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A mononuclear Rh^{III} tetraphosphine complex, $[RhCl_2(C_{25}H_{40}P_4)]BF_4\cdot C_3D_6O$, crystallized as a perdeuteroacetone solvate

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.071
Data-to-parameter ratio = 23.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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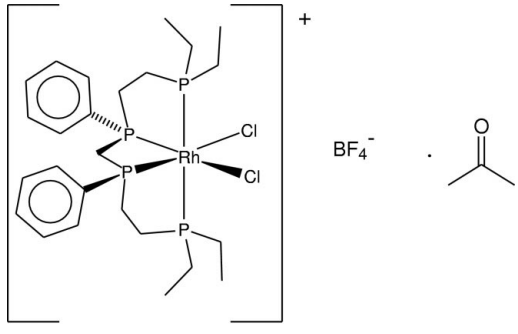
The title mononuclear Rh^{III} complex, (bis{[2-(diethylphosphino-κP)ethyl]phenylphosphino}methane)dichlororhodium(III) tetrafluoroborate perdeuteroacetone solvate, $[RhCl_2(C_{25}H_{40}P_4)]BF_4\cdot C_3D_6O$, is based on the racemic η^4-coordinated tetraphosphine ligand $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$. The Rh—Cl distances are 2.4164 (7) and 2.4282 (7) Å, and the Rh—P bond distances are in the range 2.2501 (7)–2.3649 (7) Å, with distorted octahedral coordination geometry for the Rh atom.

Comment

Hydroformylation is the most widely used homogeneous catalytic process for aldehyde synthesis (Parshall & Ittel, 1992). The dinuclear Rh complex $[Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$ [nbd = norbornadiene; et,ph-P4 = $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$ or bis{[2-(diethylphosphino)ethyl]phenylphosphino}methane], developed in our research group, is the catalyst precursor for the hydroformylation reaction of alkenes and is one of the best examples of bimetallic cooperativity (Broussard *et al.*, 1993). The main goals of our research are to explain in detail the high activity and regioselectivity of this dinuclear catalyst and to identify fully the catalytically inactive by-products formed upon fragmentation of the catalyst under hydroformylation conditions. For this purpose, $[RhCl_2(\eta^4\text{-et,ph-P4})]BF_4$, a possible by-product, was synthesized and crystallographically and spectroscopically studied. The crystal structures of the dichloromethane, methanol and toluene solvates of $[RhCl_2(\eta^4\text{-et,ph-P4})]BF_4$ were determined (Hunt *et al.*, 2001), and it was found that the complex typically cocrystallizes with 15–20% of the chloromethyl complex $[RhCl(CH_2Cl)(\eta^4\text{-et,ph-P4})]BF_4$ in a substitutional disorder. We report here the structure of the title compound, $[RhCl_2(\eta^4\text{-et,ph-P4})]BF_4\cdot C_3D_6O$, (I), as the perdeuteroacetone solvate, with no detectable chloromethyl compound present.



(I)

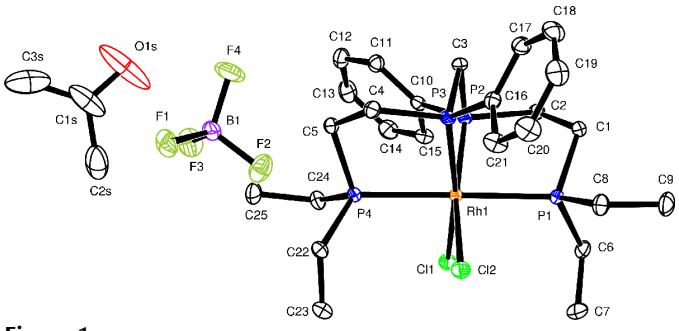


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. H atoms are not shown.

The structure of (I) (Fig. 1) contains the η^4-*rac*-et,ph-P4 ligand and two *cis*-chloro ligands coordinated to the central Rh atom. The geometry around the Rh atom is distorted octahedral. These distortions arise from the presence of the four-membered bis(phosphino)methane chelate ring (P2—Rh—P3) and two five-membered chelate rings (P1—Rh—P2 and P3—Rh—P4). The four-membered ring contributes to the 73.75 (2)° P2—Rh—P3 angle and the 94.38 (2)° Cl—Rh—Cl angle *trans* to it. Chloro ligands lie on opposite sides of the central P2—Rh—P3 plane by 0.4286 (6) (for Cl1) and 0.3921 (6) Å (for Cl2). $^{31}P\{^1H\}$ NMR spectroscopic data of the reported compound show a symmetrical set of doublets of triplets at 12.1 ($P_{internal}$) and 59.7 p.p.m. ($P_{external}$). The perdeuteroacetone molecule exhibits large displacement parameters, even at 105 K, likely indicative of unresolved disorder. A number of C—H···*X* (*X* = F, Cl, O) interactions exist in (I), the most significant of which are listed in Table 2.

Experimental

Synthetic procedures were performed under an inert atmosphere using dry-box and Schlenk-line techniques. The anhydrous solvents [dichloromethane (DCM) and d_6-acetone] packed under nitrogen were purchased from Aldrich. Complex (I) was synthesized by adding dropwise one equivalent of mixed et,ph-P4 ligand (0.633 g, 0.0013 mol) dissolved in 10 ml DCM to 1.5 equivalents of $[Rh(nbd)_2]BF_4$ (0.73 g, 0.00195 mol) in 20 ml DCM at room temperature. After 4 h of stirring under nitrogen, the solvent was removed under vacuum. The resulting yellow–orange powder was dissolved in a minimum amount of d_6-acetone and crystals of $[RhCl_2(\eta^4\text{-et,ph-P4})]BF_4{\cdot}C_3D_6O$ were obtained in 47% yield after 2 d. X-ray quality pale-yellow crystals were obtained by recrystallization from d_6-acetone.

Crystal data

$[RhCl_2(C_{25}H_{40}P_4)]BF_4{\cdot}C_3D_6O$
M_r = 789.15
Monoclinic, $P2_1/n$
a = 10.595 (2) Å
b = 14.750 (3) Å
c = 22.285 (5) Å
β = 96.186 (9)°
V = 3462.3 (12) Å^3
Z = 4
D_x = 1.514 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7957 reflections
θ = 2.5–28.7°
μ = 0.88 mm^{-1}
T = 105 K
Tablet, pale yellow
0.28 × 0.23 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.806, T_{max} = 0.900
29 400 measured reflections
8837 independent reflections
7230 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 28.7°
$h = -14 \rightarrow 14$
$k = -19 \rightarrow 14$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.071
S = 1.01
8837 reflections
377 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2 + 3.8331P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.85 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0003 (1)

Table 1
Selected geometric parameters (Å, °).

Rh1—P3	2.2501 (7)	Rh1—P4	2.3649 (7)
Rh1—P2	2.2574 (7)	Rh1—Cl1	2.4164 (7)
Rh1—P1	2.3563 (7)	Rh1—Cl2	2.4282 (7)
P3—Rh1—P2	73.75 (2)	P1—Rh1—Cl1	91.61 (2)
P3—Rh1—P1	97.29 (2)	P4—Rh1—Cl1	86.45 (2)
P2—Rh1—P1	83.30 (3)	P3—Rh1—Cl2	96.91 (2)
P3—Rh1—P4	84.47 (2)	P2—Rh1—Cl2	166.92 (2)
P2—Rh1—P4	96.21 (3)	P1—Rh1—Cl2	88.96 (3)
P1—Rh1—P4	177.94 (2)	P4—Rh1—Cl2	91.89 (3)
P3—Rh1—Cl1	165.72 (2)	Cl1—Rh1—Cl2	94.38 (2)
P2—Rh1—Cl1	96.36 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···F4^{i}	0.99	2.37	3.349 (3)	171
C3—H3B···F1^{ii}	0.99	2.32	3.302 (3)	171
C17—H17···F1^{ii}	0.95	2.41	3.240 (3)	146

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-1, y, z$.

H atoms were treated as riding in idealized positions, with C—H = 0.95–0.99 Å, depending on atom hybridization type. A torsional parameter was refined for each rigid methyl group. Displacement parameters for H atoms were assigned as $U_{iso} = 1.2U_{eq}$ of the attached atom ($1.5U_{eq}$ for methyl).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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