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A new heteronuclear trirutheniumcobalt cluster containing a bulky phosphine ligand, $[CoRu_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{10}(PCy_3)]$

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Key indicators

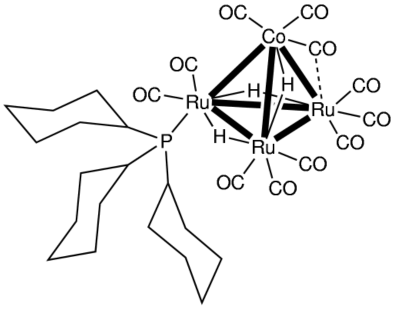
Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.007 Å
R factor = 0.036
wR factor = 0.091
Data-to-parameter ratio = 15.0

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

A mixed tetranuclear cluster of ruthenium and cobalt, namely undecacarbonyl-tri-μ-hydrido-(tricyclohexylphosphine)trirutheniumcobalt, $[CoRu_3H_3(CO)_{11}(C_{18}H_{33}P)]$, has been synthesized by reaction between $Co_2(CO)_8$ and the electron-deficient cluster $[Ru_3H_2(CO)_6(PCy_3)_3]$. The compound was characterized, both spectroscopically and crystallographically. The molecular structure of $[CoRu_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{10}(PCy_3)]$ shows a tetrahedral metal core. The tris(cyclohexyl)phosphine ligand is attached in an axial position to one of the Ru atoms of the basal face.

Comment

Mixed-metal ruthenium–cobalt clusters were first synthesized by Geoffroy and co-workers, by addition of tetracarbonylcobaltate to a dodecacarbonyltriruthenium solution (Steinhardt *et al.*, 1980). Phosphine derivatives of $[CoRu_3H_3(CO)_{12}]$ have not been extensively studied, and we could only find three examples reported in the literature, *viz.* $[CoRu_3H_3(CO)_{10}(dppe)]$ [dppe is bis(diphenylphosphido)methane; Pursiainen & Pakkanen, 1986], $[CoRu_3H_3(CO)_9\{HC(PPh_2)_3\}]$ (Kakkonen *et al.*, 1996*a*) and $[CoRu_3H_3(CO)_9\{HC(PPh_2)_3\}(PMe_2Ph)]$ (Kakkonen *et al.*, 1996*b*). We report here a new synthetic route and the X-ray crystal structure analysis of $[CoRu_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{10}(PCy_3)]$. The product, (I), was only obtained in low yield by reaction of $Co_2(CO)_8$ and the electron-deficient trinuclear ruthenium cluster $[Ru_3H_2(CO)_6(PCy_3)_3]$ (Süss-Fink *et al.*, 1998) in refluxing cyclohexane. The compound crystallizes in the monoclinic crystal system $P2_1/n$, and significant bond lengths and angles are given in Table 1.



(I)

Ten of the eleven carbonyl groups are in terminal positions, the other is in a semibridged environment between the Co and an Ru atom. The metal–carbon distances are Co1—C(19) 1.853 (5) Å and Ru2—C19 2.392 (5) Å, with a Co1—C19—Ru2 angle of 78.0 (2)°. The values compare well with the semi-bridged carbonyl ligands observed in the mixed cluster

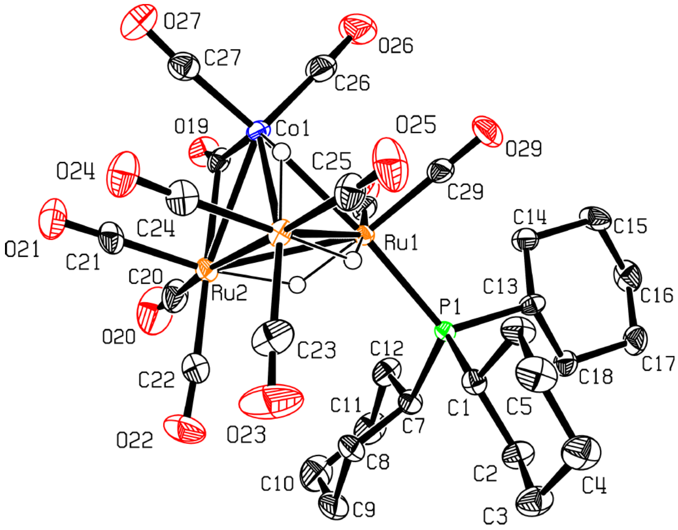


Figure 1
The molecular structure of $[CoRu_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{10}(PCy_3)]$. H atoms (except for the hydrides) have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

$[CoRu_3(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_{10}]$ (Farrugia, 1988). The hydride ligands were located from electron-density maps and fixed. The localization of the hydrides was confirmed by the metal–metal distances, being the longest of the Co—Ru and Ru—Ru bonds, which are Co1—Ru3 2.7592 (6) Å, Ru1—Ru2 2.9408 (5) Å and Ru1—Ru3 2.9240 (5) Å. The phosphine ligand is coordinated in an apical position to Ru1; the distance Ru1—P1 is 2.3651 (9) Å, and the torsion angle P1—Ru1—Ru2—Ru3 is 104.66 (3)°.

Experimental

A mixture of $[Ru_3H_2(CO)_6(PCy_3)_3]$ (200 mg, 0.15 mmol) and $Co_2(CO)_8$ (59 mg, 0.15 mmol) was dissolved in dry tetrahydrofuran, under an N_2 atmosphere, using standard Schlenk techniques. The solution was heated at 363 K for 20 min, whereupon the solution became red–brown and an abundant precipitate was observed. The solution was cooled, filtered and concentrated to a volume of 1 ml, and then chromatographed on a silica-gel (60 GF254, Merck) column, using hexane as eluent. The second band contains the known saturated cluster $[Ru_3(CO)_{11}(PCy_3)]$ in 12% yield. The mixed-metal cluster $[CoRu_3(\mu\text{-}H)_3(\mu\text{-}CO)(CO)_{10}(PCy_3)]$ was recovered from the third band (red–orange). The product was extracted with CH_2Cl_2 and isolated by evaporation of the solvent, recrystallization from acetone/hexane (8/2) at 253 K (yield 3%). ^1H NMR (200 MHz, $CDCl_3$, p.p.m.): −19.30 (*s*, 2H), −16.95 (*s*, 1H), 0.87–2.35 (*m*, 33 H); IR (cyclohexane, cm^{-1}, CO): 2086.5 (*w*), 2068 (*sh*), 2059 (*m*), 2055 (*s*), 2036 (*s*), 2018 (*m*), 2011 (*w*), 2002 (*w*), 1989 (*s*), 1870 (*m*), 1770 (*m*).

Crystal data

$[CoRu_3H_3(CO)_{11}(C_{18}H_{33}P)]$
$M_r = 953.69$
Monoclinic, $P2_1/n$
$a = 9.6492$ (8) Å
$b = 16.4487$ (9) Å
$c = 21.6012$ (17) Å
$\beta = 92.583$ (10)°
$V = 3425.0$ (4) Å^3
$Z = 4$

$D_x = 1.850$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 2.3$–25.9°
$\mu = 1.88$ mm^{-1}
$T = 153$ (2) K
Plate, red
0.75 × 0.45 × 0.10 mm

Data collection

Stoe IPDS diffractometer
φ-oscillation scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{min} = 0.375$, $T_{max} = 0.830$
23765 measured reflections
6430 independent reflections

4807 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.9°$
$h = -11 \rightarrow 11$
$k = -19 \rightarrow 19$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.091$
$S = 0.92$
6430 reflections
430 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 2.87$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C19—O19	1.151 (6)	Ru1—Ru3	2.9240 (5)
C19—Co1	1.853 (5)	Ru1—Ru2	2.9408 (5)
C19—Ru2	2.392 (5)	Ru2—Co1	2.7041 (6)
P1—Ru1	2.3651 (9)	Ru2—Ru3	2.8331 (5)
Ru1—Co1	2.7179 (6)	Ru3—Co1	2.7592 (6)
O19—C19—Co1	153.4 (4)	Ru3—Ru2—Ru1	60.817 (11)
O19—C19—Ru2	128.5 (4)	Co1—Ru3—Ru2	57.817 (14)
Co1—C19—Ru2	78.00 (18)	Co1—Ru3—Ru1	57.052 (13)
P1—Ru1—Co1	173.52 (3)	Ru2—Ru3—Ru1	61.412 (12)
Co1—Ru1—Ru3	58.420 (14)	Ru2—Co1—Ru1	65.690 (15)
Co1—Ru1—Ru2	56.929 (14)	Ru2—Co1—Ru3	62.463 (15)
Ru3—Ru1—Ru2	57.772 (12)	Ru1—Co1—Ru3	64.528 (15)

Atoms Ru3 and Co1 are disordered and occupy the same positions, with an occupancy-factor ratio of 85:15. In a similar manner, the semi-bridged carbonyl (C19—O19), as well as the hydride H3*h*, are disordered and occupy two equivalent sites. The carbonyl groups, especially their O atoms, exhibited a high degree of thermal motion, but only two have been treated as disordered (C22–O22 and C25–O25), with occupancy-factor ratios of 85:15. The hydride ions were located from difference Fourier maps and were fixed in their positions, while the remaining H atoms were included in calculated positions and treated as riding, using *SHELXL*97 default parameters. Atoms having occupancies less than 0.15 were refined isotropically. Residual electron densities greater than 1 e Å^{-3} were observed, located at 1.54 Å from C14, 1.42 Å from C29, 1.85 Å from C15 and 0.53 Å from C13.

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: *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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