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(η^6-Benzene)dichloro[tris(2-isopropylphenyl) phosphite]ruthenium(II) dichloromethane solvate

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Key indicators

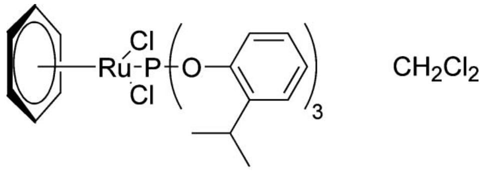
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.023
wR factor = 0.058
Data-to-parameter ratio = 21.8

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

In the title compound, $[RuCl_2(C_{27}H_{33}O_3P)(C_6H_6)]\cdot CH_2Cl_2$, the Ru—P bond distance is 2.2790 (4) Å, and the Ru—Cl bond distances are 2.4052 (4) and 2.4046 (4) Å. The title compound is the first reported structure containing tris(2-isopropylphenyl)phosphite as a ligand. The effective cone angle (θ_E) for the tris(2-isopropylphenyl) phosphite was calculated to be 160°.

Comment

η^6-Arene ruthenium complexes play a vital role in organometallic chemistry (Moriarty *et al.*, 1988; Noyori & Hashiguchi, 1997; Bennett, 1995, 1997), and ruthenium(II) complexes of the type Ru(η^6-arene)$^{2+}$ were first synthesized by Fisher & Böttcher (1957) from anhydrous $RuCl_3$. However, these complexes were not convenient precursors to the half-sandwich arene complexes. Winkaus & Singer (1967) reported that 1,3-cyclohexadiene undergoes dehydrogenation on reaction with an ethanol solution of $RuCl_3$ to give the insoluble benzene complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. The arene ruthenium halide compounds are key starting materials for the formation of a wide range of neutral and cationic ligand derivatives (Bennett, 1995; De los Ríos *et al.*, 1996; Schlüter *et al.*, 2002; Chen *et al.*, 2002; Singh *et al.*, 2002). The half-sandwich arene ruthenium complexes may serve as excellent catalyst precursors for hydrogenation (Mashima *et al.*, 1994; Hashiguchi *et al.*, 1995; Fujii *et al.*, 1996; Kathó *et al.*, 2000; Chen *et al.*, 2002; De Clercq & Verpoort, 2002) and for ring-opening metathesis polymerization (Stumpf *et al.*, 1995).



(I)

The title compound, (I), crystallizes in the monoclinic space group $P2_1/n$ as a dichloromethane solvate with Z = 4. The molecular structure of (I) is shown in Fig. 1, and it is the first reported structure containing tris(2-isopropylphenyl) phosphite as a ligand. The Ru atom is in a formally six-coordinate environment and the structure adops a distorted 'bar-stool' type of geometry.

The Ru—P bond length is of the same order as in related compounds (Table 3) with Ru—P = 2.2790 (4) Å. The Ru—Cl bond distances are also typical of this type of compound, with Ru—Cl1 = 2.4052 (4) Å and Ru—Cl2 = 2.4046 (4) Å (see

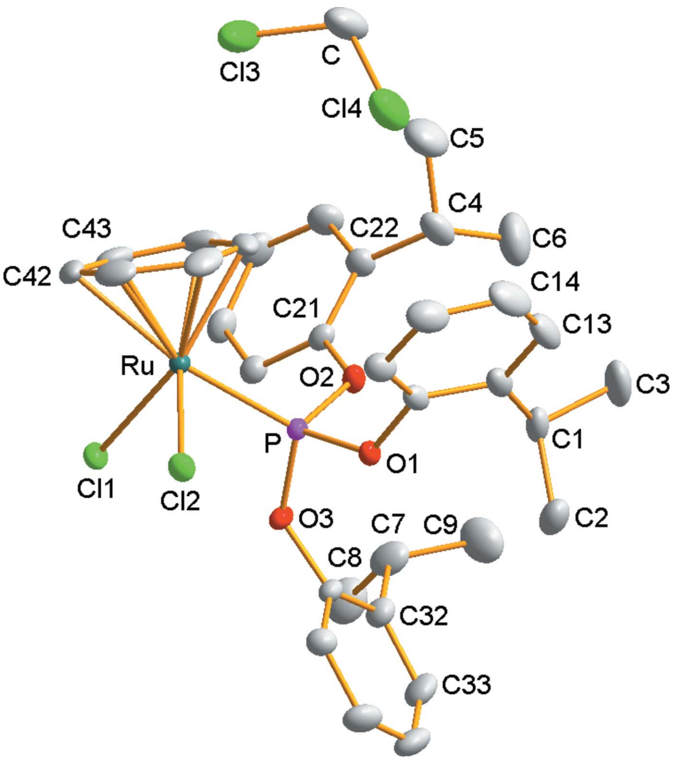


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. For C atoms in rings, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring.

Table 3). The ruthenium-to-benzene centroid distance is 1.7165 (1) Å. The Ru—C bond distances are almost equal, with an average bond length of 2.2147 (18) Å.

The most widely used method for determining ligand steric behaviour at a metal centre is the calculation of the Tolman cone angle (θ_T), as described previously by Tolman (1977). For the current study, actual Rh—P bond distances were used (Otto *et al.*, 2000), with a van der Waals radius of 1.20 Å for H atoms, yielding effective cone angles (θ_E). The substituents of the phosphite may have different orientations, resulting in variations in cone angle sizes, as observed by Ferguson *et al.* (1978), and may not necessarily be a true indication of the steric properties of the phosphite in solution. A value of 160° was calculated for tris(2-isopropylphenyl) phosphite. However, this is the first reported structure containing the phosphite and therefore no comparison can currently be made.

Experimental

The dinuclear ruthenium complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was synthesized according to the literature (Bennett & Smith, 1974). The phosphite was synthesized by reacting 2-isopropylphenol with PCl_3 in the presence of NEt_3 according to the method of Van Leeuwen & Roobeek (1983). The title compound was obtained by heating a mixture of $[(C_6H_6)RuCl_2]_2$ (0.250 g, 0.499 mmol) and the phosphite (0.872 g, 1.996 mmol) under reflux in benzene (35 ml) for 4 h. Recrystallization of the title compound from CH_2Cl_2 gave crystals suitable for X-ray diffraction in quantitative yield.

Crystal data

$[RuCl_2(C_{27}H_{33}O_3P)(C_6H_6)]\cdot CH_2Cl_2$
M_r = 771.51
Monoclinic, $P2_1/n$
a = 10.7593 (6) Å
b = 18.6163 (11) Å
c = 17.5744 (10) Å
β = 101.029 (2)°
V = 3455.1 (3) Å^3
Z = 4
D_x = 1.483 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.84 mm^{-1}
T = 150 (2) K
Block, red
0.3 × 0.28 × 0.19 mm

Data collection

Bruker X8 APEX-II diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min}$ = 0.786, $T_{\max}$ = 0.856
80414 measured reflections
8585 independent reflections
7855 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.038
$\theta_{\max}$ = 28.3°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.058
S = 1.06
8585 reflections
394 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 2.6184P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.78 e Å^{-3}
$\Delta\rho_{\min}$ = −0.88 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru—P	2.2790 (4)	Ru—Cl2	2.4046 (4)
Ru—Cl1	2.4052 (4)		
P—Ru—Cl2	84.400 (13)	O3—P—Ru	114.60 (4)
P—Ru—Cl1	89.504 (13)	O1—P—Ru	120.05 (4)
Cl2—Ru—Cl1	88.787 (14)	O2—P—Ru	116.60 (4)
Cl2—Ru—P—O3	71.81 (5)	Cl1—Ru—P—O1	−135.37 (5)
Cl1—Ru—P—O3	−17.02 (5)	Cl2—Ru—P—O2	−164.71 (5)
Cl2—Ru—P—O1	−46.54 (5)	Cl1—Ru—P—O2	106.46 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O2	1.00	2.44	3.308 (2)	145
C2—H2C···O1	0.98	2.57	3.149 (2)	118
C4—H4···O2	1.00	2.36	2.851 (2)	109
C7—H7···O3	1.00	2.47	2.938 (2)	108
C16—H16···Cl2	0.95	2.76	3.5885 (17)	146
C41—H41···Cl1$^{\rm i}$	0.95	2.80	3.5863 (19)	141
C42—H42···Cl2$^{\rm i}$	0.95	2.76	3.6875 (17)	164
C—H0A···Cl2$^{\rm ii}$	0.99	2.52	3.442 (2)	155

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

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Table 3
Comparative geometric parameters for selected $[(\eta^6\text{-}C_6H_6)RuCl_2(L)]$ (L = ligand) complexes..

L	Ru—L (Å)	Ru—Cl1 (Å)	Ru—Cl2 (Å)	notes
$P(2\text{-}^i\text{Pr}—C_6H_4)_3$	2.2790 (4)	2.4052 (4)	2.4046 (4)	TW
Me_2HPz	2.122 (7)	2.423 (1)	2.410 (2)	(i)
Me_2HPz	2.125 (7)	2.417 (2)	2.412 (2)	(i)
PPh_3	2.364 (1)	2.412 (1)	2.406 (2)	(ii)
pta	2.237 (4)	2.4155 (18)	s	(iii)
PPh_2MeIm	2.3529 (10)	2.4085 (11)	2.4055 (10)	(iv)
PPh_2MeIm^+	2.3404 (14)	2.4221 (15)	2.398 (13)	(iv)

Notes: TW = this work; Pz = pyrazole; pta = 1,3,5-triaza-7-phophaadamantane; s = generated by symmetry; MeIm = 1-methylimidazol-2-yl; $MeIm^+$ = 1-methylimidazol-3-ium-2-yl. (i) Małecki *et al.* (2004). (ii) Elsegood & Tocher (1995). (iii) Horváth *et al.* (2004). (iv) Caballero *et al.* (2004).

The methyl, methine and aromatic H atoms were placed in geometrically idealized positions (C—H = 0.95–1.00 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$ for the methyl and methine and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$ for aromatic H atoms. The methyl H atoms were located in a difference Fourier map and the group was refined as a rigid rotor.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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