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A cluster containing a pyrazole ligand: $[Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3H_3)(CO)_{10}]$

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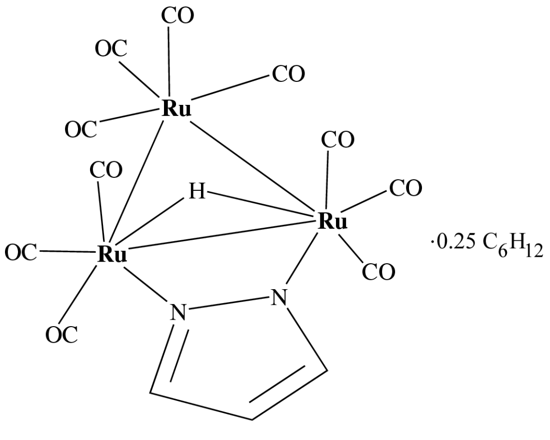
Key indicators
Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.022 Å
R factor = 0.041
wR factor = 0.107
Data-to-parameter ratio = 8.9

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

The title cluster decacarbonyl-1κ^4C,2κ^3C,3κ^3C-μ-hydrido-2:3κ^2H:H-μ-pyrazolyl-2:3κ^2N^1:N^2-*triangulo*-triruthenium, (I), $[Ru_3(\mu\text{-}H)(\mu\text{-}C_3H_3N_2)(CO)_{10}]$, which contains a pyrazole ligand, has been synthesized and characterized, both spectroscopically and crystalographically, as a cyclohexane solvate. The molecular structure of (I) is very similar to that of the known dimethylpyrazole derivative $[Ru_3(\mu\text{-}H)\{\mu\text{-}N_2C_3H\text{-}(CH_3)_2\text{-}3,5\}(CO)_{10}]$.

Comment

The parent cluster (I), as well as its derivatives $[Ru_3(\mu\text{-}H)\{\mu\text{-}N_2C_3H(CH_3)_2\text{-}3,5\}(CO)_{10}]$, (II), and $[Ru_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}]$, (III), were first synthesized by Bruce *et al.* (1986) from the reaction of $Ru_3(CO)_{12}$ and the corresponding pyrazole in refluxing cyclohexane. Only the di(trifluoromethyl)pyrazolyl derivative, (III), was obtained in good yield and studied by X-ray diffraction. More recently, Cabeza *et al.* (1995) synthesized (II) by protonation of the anionic cluster $[Ru_3\{\mu\text{-}N_2C_3H(CH_3)_2\text{-}3,5\}(\mu\text{-}CO)_3(CO)_7]^-$, which was synthesized by reaction between 3,5-dimethylpyrazole and the anionic cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ in refluxing tetrahydrofuran. Here were report a new synthetic route and the X-ray crystal structure analysis of (I), which can be obtained in good yield by reaction of potassium dihydrobis(1-pyrazolyl)borate (Trofimenko, 1970) with $Ru_3(CO)_{12}$ in refluxing MeOH.



(I)

The molecular structure of $[Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3H_3)(CO)_{10}]$, (I), was confirmed by single-crystal X-ray analysis. The asymmetric unit comprises two independent molecules of (I) and half a molecule of cyclohexane. Fig. 1 shows only one independent molecule of (I), and significant bond lengths and

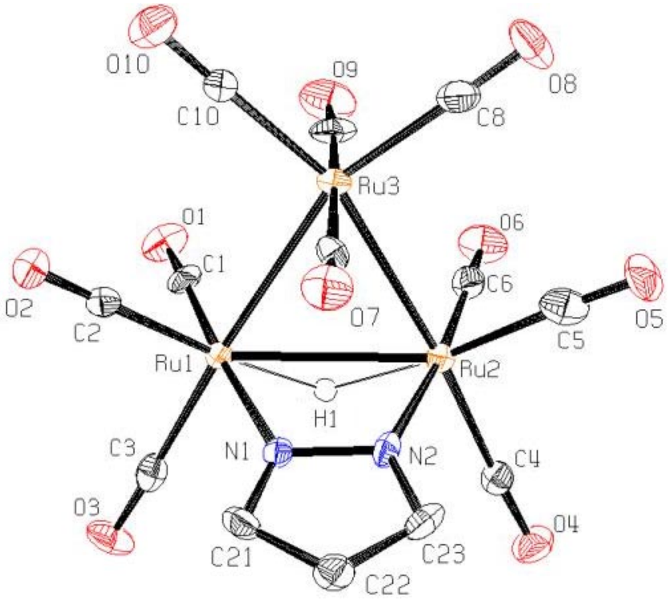


Figure 1
The molecular structure of one molecule of $[Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3H_3)(CO)_{10}]$. Displacement ellipsoids are drawn at the 50% probability level.

angles are given in Table 1. The triruthenium core of (I) consists of an asymmetric Ru_3 triangle; the three metal–metal bonds (average of the two molecules in the asymmetric unit) [2.850 (1), 2.907 (1) and 2.843 (1) Å] are comparable to those observed in (III) [2.849 (1), 2.902 (1) and 2.846 (1) Å]. The pyrazole ligand and the hydrido bridge two Ru atoms in an axial fashion. The Ru—N bond distances [average 2.095 (9) and 2.109 (9) Å] are sligthly shorter than those in (III) [Ru—N 2.146 (3) and 2.137 (3) Å]. The angles between the planar pyrazolyl ligands and the Ru_3 planes are 75.5° for molecule 1 and 76.8° for molecule 2.

Experimental

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and potassium dihydrobis(1-pyrazolyl)borate (58 mg, 0.31 mmol) was dissolved in MeOH (30 ml), under an N_2 atmosphere using standard Schlenk techniques. The solution was refluxed for 20 min, the solution became red–brown, and the characteristic $Ru_3(CO)_{12}$ absorption at ν_{CO} = 2061 cm^{-1} had disappeared. The solution was cooled, concentrated to 1 ml, and chromatographed on a silica-gel (60 GF254, Merck) column, using hexane as eluent, until the first yellow fraction [a mixture of $Ru_3(CO)_{12}$ and $Ru_4H_4(CO)_{12}$ (15%)] separated. Then an orange–red fraction containing (I) was extracted using acetone as eluent. The product was isolated by evaporation of the solvent and recrystallization from cyclohexane, and dried *in vacuo*. Yield: 52%; ^{1}H NMR (200 MHz, ν_{CO}, $CDCl_3$): −13.42 (*s*, 1H), 6.23 (*t*, 1H), 7.24 (*d*, 2H); IR (KBr, cm^{-1}, CO): 2106 (*w*), 2093 (*w*), 2069 (*s*), 2060 (*s*), 2026 (*s*), 2019 (*m*), 2011 (*m*), 1991 (*w*). An orange crystal of compound (I) was mounted at 153 K on a Stoe Image Plate Diffraction System (Stoe & Cie, 2000) using Mo $K\alpha$ graphite-monochromated radiation (Image plate distance 90 mm, φ oscillation scans 0–195°, step $\Delta\varphi$ = 0.7°, 2θ range 2.15–22.5°, d_{max}–d_{min} = 16.00–0.93 Å).

Crystal data

$[Ru_3H(C_3H_3N_2)(CO)_{10}]\cdot 0.25C_6H_{12}$
$M_r = 672.43$
Monoclinic, $I2/a$
$a = 14.2248\ (11)$ Å
$b = 9.1670\ (5)$ Å
$c = 59.834\ (5)$ Å
$\beta = 90.380\ (9)°$
$V = 7802.1\ (10)$ Å^3
$Z = 16$
$D_x = 2.290$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 2.2$–$22.5°$
$\mu = 2.35$ mm^{-1}
$T = 153\ (2)$ K
Block, orange
0.50 × 0.45 × 0.40 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.224$, $T_{max} = 0.251$
18544 measured reflections
4743 independent reflections
4474 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 22.3°$
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 9$
$l = -60 \rightarrow 63$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.107$
$S = 1.36$
4743 reflections
532 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 252.1712P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -0.81$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	2.097 (8)	Ru4—H2	1.55
Ru1—Ru3	2.8544 (12)	Ru5—N4	2.115 (9)
Ru1—Ru2	2.8992 (11)	Ru5—Ru6	2.8357 (12)
Ru1—H1	1.69	Ru5—H2	1.92
Ru2—N2	2.103 (8)	C21—N1	1.336 (13)
Ru2—Ru3	2.8509 (11)	C23—N2	1.356 (13)
Ru2—H1	1.75	C24—N3	1.344 (14)
Ru4—N3	2.094 (9)	C26—N4	1.338 (15)
Ru4—Ru6	2.8457 (12)	N1—N2	1.351 (11)
Ru4—Ru5	2.9124 (12)	N3—N4	1.344 (12)
N1—Ru1—Ru2	68.1 (2)	N4—Ru5—Ru4	67.9 (2)
Ru3—Ru1—Ru2	59.40 (3)	Ru6—Ru5—Ru4	59.33 (3)
N2—Ru2—Ru1	68.6 (2)	Ru5—Ru6—Ru4	61.68 (3)
Ru3—Ru2—Ru1	59.52 (3)	N2—N1—Ru1	112.3 (6)
Ru2—Ru3—Ru1	61.08 (3)	N1—N2—Ru2	110.8 (6)
N3—Ru4—Ru5	68.3 (2)	N4—N3—Ru4	112.2 (6)
Ru6—Ru4—Ru5	58.99 (3)	N3—N4—Ru5	111.5 (7)

The hydride ions were located from difference Fourier maps and fixed in their positions, while the remaining H atoms were included in calculated positions and treated as riding atoms using *SHELXL*97 default parameters.

Data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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