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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 R factor = 0.032
 wR factor = 0.097
 Data-to-parameter ratio = 15.7

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

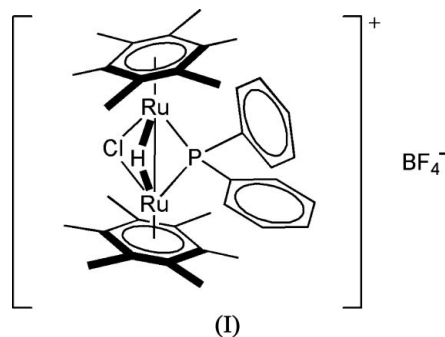
μ -Chloro- μ -diphenylphosphido- μ -hydrido-
 bis[(η^6 -hexamethylbenzene)ruthenium(II)]
 tetrafluoroborate

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The new triple-bridged dinuclear cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-Cl})(\mu_2\text{-H})(\mu_2\text{-PPh}_2)]^+$ was formed in chloroform from the precursor $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)]^+$ and characterized as the tetrafluoroborate salt $[(\eta^6\text{-C}_{12}\text{H}_{18})_2\text{Ru}_2(\mu_2\text{-Cl})(\mu_2\text{-H})(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)]\text{BF}_4$. The single-crystal X-ray structure analysis confirms the formation of the *meso* form. Despite the presence of two stereogenic centres, the complex is not chiral.

Comment

The formation of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-Cl})(\mu_2\text{-H})(\mu_2\text{-PPh}_2)]\text{BF}_4$, (I), occurred in deuterated chloroform under atmospheric pressure from the dihydrido precursor $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)]\text{BF}_4$ (Tschan *et al.*, 2005). The complete reaction took about two weeks, as demonstrated by ^1H NMR spectroscopy, and only one product was isolated after work-up. In the ^1H NMR spectrum, the chemical shift of the hydrido ligand is observed at -12.10 p.p.m., which is comparable to those found in the compounds $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\{\mu_2\text{-}(p\text{-Me-C}_6\text{H}_4)\text{-S}\}_2(\mu_2\text{-H})]\text{BF}_4$ and $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\{\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4)\text{-S}\}_2(\mu_2\text{-H})]\text{BF}_4$ (Tschan *et al.*, 2004). In addition, despite the presence of two stereogenic centres, the complex is not chiral, with only the *meso* form being generated. The ^1H NMR spectrum of (I) shows a series of unresolved multiplets for the aromatic protons of the diphenylphosphido ligand. This is in accord with the presence of diastereotopic protons within the phenyl rings.



The single-crystal X-ray structure analysis of (I) reveals a trigonal-bipyramidal Ru_2X_3 core, in which each Ru atom is coordinated by a $\eta^6\text{-C}_6\text{Me}_6$ ligand and linked to the other by three different bridging ligands, *viz.* $\mu_2\text{-Cl}$, $\mu_2\text{-H}$ and $\mu_2\text{-PPh}_2$. The bond angle for the bridging chloro ligand is only $71.09(3)^\circ$, compared to $83.1(1)$, $84.9(1)$ and $84.4(1)^\circ$ for the triple chloro-bridged complex $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu_2\text{-Cl})_3]\text{PF}_6$ (Pandey *et al.*, 1999). This difference in bridging angles is due to the shorter Ru–Ru distance in (I) [$2.8256(4) \text{ \AA}$] compared

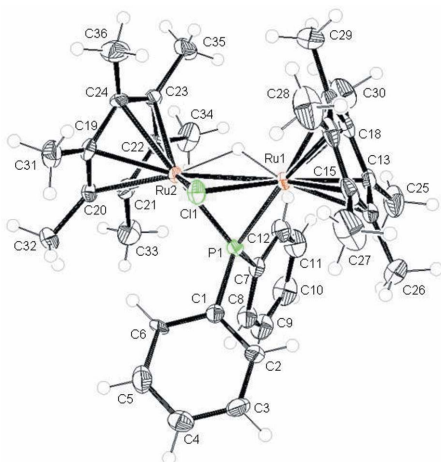


Figure 1

The structure of the cation of (I) (ORTEP-3; Farrugia, 1997). The tetrafluoroborate anion has been omitted for clarity. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

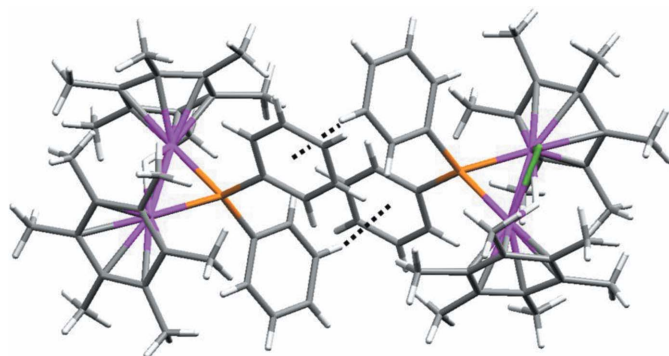


Figure 2

T-shaped π -stacking interactions (dashed lines) between two neighbouring cations of (I) (MERCURY; Bruno *et al.*, 2002).

to that found in $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu_2\text{-Cl})_3]\text{PF}_6$ [3.277 (1) Å]. The Ru–Ru distance is in accordance with a single metal–metal bond and is comparable to that in $[(\eta^6\text{-}p\text{-cymene})_2\text{Ru}_2(\mu_2\text{-S}_2\text{fc})(\mu_2\text{-H})_2]\text{CF}_3\text{SO}_3$ [2.7698 (7) Å; Takemoto *et al.*, 2000]. The presence of diphenylphosphido- and chloro-bridging ligands forces the arene–Ru–Ru–arene unit to adopt a distorted geometry. The two C_6Me_6 ligands are not parallel to each other, the angle between the C_6Me_6 planes being 46.78 (8)°. Selected bond lengths and angles are listed in Table 1.

The two phenyl rings interact weakly through T-shaped π -stacking interactions with the phenyl rings of a neighbouring cation. The symmetrical C–H...centroid distances are 3.7 Å with C–H...centroid angles of 162.9°. Thus, in the solid state a compact dicationic unit is generated (Fig. 2).

Experimental

A brown solution of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-PPh}_2)]\text{BF}_4$ (10 mg, 0.012 mmol) in CDCl_3 (1 ml) was left to stand for two weeks. *n*-Hexane was added to the resulting red solution and a dark solid precipitated. This was filtered off, washed with hexane and then dissolved in dichloromethane. After filtration through Celite, the solvent was evaporated to give (I) (6 mg, 0.008 mmol) in 60% yield.

Dark-red crystals suitable for single-crystal X-ray analysis were obtained by the slow evaporation of a chloroform solution. ^1H NMR (200 MHz, *d*₆-acetone, 298 K): 7.7–7.5 (*m*, 6H, H–Ar), 7.47–6.95 (*m*, 2H, H–Ar), 6.93–6.82 (*m*, 2H, H–Ar), 2.19 [s, 36H, $\text{C}_6(\text{CH}_3)_6$], –12.10 [*d*, $^2J(\text{H}, \text{P}) = 40$ Hz, 1H, hydride]. $^{31}\text{P}\{^1\text{H}\}$ NMR (80 MHz, *d*₆-acetone, 298 K): 94.75 [*d*, $^2J(\text{H}, \text{P}) = 40$ Hz]. MS (ESI): *m/z*: 749 [$M^+ + \text{H}$].

Crystal data

$[\text{Ru}_2\text{ClH}(\text{C}_{12}\text{H}_{10}\text{P})(\text{C}_{12}\text{H}_{18})_2]\text{BF}_4$
 $M_r = 835.11$
 Monoclinic, $P2_1/c$
 $a = 13.5299$ (8) Å
 $b = 12.8959$ (12) Å
 $c = 20.6136$ (13) Å
 $\beta = 104.778$ (7)°
 $V = 3477.7$ (5) Å³

$Z = 4$
 $D_x = 1.595$ Mg m^{−3}
 Mo $K\alpha$ radiation
 $\mu = 1.04$ mm^{−1}
 $T = 173$ (2) K
 Block, red
 $0.39 \times 0.14 \times 0.11$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
 $T_{\min} = 0.593$, $T_{\max} = 0.877$

22538 measured reflections
 6613 independent reflections
 4899 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 25.9^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.097$
 $S = 1.02$
 6613 reflections
 422 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.05$ e Å^{−3}
 $\Delta\rho_{\min} = -1.32$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

P1–Ru2	2.3221 (10)	Ru1–Ru2	2.8256 (4)
P1–Ru1	2.3274 (10)	Ru1–H1H	1.57 (5)
Cl1–Ru1	2.4287 (10)	Ru2–H1H	1.67 (5)
Cl1–Ru2	2.4319 (10)		
Ru2–P1–Ru1	74.85 (3)	Ru1–Cl1–Ru2	71.09 (3)

The hydride atom was located in a difference map and refined isotropically. All other H atoms were placed in calculated positions (C–H = 0.93 Å) and treated as riding atoms with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ applied. The highest density is located at 1.42 Å from atom F3, whereas the deepest hole is located at less than 1 Å from atom Ru2.

Data collection: EXPOSE in IPDS Software (Stoe & Cie, 2000); cell refinement: CELL in IPDS Software; data reduction: INTEGRATE in IPDS Software; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and MERCURY (Bruno *et al.*, 2002).

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