Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Dichlorotris(triphenylphosphine)ruthenium(II) dichloromethane hemisolvate

Andrew R. Cowley, Jonathan R. Dilworth* and Carlo A. Maresca von Beckh W.

University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, Oxford OX1 3TA, England

Correspondence e-mail: jon.dilworth@chem.ox.ac.uk

Received 16 May 2005
Accepted 20 May 2005
Online 31 May 2005

Key indicators

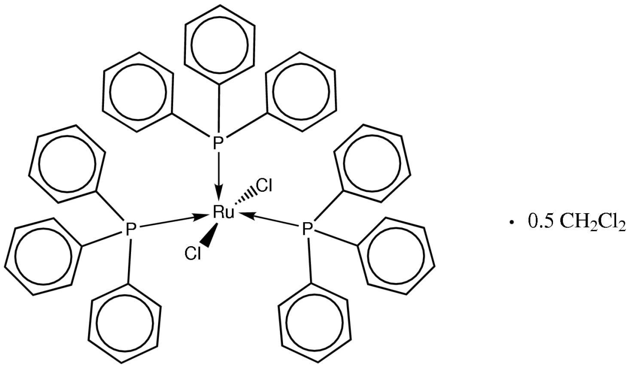
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.039
wR factor = 0.041
Data-to-parameter ratio = 10.8

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

A third modification of [$RuCl_2(PPh_3)_3$] has been characterized, this time as the title compound, [$RuCl_2(C_{18}H_{15}P)_3$]·0.5CH_2Cl_2. As seen for the previous modifications, the complex has a distorted square-pyramidal geometry with an *ortho*-H atom 'blocking' the site *trans* to the apical PPh_3 ligand. There is no evidence for a strong C—H···Ru interaction nor any specific directional force in the solid state.

Comment

Two different modifications of [$RuCl_2(PPh_3)_3$] have been solved in the space groups $P2_1/c$ (La Placa & Ibers, 1965) and $P2_1/n$ (Ernst *et al.*, 2003). Both show a distorted square-pyramidal geometry about Ru, with an *ortho*-H atom approaching the metal and 'blocking' the site *trans* to the apical PPh_3 ligand. As part of our studies on Ru^{II} thioether complexes, we discovered the title compound, (I), (Fig. 1), also containing the [$RuCl_2(PPh_3)_3$] complex, as the dichloromethane hemisolvate in the space group $C2/c$.



(I)

The metal complex in (I) adopts a distorted square-pyramidal geometry with bond lengths, angles and phenyl ring orientations virtually identical to the $P2_1/c$ modification of [$RuCl_2(PPh_3)_3$]. In fact, most [$Ru^{II}X_2(PPh_3)_3$] complexes are distorted square-pyramidal (Anillo *et al.*, 1993; MacFarlane *et al.*, 1996), due to electronic (vibrational distortions, Jahn–Teller effects) and/or steric reasons.

The shortest Ru···H distance in (I) is due to an *ortho*-H atom located approximately *trans* to P2 [Ru1···H2 = 2.83 (4) Å and P2—Ru1···H2 = 168 (2)°]. The shortest Ru···C distance in (I) [Ru1···C2 3.445 (4) Å] is average for penta-coordinate [$Ru^{II}(PPh_3)_3$] complexes (Anillo *et al.*, 1993; MacFarlane *et al.*, 1996) and some 0.2 Å shorter than in [$Ru^0(CO)_2(PPh_3)_3$] (Hiraki *et al.*, 1997). It is 0.1–0.3 Å shorter than the analogous distance in hexa-coordinate [$Ru^{II}(PPh_3)_3$] complexes (Skapski & Stephens, 1974; Alexander *et al.*, 1988;

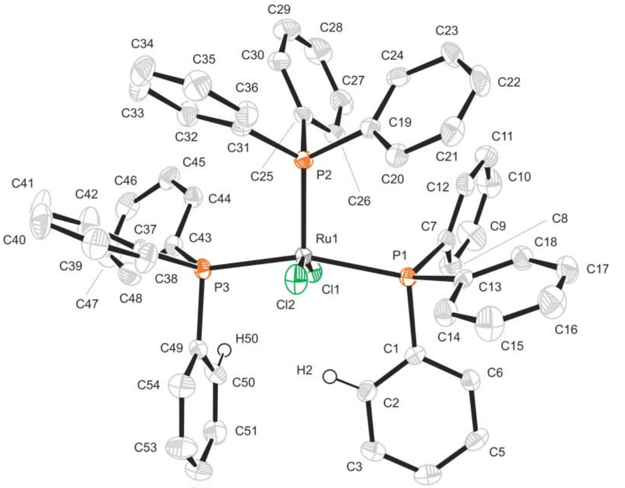


Figure 1
A view of (I), with displacement ellipsoids shown at the 50% probability level. The solvent molecule and most H atoms have been omitted for clarity.

Mizuho *et al.*, 1991; Poulton *et al.*, 1992; Junk & Steed, 1999; Jazzar *et al.*, 2001) and some 0.2 Å longer than in tetra-coordinate [$Ru^{II}(SC_6F_5)_2(PPh_3)_2$] (Catalá *et al.*, 1987, 1989). There is no elongation of the C2—H2 bond in (I) as observed in the $P2_1/n$ modification of [$RuCl_2(PPh_3)_3$], so overall there appears to be no strong C2—H2···Ru1 interaction in (I).

[$RuCl_2(PPh_3)_3$] has been referred to as an agostic complex (Leung *et al.*, 2000; Perera & Shaw, 1994, 1995; Catalá *et al.*, 1987, 1989), but much shorter and stronger agostic C—H···Ru bonds are known (Huang *et al.*, 1999, 2000; Jiménez Tenorio *et al.*, 2000). The close approach of the *ortho*-H atom to Ru and subsequent 'blocking' of the site *trans* to the apical PPh_3 ligand may therefore be due to a weak C—H···Ru interaction, steric crowding of the metal centre and/or crystal packing forces in the solid state.

The crystal packing in (I) is unexceptional and gives no indication of any specific directional force being present. The CH_2Cl_2 solvent molecule lies on a twofold symmetry axis and plays no role in metal coordination.

Experimental

[$RuCl_2(PPh_3)_3$] was synthesized according to the literature method of Hallman *et al.* (1970) but using only one-quarter the specified volume of methanol. Suitable single crystals of (I) were grown by two-phase dichloromethane–methanol liquid diffusion.

Crystal data

[$RuCl_2(C_{18}H_{15}P)_3$]·$0.5CH_2Cl_2$
M_r = 1001.31
Monoclinic, $C2/c$
a = 22.2083 (2) Å
b = 12.84460 (10) Å
c = 33.9272 (5) Å
β = 107.5681 (5)°
V = 9226.57 (18) Å^3
Z = 8

D_x = 1.442 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17441 reflections
θ = 5.0–27.5°
μ = 0.66 mm^{-1}
T = 150 K
Block, purple–brown
0.10 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.93, T_{max} = 0.94
17441 measured reflections

10441 independent reflections
6083 reflections with $I > 3\sigma(I)$
R_{int} = 0.05
θ_{max} = 27.5°
$h = -28 \rightarrow 28$
$k = -14 \rightarrow 16$
$l = -44 \rightarrow 43$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.041
S = 1.11
6083 reflections
563 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = [1 - (F_o - F_c)^2/36\sigma(F_o)^2]^2/ 0.437T_0(x) + 0.0688T_1(x) + 0.16T_2(x)]$, where $T_n(x)$ are Chebychev polynomials and $x = F_c/F_{max}$ (Watkin, 1994; Prince, 1982)
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.76 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—P3	2.3557 (9)	Ru1—Cl1	2.3916 (9)
Ru1—P2	2.2118 (10)	C2—H2	0.94 (4)
Ru1—P1	2.4334 (9)	C50—H50	0.96 (5)
Ru1—Cl2	2.3732 (9)		
P3—Ru1—P2	98.27 (4)	P1—Ru1—Cl2	91.36 (3)
P3—Ru1—P1	160.12 (4)	P3—Ru1—Cl1	86.29 (3)
P2—Ru1—P1	101.08 (4)	P2—Ru1—Cl1	107.46 (4)
P3—Ru1—Cl2	92.05 (3)	P1—Ru1—Cl1	83.63 (3)
P2—Ru1—Cl2	93.27 (4)	Cl2—Ru1—Cl1	159.24 (4)

Atoms H2 and H50 were located in a difference Fourier map and their coordinates and isotropic displacement parameters were subsequently refined. All other H atoms were positioned geometrically with C—H = 1.00 Å. The most positive and negative residual electron densities are located 1.11 and 1.05 Å from Cl61, respectively, possibly indicating disorder in the CH_2Cl_2 solvent molecule. No attempt was made to model this disorder.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

References

Alexander, B. D., Gomez-Sal, M. P., Gannon, P. R., Blaine, C. A., Boyle, P. D., Mueting, A. M. & Pignolet, L. H. (1988). *Inorg. Chem.* **27**, 3301–3308.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Anillo, A., Barrio, C., García-Granda, S. & Obeso-Rosete, R. (1993). *J. Chem. Soc. Dalton Trans.* pp. 1125–1130.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, C. K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Catalá, R.-M., Cruz-Garritz, D., Terreros, P., Torrens, H., Hills, A., Hughes, D. L. & Richards, R. L. (1987). *J. Organomet. Chem.* **328**, C37–C39.

Catalá, R.-M., Cruz-Garritz, D., Sosa, P., Terreros, P., Torrens, H., Hills, A., Hughes, D. L. & Richards, R. L. (1989). *J. Organomet. Chem.* **359**, 219–232.

Ernst, R. D., Basta, R. & Arif, A. M. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 49–51.

Hallman, P. S., Stephenson T. A. & Wilkinson, G. (1970). *Inorg. Synth.* **12**, 237–240.

Hiraki, K., Kira, S. & Kawano H. (1997). *Bull. Chem. Soc. Jpn*, **70**, 1583–1592.

m1238 Cowley *et al.* • [$RuCl_2(C_{18}H_{15}P)_3$]·$0.5CH_2Cl_2$ *Acta Cryst.* (2005). E**61**, m1237–m1239

Huang, D., Bollinger, J. C., Streib, W. E., Folting, K., Young, V. Jr, Eisenstein, O. & Caulton, K. G. (2000). *Organometallics*, **19**, 2281–2290.

Huang, D., Streib, W. E., Bollinger, J. C., Caulton, K. G., Winter, R. F. & Scheiring T. (1999). *J. Am. Chem. Soc.* **121**, 8087–8097.

Jazzar, R. F. R., Mahon, M. F. & Whittlesey, M. K. (2001). *Organometallics*, **20**, 3745–3751.

Jiménez Tenorio, M., Mereiter, K., Puerta, M. C. & Valerga, P. (2000). *J. Am. Chem. Soc.* **122**, 11230–11231.

Junk, P. C. & Steed, J. W. (1999). *J. Organomet. Chem.* **587**, 191–194.

La Placa, S. J. & Ibers, J. A. (1965). *Inorg. Chem.* **4**, 778–783.

Leung, W.-H., Zheng, H., Chim, J. L. C., Chan, J., Wong, W.-T. & Williams, I. D. (2000). *J. Chem. Soc. Dalton Trans.* pp. 423–430.

MacFarlane, K. S., Joshi, A. M., Rettig, S. J. & James, B. R. (1996). *Inorg. Chem.* **35**, 7304–7310.

Mizuho, Y., Kasuga, N. & Komiya, S. (1991). *Chem. Lett.* pp. 2127–2130.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.

Perera, S. D. & Shaw, B. L. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1201–1202.

Perera, S. D. & Shaw, B. L. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3861–3866.

Poulton, J. T., Folting, K. & Caulton, K. G. (1992). *Organometallics,* **11**, 1364–1372.

Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.

Skapski, A. C. & Stephens, F. A. (1974). *J. Chem. Soc. Dalton Trans.* pp. 390–395.

Watkin, D. J. (1994). *Acta Cryst.* A**50**, 411–437.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (2005). E**61**, m1237–m1239 Cowley *et al.* • $[RuCl_2(C_{18}H_{15}P)_3]\cdot0.5CH_2Cl_2$ **m1239**