}\text{H}_{40}\text{O}_3\text{P})_2(\text{C}_2\text{H}_3\text{N})_2(\text{CO})_2] \cdot \sim 1.5\text{CH}_2\text{Cl}_2$, contains a dimeric rhodacyclic complex, having inversion symmetry. The Rh atoms are joined by bridging phosphites and additionally each is coordinated by a CO and an acetonitrile. Half of the *tert*-butyl groups are rotationally disordered, but weak C—H...O interactions prevent this from occurring in the other two groups.

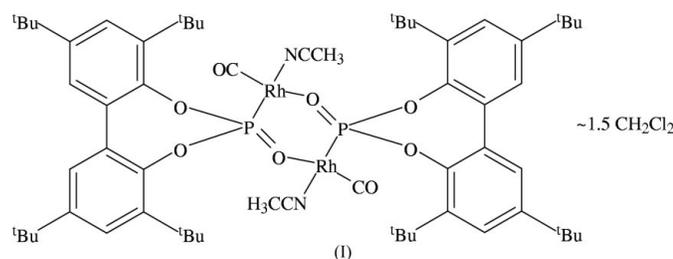
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Comment

During the course of research into novel ligand systems for catalysis and coordination chemistry, monodentate (van der Vlugt, Grutters *et al.*, 2003) and bidentate (van der Vlugt, Fioroni *et al.*, 2003) phosphorus-functionalized silsesquioxane frameworks were prepared (van der Vlugt, Ackerstaff *et al.*, 2004). From the stoichiometric reaction of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with a silsesquioxane-based diphosphite ligand, the unexpected title compound, (I), was obtained (Fig. 1).



Compound (I) is a centrosymmetric dinuclear rhodium complex. Two $\{(\mu_2\text{-}O,P)(\text{dibenzo-}[d,f]\text{-}2,2,4,4\text{-tetra-}tert\text{-butyl-}[1,3,2]\text{dioxaphosphito})\}$ ligands are present in the molecule, each coordinating to one rhodium cation *via* the P atom. There are three O atoms attached to the P atom, and the bridging coordination of the phosphito ligand results in a metallomacrocyclic complex. The remaining coordination sites on the rhodium cations are filled by one CO and one acetonitrile each.

A search of the Cambridge Structural Database (CSD) (Jan 2004 update of the November 2003 version; Allen, 2002) reveals that such a dinuclear rhodium structure has not been reported before and, to the best of our knowledge, has also never been reported in solution. Recently, Bedford *et al.* (2003) have published the structure of a palladium dimer that bears a close resemblance to the structural motif found in this complex. Earlier Geldbach *et al.* (2001) published the structure of a dimeric ruthenium complex with similar features.

There is no indication that the rhodium–phosphorus bridging oxygen has any oxide character, since the P1—O1 bond length is shorter [1.507 (3) Å] than the P1—O3 and P1—

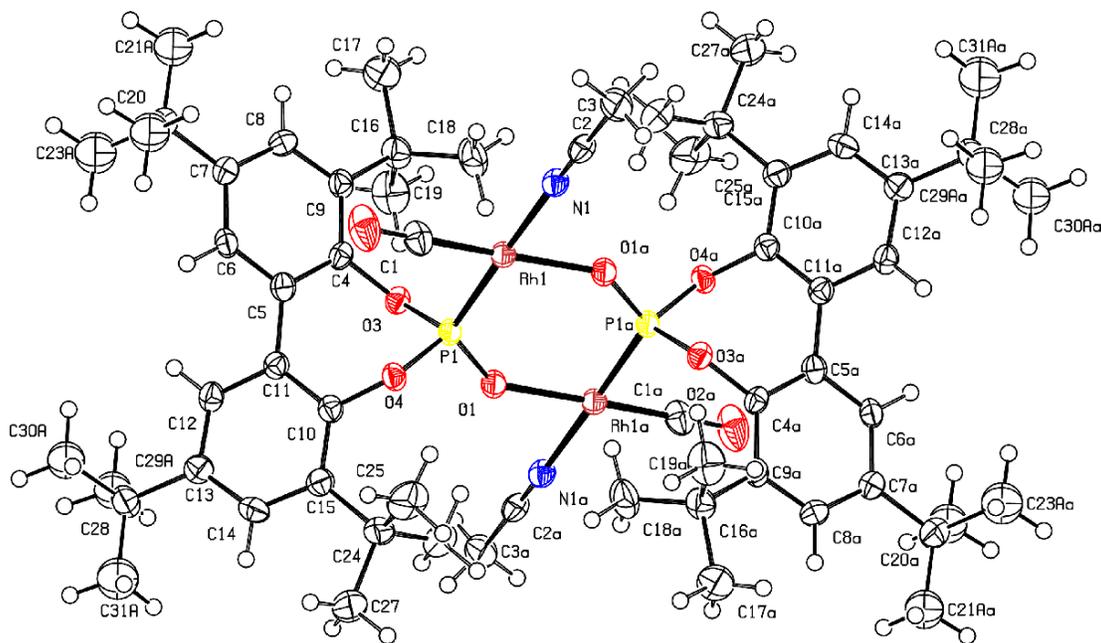


Figure 1
View of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. The minor disorder components of the *tert*-butyl groups and the disordered solvent molecules have been omitted for clarity.

O4 bonds [1.642 (3) and 1.625 (3) Å respectively]. The dinuclear complex shows a mutual *anti* configuration for both Rh atoms, in relation to the other atoms in the six-membered ring. The geometry around the Rh atoms is square planar, with a maximum deviation of 0.002 (1) Å from the P/N/O/C mean plane. The rhodium cation is displaced by 0.027 (3) Å from the mean plane and the N1–Rh1–P1 bond angle is 178.42 (8)°. The Rh1–N1 and the Rh1–C1 bond lengths are normal at 2.119 (3) Å and 1.799 (5) Å respectively, comparable to other Rh(CO)(NCCH₃)_xL_x complexes in the literature (Siedle *et al.*, 1990).

The *tert*-butyl groups containing C20 and C28 are rotationally disordered, whilst those containing C18 and C26 are not. This lack of disorder may be attributable to the presence of weak C–H···O interactions of C18, C19, C25 and C26 with O3, O3, O4 and O1 respectively (see Table 2).

Experimental

112.5 mg (0.06 mmol) of {*c*-(C₅H₉)₇Si₇O₉(OSiMePh₂)}{C₂₈H₄₀O₂P}₂(CO)₂ and 14.9 mg (0.06 mmol) [Rh(acac)(CO)₂] in CH₂Cl₂ were used. After removal of the solvent, a light green powder was obtained. Layering with CH₂Cl₂ and CH₃CN produced tiny crystals after three d. The saturated solution was filtered, giving slightly bigger crystals after a further two d.

Crystal data

[Rh₂(C₂₈H₄₀O₃P)₂(C₂H₃N)₂(CO)₂].1.5CH₂Cl₂

M_r = 1255.09

Monoclinic, C₂/c

a = 29.2584 (4) Å

b = 12.4252 (2) Å

c = 21.7240 (3) Å

β = 118.3548 (5)°

V = 6950.05 (18) Å³

Z = 4

D_x = 1.199 Mg m⁻³

Mo Kα radiation

Cell parameters from 7134

reflections

θ = 1.0–26.0°

μ = 0.57 mm⁻¹

T = 150 K

Needle, yellow

0.39 × 0.15 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1990)

T_{min} = 0.750, *T_{max}* = 0.950

28137 measured reflections

6085 independent reflections

4468 reflections with *I* > 2σ(*I*)

R_{int} = 0.053

θ_{max} = 25.0°

h = -34 → 34

k = -14 → 14

l = -25 → 25

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.043

wR(*F*²) = 0.098

S = 1.05

6085 reflections

340 parameters

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0431*P*)²

+ 7.5648*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.004

Δρ_{max} = 0.68 e Å⁻³

Δρ_{min} = -0.49 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Rh1–P1	2.2074 (10)	P1–O4	1.625 (3)
Rh1–N1	2.119 (3)	O2–C1	1.161 (6)
Rh1–C1	1.799 (5)	O3–C4	1.405 (4)
Rh1–O1 ⁱ	2.071 (3)	O4–C10	1.394 (5)
P1–O1	1.507 (3)	N1–C2	1.126 (5)
P1–O3	1.642 (3)		
P1–Rh1–N1	178.42 (8)	Rh1–P1–O4	107.22 (10)
P1–Rh1–C1	87.84 (13)	O1–P1–O3	100.47 (13)
P1–Rh1–O1 ⁱ	94.91 (7)	O1–P1–O4	108.41 (14)
N1–Rh1–C1	92.47 (15)	O3–P1–O4	101.82 (13)
O1 ⁱ –Rh1–N1	84.74 (11)	Rh1 ⁱ –O1–P1	143.09 (16)
O1 ⁱ –Rh1–C1	176.86 (15)	O4–C10–C11	118.4 (3)
Rh1–P1–O1	119.91 (11)	O4–C10–C15	119.5 (3)
Rh1–P1–O3	117.37 (9)		

Symmetry code: (i) -*x*, 1 - *y*, -*z*.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C18–H18C···O3	0.98	2.42	3.067 (5)	123
C19–H19C···O3	0.98	2.42	3.082 (5)	124
C25–H25B···O4	0.98	2.26	2.923 (4)	124
C26–H26B···O1	0.98	2.34	3.306 (5)	168

H atoms were placed in geometrically idealized positions [$d(C-H) = 0.98$ Å for methyl H atoms and 0.95 Å for other H atoms] and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other H atoms.

The *tert*-butyl groups containing C20 and C28 were found to be rotationally disordered, and were modeled using partial occupancies and isotropic displacement parameters. The unit cell contains two voids of about 371 Å³ each, filled with disordered CH₂Cl₂. Their contribution to the structure factor calculation was taken into account by back-Fourier transformation using *PLATON-SQUEEZE* (van der Sluis & Spek, 1990; Spek, 2003). The total electron density taken into account was 128.4 e⁻ per void, equivalent to three dichloromethane molecules. The derived quantities (M_r , $F(000)$, μ and D_x) in the *Crystal data* do not contain the contribution from this disordered solvent.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *HKL2000* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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