

Decacarbonyltetra- μ -hydrido-bis(tricyclohexylphosphine)-tetrahedro-tetraruthenium

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
Disorder in main residue
R factor = 0.027
wR factor = 0.045
Data-to-parameter ratio = 17.2

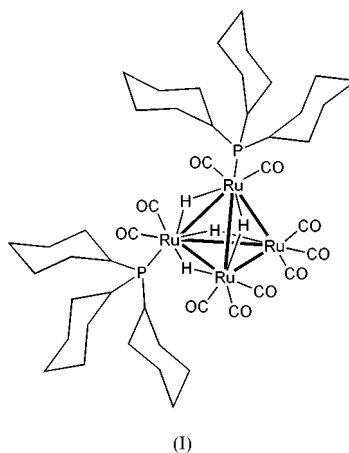
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title cluster, $[\text{Ru}_4\text{H}_4(\text{C}_{18}\text{H}_{33}\text{P})_2(\text{CO})_{10}]$, which contains two tricyclohexylphosphine ligands, has been synthesized and characterized both spectroscopically and crystallographically. The molecular structure is very similar to that of the known triphenylphosphine derivative $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2]$.

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Comment

It has been shown by Bruce *et al.* (1986) that the hydrogenation of $\text{Ru}_3(\text{CO})_{12}$ in the presence of tertiary phosphines [$L = \text{P}(\text{OMe})_3$, PMe_3 , PPh_3 or $\text{PPh}(\text{OMe})_2$] gives a mixture of tetranuclear complexes $[\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{L})_n]$ ($n = 1-3$). From a different starting material, $[\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3]$ (Süss-Fink *et al.*, 1998), and also by hydrogenation in an autoclave, we have obtained the analogous compound $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PCy}_3)_2]$, (I), which contains two tricyclohexylphosphine (PCy_3) ligands. The ^1H NMR spectrum displays four non-equivalent hydrides, as opposed to the parent cluster, $[\text{H}_4\text{Ru}_4(\text{CO})_{10}[\text{P}(\text{OCH}_3)_3]_2]$, which shows only one hydride resonance (Knox & Kaesz, 1971). The hydride ligands adopt a similar arrangement to that observed for $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PH}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (Shapley & Richter, 1977).



The molecular structure of (I) (Fig. 1) was confirmed by single-crystal X-ray analysis. The geometry of (I) consists of an asymmetric Ru_4 tetrahedral core, with four long metal-metal distances and two shorter ones. The four hydrido ligands bridge the long $\text{Ru}-\text{Ru}$ bonds, as suggested for $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2]$ (Wilson *et al.*, 1978; Sasvári *et al.*, 1979). The metal-metal distances (long $\text{Ru}-\text{Ru}$, average 3.01 \AA ; short 2.79 \AA) are slightly longer than those in $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2]$ (long 2.97 \AA ; short 2.77 \AA) and in $[\text{H}_4\text{Ru}_4(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$ (long 2.973 \AA ; short 2.792 \AA)

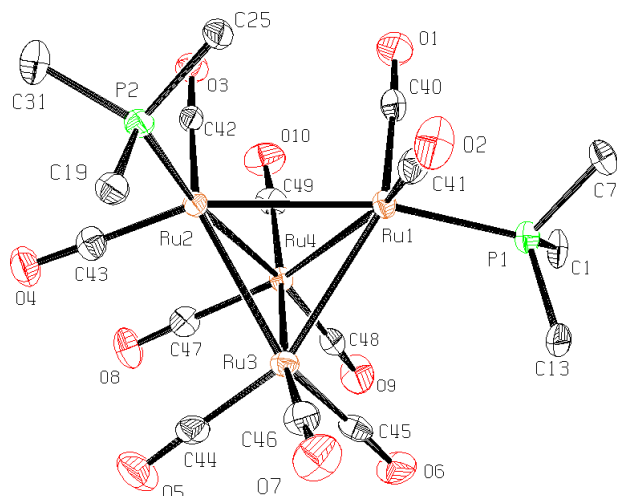


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. The cyclohexyl groups and H atoms have been omitted for clarity.

(Aime *et al.*, 1995). The phosphine ligands are coordinated to Ru1 and Ru2 with Ru–P distances of 2.389 (1) and 2.382 (1) Å, respectively. The P1–Ru1–Ru2–P2 torsion angle is 143.6 (1)°. All the carbonyl groups adopt a staggered conformation with respect to the metal edges. The carbonyl groups opposite to the unbridged Ru–Ru bonds (C46 and C48) show longer Ru–C distances (average 1.913 Å) than those opposite to bridged Ru–Ru bonds (average 1.878 Å). Otherwise no significant difference was observed in the carbonyl envelopes of the three analogous clusters.

Experimental

A solution of $[\text{H}_2\text{Ru}_3(\text{CO})_6(\text{PCy}_3)_3]$ (Süss-Fink *et al.*, 1998) (127 mg, 0.1 mmol) in degassed cyclohexane (40 ml) was placed in a stainless-steel autoclave. After purging with hydrogen, the autoclave was pressurized with hydrogen (30 bar) and heated to 373 K. After 18 h, the autoclave was placed in an ice-bath and the pressure released. The solution was evaporated to dryness and the brown residue dissolved in dichloromethane (3 ml) before being chromatographed on a silica gel (100 GF254, Merck) column, using a mixture of hexane– CH_2Cl_2 (4:1) as eluant. The major red fraction gave $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{PCy}_3)_2]$ in 30% yield. ^1H NMR (200 MHz, CDCl_3): δ –19.6 (s, 1H), –18.0 (s, 1H), –17.1 (s, 1H), –15.7 (s, 1H), 1.25–2.10 (m, 66H); ^{31}P NMR (200 MHz, CDCl_3): δ 57.3 (s, 1P), 53.2 (s, 1P). IR (cyclohexane, cm^{-1} , CO): 2069 (w), 2062 (sh), 2022 (vs), 2003 (w), 1993 (s), 1982 (m), 1971 (w), 1966 (w). MS (ESI, m/z): 1248.0 Analysis calculated for $\text{C}_{46}\text{H}_{70}\text{O}_{10}\text{P}_2\text{Ru}_4$: C 44.23, H 5.65%; found: C 43.66, H 5.62%. Red crystals of compound (I) were obtained at room temperature by slow evaporation of a CH_3OH – CH_2Cl_2 (3:7) solution.

Crystal data

$[\text{Ru}_4\text{H}_4(\text{C}_{18}\text{H}_{33}\text{P})_2(\text{CO})_{10}]$
 $M_r = 1249.24$
 Monoclinic, $P2_1/c$
 $a = 12.461$ (5) Å
 $b = 23.934$ (5) Å
 $c = 18.541$ (5) Å
 $\beta = 96.545$ (5)°
 $V = 5494$ (3) Å³
 $Z = 4$

$D_x = 1.510$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 7997 reflections
 $\theta = 2.0$ – 25.9°
 $\mu = 1.19$ mm^{-1}
 $T = 153$ (2) K
 Block, red
 $0.30 \times 0.30 \times 0.12$ mm

Data collection

Stoe & Cie IPDS diffractometer
 φ scans
 Absorption correction: refined from ΔF (Walker & Stuart, 1983)
 $T_{\min} = 0.641$, $T_{\max} = 0.895$
 38794 measured reflections
 10053 independent reflections

6046 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\max} = 25.9^\circ$
 $h = -14 \rightarrow 15$
 $k = -29 \rightarrow 29$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.045$
 $S = 0.75$
 10053 reflections
 586 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0085P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1–Ru1	2.3894 (12)	Ru1–Ru2	3.0484 (12)
P2–Ru2	2.3824 (11)	Ru2–Ru4	2.7977 (6)
Ru1–Ru4	3.0031 (9)	Ru2–Ru3	2.9600 (7)
Ru1–Ru3	3.0267 (7)	Ru3–Ru4	2.7824 (8)
P1–Ru1–Ru4	113.69 (3)	P2–Ru2–Ru1	107.43 (3)
P1–Ru1–Ru3	109.62 (3)	Ru4–Ru2–Ru1	61.642 (11)
Ru4–Ru1–Ru3	54.960 (18)	Ru3–Ru2–Ru1	60.475 (14)
P1–Ru1–Ru2	166.33 (3)	Ru4–Ru3–Ru2	58.216 (12)
Ru4–Ru1–Ru2	55.07 (2)	Ru4–Ru3–Ru1	62.088 (18)
Ru3–Ru1–Ru2	58.316 (16)	Ru2–Ru3–Ru1	61.21 (2)
P2–Ru2–Ru4	169.05 (3)	Ru3–Ru4–Ru2	64.070 (18)
P2–Ru2–Ru3	118.85 (3)	Ru3–Ru4–Ru1	62.952 (13)
Ru4–Ru2–Ru3	57.714 (18)	Ru2–Ru4–Ru1	63.29 (2)

The hydride ions were located in a difference Fourier map and their positions fixed, while the remaining H atoms were included in calculated positions and treated as riding atoms. One cyclohexyl group has been treated as disordered over two sites (C34–C36), with partial occupancy factors of 0.5.

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, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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