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Chloro(pentamethyl-η^5-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II)

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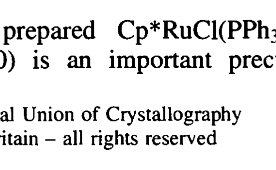
Abstract

The crystal structure of the title compound, $[RuCl(C_{10}H_{15})(C_{18}H_{15}P)_2]$, is reported. A structural discussion and a comparison with similar ruthenium(II) complexes are presented.

Comment

The crystal structure of the title compound, (1), completes our structural characterization of the series of pentamethylcyclopentadienyl- and cyclopentadienylruthenium(II) bis(triphenylphosphine) complexes (Torres-Lubián & Paz-Sandoval, 1997).



(1)

The easily prepared $Cp^*RuCl(PPh_3)_2$ (Chinn & Heinekey, 1990) is an important precursor to other half-sandwich complexes of ruthenium(II). It has been widely used due to the lability of the ligands (Yi *et al.*, 1997, 1998; Sato & Kawata, 1997; Bruce *et al.*, 1996; Davies *et al.*, 1990, and references therein). Despite its wide use as a starting material in many syntheses by many research groups, compound (1) has not been structurally characterized. There are several analogous compounds, however, and we deemed it imperative to compare them to (1).

The molecular structure of the neutral complex (1) is shown in Fig. 1. The relevant bond distances and angles are listed in Table 1. The molecule can be considered as a member of the $M(C_5R_5)(PR'_3)_2Cl$ series, and the geometry around the Ru atom can be described as distorted octahedral if the Cp* group is viewed as a tridentate ligand. The ruthenium–carbon distances range between 2.224 (2) and 2.274 (2) Å [average 2.24 (2) Å]. These bond lengths are in good agreement with the corresponding distances in related compounds: $CpRu(PPh_3)_2Cl$ [(2); Bruce *et al.*, 1981], $Cp^*Ru[P(p\text{-}CF_3C_6H_4)_3]_2Cl$ [(3); Serron *et al.*, 1995], $CpRu[P(p\text{-}CF_3C_6H_4)_3]_2Cl$ [(4); Serron *et al.*, 1995], $Cp^*Ru(PPh_3)(PPh_2H)Cl$ [(5); Torres-Lubián & Paz-Sandoval, 1997], $CpRu(PPh_3)(PPh_2H)Cl$ [(6); Torres-Lubián & Paz-Sandoval, 1997], $Cp^*Ru(PPh_2H)_2Cl$ [(7); Torres-Lubián & Paz-Sandoval, 1997] and $CpRu(\eta^1\text{-dppm})_2Cl$ [(8); Orth *et al.*, 1996]. The Ru—C bond lengths in (1) are slightly longer than the Ru—C distances [2.192 (3)–2.220 (3) Å] in (2) due to the steric strain introduced by the Cp* moiety. The bulkiness of the Cp* ligand also results in a wider variation of the ruthenium–carbon distances in (1). The Ru–centroid distance [1.887 (2) Å] is somewhat longer than that in (2) [1.847 (4) Å], but is

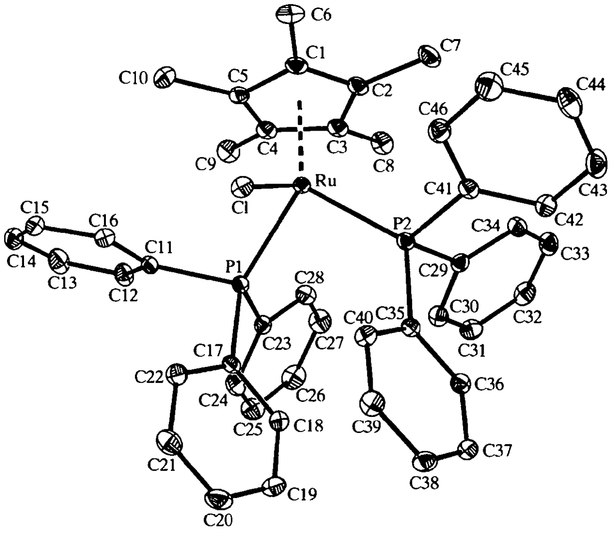


Fig. 1. The molecular structure of (1). The displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

in excellent agreement with the corresponding values in (3) [1.890 (11) Å] and (4) [1.890 (2) Å], and compares well with similar values in compounds (5)–(8).

The ruthenium–chlorine distance in (1) [2.4575 (5) Å] is similar to the corresponding distances in (2), (5), (7) and (8), but is significantly longer than the ruthenium–chlorine distances in (3) [2.439 (5) Å], (4) [2.4294 (6) Å] and (6) [2.434 (2) Å]. There is no substantial evidence that the Ru—Cl distance in ruthenium complexes bearing a Cp ligand is generally shorter than that in analogous complexes with a Cp* substituent. The ruthenium–phosphorous bond length in (1) [average 2.341 (6) Å] is slightly shorter than the typical Ru—P bond of 2.370 Å, and agrees well with the corresponding distances in (2) and other complexes. The present value indicates substantial $d(\pi)$–$d(\pi)$ multiple bonding. As expected, the substituents of the phosphine group and intermolecular interactions among them affect the ruthenium–phosphorous separation. The general trend is that less sterically demanding phosphines coordinate with shorter distances. This trend is illustrated in complexes (5) and (6) which have Ru—P distances to the PPh_3 ligand of 2.309 (2) and 2.302 (2) Å, respectively; the Ru—P distances to the PPh_2H ligands in (5) and (6) are 2.283 (2) and 2.282 (2) Å, respectively.

The environment around the Ru atom can be considered distorted octahedral. The degree of distortion can be estimated as the difference between the observed P—Ru—P and two Cl—Ru—Cl angles and the right angle. While there is no certain dependency between the degree of distortion and the presence of a Cp *versus* a Cp* moiety or the composition of the phosphine ligands, it is interesting to notice that in the complex pairs (1)/(2), (3)/(4) and (5)/(6), the former compounds bear Cp* ligands and the latter Cp moieties. In the two latter pairs, the complexes with a Cp* ligand are more severely distorted. The sum of the variations of the three angles from 90° are *ca* 12.13/15.35, 7.40/5.64 and 10.21/4.33° for the three pairs, respectively. The large P—Ru—P angle in (2) [103.99 (4)°] is quite unusual since in complexes (1) and (3)–(8) it spans the range 90.68 (4) to 97.20 (4)°. Large P—Ru—P angles were observed in two other related complexes, namely η^5-$(C_5H_4C_2CO_2Me)RuCl(PPh_3)_2$ (Bruce *et al.*, 1989) and $Cr(CO)_3$-$(\eta^6$-η^5-$C_6H_5C_5H_4)Ru(PPh_3)_2Cl$ (Qian *et al.*, 1997), in which the angle measured 99.9 (1) and 101.5 (1)°, respectively. Close examination of complex (1) shows that the potential pseudo-*m* symmetry is not preserved due to intramolecular interactions between sterically demanding Cp* ligands and bulky PPh_3 moieties. No significant intermolecular interactions were observed.

Experimental

Complex (1) was prepared according to a published procedure (Chinn & Heinekey, 1990). Crystals were grown from an acetone/diethyl ether mixture at room temperature.

Crystal data

$[RuCl(C_{10}H_{15})(C_{18}H_{15}P)_2]$
$M_r = 796.28$
Monoclinic
$P2_1/c$
$a = 17.1543 (8)$ Å
$b = 10.7312 (5)$ Å
$c = 20.6138 (10)$ Å
$\beta = 101.618 (1)°$
$V = 3717.0 (3)$ Å^3
$Z = 4$
$D_x = 1.423$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 268 reflections
$\theta = 11$–$15°$
$\mu = 0.613$ mm^{-1}
$T = 173 (2)$ K
Block
0.36 × 0.28 × 0.19 mm
Orange

Data collection

Bruker CCD-1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.80$, $T_{\max} = 0.90$
27 327 measured reflections
8779 independent reflections

6670 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 28.86°$
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 14$
$l = -26 \rightarrow 27$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.065$
$S = 1.04$
8779 reflections
451 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0260P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ru—centroid	1.887 (2)	Ru—P2	2.3449 (5)
Ru—P1	2.3364 (6)	Ru—Cl	2.4575 (5)
P1—Ru—P2	96.43 (2)	P2—Ru—Cl	93.415 (18)
P1—Ru—Cl	87.718 (19)		

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART*. Data reduction: *SHELXTL* (Sheldrick, 1997). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1451). Services for accessing these data are described at the back of the journal.

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A copper(I) complex of 4-amino-3-thioxo-6-methyl-2,3,4,5-tetrahydro-1,2,4-triazin-5-one

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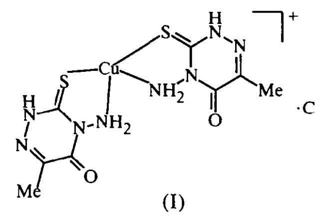
Abstract

In the crystal of the title compound, bis(4-amino-κN-3-thioxo-κS-6-methyl-2,3,4,5-tetrahydro-1,2,4-triazin-5-one)copper(I) chloride, [$Cu(C_4H_6N_4O)_2$]Cl, the asymmetric unit contains one-half of the cation, with the other half related by a crystallographic twofold axis; the Cl and Cu atoms lie on the twofold axis. The Cu atom is in a distorted tetrahedral geometry. The inversion-related molecules are linked by N···O [2.805 (3) Å] short contacts to form an infinite zigzag chain along the *c* direction. The Cl atom is involved in both intra- and interchain N—H···Cl hydrogen bonds.

Comment

Many metal complexes of chelating agents derived from 4-amino-3-thioxo-6-methyl-2,3,4,5-tetrahydro-1,2,4-triazin-5-one have been studied (Iskander *et al.*, 1989; Sharda *et al.*, 1994; Dubey & Beena, 1991). Some complexes of triazine have been shown to possess fungicidal activity (Bala *et al.*, 1978). As part of our studies on the synthesis and characterization, as well as the potential fungicidal activities, of triazine derivatives, we report here the crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) contains one-half of the [$Cu(C_4H_6N_4O)_2$]$^+$ cation, with the other half related by a crystallographic twofold axis; both the Cl^- anion and Cu atom lie on the twofold axis. The Cu atom is in a heavily distorted tetrahedral geometry, with the bond angles around it ranging from 84.75 (5) to 120.78 (6)°. The Cu1—S and Cu1—N bond lengths agree with reported values (Orpen *et al.*, 1989).

The inversion-related molecules are linked by N4···O1($1-x$, $1-y$, $1-z$) [2.805 (3) Å] short contacts to form an infinite zigzag ribbon-like structure along the *c* direction. Interestingly, the narrow N—H···O angles involving N4 and O1 (103 and 102°) decrease the involvement of any N—H···O hydrogen bonding in the chain. The Cl^- anion is located in the cavity of the chain and is linked to it through N4—H4*A*···Cl($1-x$, $1-y$, $1-z$) and N4—H4*B*···Cl1 hydrogen bonds (Table 3). Adjacent chains are interlinked by N1—H1···Cl1($x-\frac{1}{2}$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) hydrogen bonds. Other short contacts observed in the

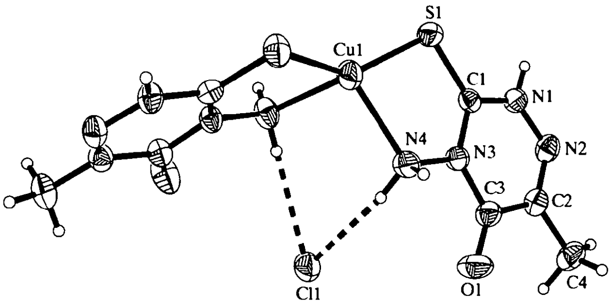


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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