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Structure of Nonacarbonyl-tri-μ-hydrido-μ_3-(p-tolylmethylidyne)-*triangulo*-triruthenium, $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9[\mu_3\text{-CC}_6\text{H}_4(p\text{-CH}_3)]$*

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Abstract. $C_{17}H_{10}O_9Ru_3$, $M_r = 661{\cdot}5$, triclinic, $P\bar{1}$, $a = 9{\cdot}617$ (2), $b = 9{\cdot}869$ (2), $c = 11{\cdot}777$ (2) Å, $\alpha = 104{\cdot}57$ (2), $\beta = 91{\cdot}94$ (2), $\gamma = 93{\cdot}22$ (2)°, $V = 1078{\cdot}6$ (4) Å^3, $Z = 2$, $D_x = 2{\cdot}04$ g cm^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu(\text{Mo }K\alpha) = 20{\cdot}7$ cm^{-1}, $F(000) = 632$, $T = 294$ K, $R(F) = 3{\cdot}3\%$, $R(wF) = 3{\cdot}2\%$ for all 2847 unique data, none rejected. The three ruthenium atoms define an equilateral triangle and each is bonded to three terminal carbonyl ligands, two edge-bridging hydrides, and the methylidyne carbon of the C-tolyl group. The three hydride ligands and all but the methyl hydrogens on C(6) were located from a series of difference-Fourier syntheses.

Introduction. As a continuation of recent structural studies on ruthenium carbonyl hydrides (Churchill, Ziller & Keister, 1985; Churchill, Fettinger, Keister, See & Ziller, 1985; Churchill, Fettinger & Keister, 1985), the tri-μ-hydrido complex $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9[\mu_3\text{-CC}_6\text{H}_4(p\text{-CH}_3)]$ has been subjected to a single-crystal X-ray structural analysis.

Experimental. The compound was prepared as described (Keister & Horling, 1980). A suitable parallelepiped crystal of $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CC}_6\text{H}_4\text{-CH}_3)$ with approximate dimensions $0{\cdot}13 \times 0{\cdot}25 \times 0{\cdot}40$ mm was mounted and aligned on the Syntex $P2_1$ automated diffractometer. Determination of unit-cell parameters and the crystal's orientation matrix and data collection [$2\theta = 4{\cdot}5$–$45{\cdot}0°$; $(\sin\theta)/\lambda_{\text{max}} = 0{\cdot}539$ Å^{-1}] were performed as previously described (Churchill, Lashewycz & Rotella, 1977). Three standard reflections were measured after each batch of 97 data; no significant fluctuations or decay were observed. Diffraction data were corrected for absorption (by interpolation in 2θ and φ between a set of close-to-axial ψ scans in which $T_{\text{min}}/T_{\text{max}} = 0{\cdot}801/1{\cdot}000$), averaged to provide a unique data set, corrected for Lorentz and polarization factors and reduced to observed structure factor amplitudes. Any reflection with a net intensity less than zero was assigned an $|F_o|$ value of zero.

The coordinates of the three ruthenium atoms were derived from a three-dimensional Patterson map. The positions of all remaining atoms except the methyl hydrogens on C(6) were located from a series of difference-Fourier syntheses. Full-matrix least-squares refinement of the model led to convergence [$(\Delta/\sigma)_{\text{max}} = 0{\cdot}10$ in final refinement cycle] with $R(F) = 3{\cdot}3\%$, $R(wF) = 3{\cdot}2\%$ and GOF = 1·31 for 290 variables refined against all 2847 unique data [$R(F) = 2{\cdot}3\%$, $R(wF) = 2{\cdot}8\%$ for those 2359 reflections with $|F_o| > 6\sigma(|F_o|)$]. A final difference-Fourier map was 'clean' with $(\Delta\rho)_{\text{max}} = 0{\cdot}26$ e Å^{-3}. Methyl hydrogens were included in calculated positions based on idealized tetrahedral geometry with $d(\text{C—H}) = 0{\cdot}95$ Å (Churchill, 1973). A listing of fractional coordinates and equivalent isotropic thermal parameters is given in Table 1.†

The analytical form of the appropriate neutral-atom scattering factor was corrected for both the real (f') and imaginary (if'') components of anomalous dispersion using the values compiled in *International Tables for X-ray Crystallography* (1974). The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $1/w = (\sigma|F_o|)^2 + (0{\cdot}015|F_o|)^2$.

Discussion. The molecular structure and atomic labelling scheme are shown in Fig. 1. Selected bond lengths and angles are collected in Table 2. There are no abnormally short intermolecular distances.

The $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-C})$ portion of the molecule has approximate C_{3v} symmetry. The three Ru atoms define a triangle of sides 2·837 (1), 2·845 (1) and 2·856 (1) Å. Each Ru atom is linked to two 'equatorial' carbonyl ligands which are *trans* to μ-hydrido ligands and to one 'axial' carbonyl ligand which is *trans* to the μ_3-methylidyne carbon, C(1). Ru—CO(eq.) distances range 1·903 (6)–1·914 (6) Å and are significantly shorter than the Ru—CO(ax.) distances of 1·984 (6)–

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* Ruthenium Carbonyl Hydrides. 11. Part 10: Churchill, Ziller & Keister (1985).

† Lists of structure factors, anisotropic thermal parameters and bond distances and angles within the p-tolyl group have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43341 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final fractional atomic coordinates and isotropic thermal parameters*

E.s.d.'s are given in parentheses.

	x	*y*	*z*	U_{eq}(Å²)
Ru(1)	0·27325 (4)	0·21713 (4)	0·44753 (3)	0·047
Ru(2)	0·07144 (4)	0·24933 (4)	0·27653 (3)	0·050
Ru(3)	0·24712 (4)	0·01998 (4)	0·22409 (3)	0·049
O(11)	0·14773 (49)	0·12674 (53)	0·65931 (41)	0·112
O(12)	0·31654 (50)	0·53081 (47)	0·56043 (40)	0·092
O(13)	0·57517 (42)	0·17308 (49)	0·50830 (38)	0·089
O(21)	0·04229 (48)	0·56115 (47)	0·38209 (41)	0·095
O(22)	−0·23850 (41)	0·16736 (46)	0·30843 (41)	0·090
O(23)	0·03945 (55)	0·28285 (64)	0·02756 (44)	0·127
O(31)	0·24591 (56)	0·00635 (54)	−0·03691 (40)	0·108
O(32)	0·11692 (50)	−0·28177 (46)	0·20305 (42)	0·099
O(33)	0·54186 (44)	−0·07375 (43)	0·23271 (44)	0·092
C(11)	0·19703 (58)	0·15896 (71)	0·58433 (51)	0·069
C(12)	0·30042 (55)	0·41357 (63)	0·52001 (48)	0·063
C(13)	0·46274 (59)	0·19159 (55)	0·48418 (44)	0·059
C(21)	0·05467 (55)	0·44551 (65)	0·34071 (49)	0·067
C(22)	−0·12752 (58)	0·19984 (55)	0·29674 (48)	0·062
C(23)	0·05168 (58)	0·26985 (66)	0·12026 (57)	0·075
C(31)	0·24717 (60)	0·00905 (59)	0·06045 (53)	0·075
C(32)	0·16220 (56)	−0·17138 (62)	0·21186 (48)	0·065
C(33)	0·43385 (61)	−0·03662 (56)	0·22949 (52)	0·067
C(1)	0·28897 (44)	0·24009 (48)	0·27529 (40)	0·046
C(2)	0·39335 (46)	0·32599 (49)	0·22910 (39)	0·048
C(3)	0·50069 (59)	0·27070 (67)	0·16019 (55)	0·069
C(4)	0·59760 (63)	0·35067 (71)	0·11644 (57)	0·082
C(5)	0·59411 (55)	0·49225 (70)	0·14205 (48)	0·069
C(6)	0·70312 (75)	0·57783 (77)	0·09469 (65)	0·103
C(7)	0·49110 (76)	0·55120 (70)	0·20933 (62)	0·080
C(8)	0·38978 (63)	0·47008 (60)	0·25409 (53)	0·068
H(12)	0·0933 (54)	0·2111 (57)	0·4139 (49)	0·09 (1)
H(13)	0·2354 (56)	0·0401 (59)	0·3814 (50)	0·10 (2)
H(23)	0·0627 (70)	0·0380 (75)	0·2274 (61)	0·14 (3)
H(3)	0·498 (5)	0·180 (6)	0·129 (4)	0·06 (2)
H(4)	0·685 (4)	0·335 (3)	0·055 (3)	0·02 (1)
H(7)	0·477 (5)	0·634 (5)	0·235 (4)	0·05 (2)
H(8)	0·317 (5)	0·517 (5)	0·301 (4)	0·04 (1)
H(6*A*)	0·689	0·677	0·119	0·08
H(6*B*)	0·701	0·552	0·010	0·08
H(6*C*)	0·796	0·566	0·122	0·08

For non-hydrogen atoms $U_{eq} = [\frac{1}{3}(B_{11} + B_{22} + B_{33})]/8\pi^2$.

1·990 (6) Å. The H—Ru—CO(eq.) angles lie in the range 167·5 (23)–175·8 (19)°; the refined Ru—H distances are of limited accuracy, ranging from 1·74–2·02 Å. The μ_3-CC$_6$H$_4$(p-CH$_3$) moiety takes up a symmetric capping location with Ru—C(1) distances of 2·099 (4)–2·114 (5) Å (average 2·106 Å). The μ-CC$_6$H$_4$(p-CH$_3$) ligand is associated with longer Ru—C distances than the μ_3-CCl ligand in (μ-H)$_3$Ru$_3$(CO)$_9$(μ_3-CCl), where Ru—C = 2·056 (2)–2·067 (2) Å (average 2·063 Å) (Zhu, Lecomte, Coppens & Keister, 1982), or the μ_3-CCH$_3$ ligand in (μ-H)$_3$Ru$_3$(CO)$_9$(μ_3-CCH$_3$), where Ru—C = 2·078 (12)–2·086 (10) Å (average 2·083 Å) (Sheldrick & Yesinowski, 1975), and has Ru—C distances comparable to those of the μ_3-CCH$_2$CMe$_3$ ligand in (μ-H)$_3$Ru$_3$(CO)$_9$[μ_3-CCH$_2$C(CH$_3$)$_3$], where Ru—C = 2·091 (5)–2·116 (5) Å (average 2·102 Å) (Castiglioni, Gervasio & Sappa, 1981). The trend of increasing Ru—CX bond length [X = Cl < CH$_3$ < C$_6$H$_4$(p-CH$_3$)] parallels the expected decrease in Ru—CX bond strength [*e.g.*, H—CH$_2X$ bond dissociation energy, X = Cl (430 kJ mol^{-1}) > CH$_3$ (410 kJ mol^{-1}) > C$_6$H$_5$ (355 kJ mol^{-1}) (Sanderson, 1976; Weissman & Benson, 1983).

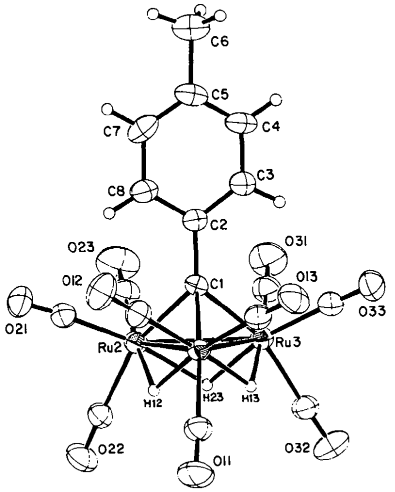

Fig. 1. The molecular structure and atomic labelling.

Table 2. *Bond lengths* (Å) *and angles* (°)

Ru(1)—Ru(2)	2·837 (1)	Ru(1)—C(1)	2·106 (5)
Ru(1)—Ru(3)	2·845 (1)	Ru(2)—C(1)	2·099 (4)
Ru(2)—Ru(3)	2·856 (1)	Ru(3)—C(1)	2·114 (5)
Ru(1)—C(11)	1·990 (6)	C(11)—O(11)	1·122 (8)
Ru(1)—C(12)	1·910 (6)	C(12)—O(12)	1·134 (8)
Ru(1)—C(13)	1·903 (6)	C(13)—O(13)	1·145 (7)
Ru(2)—C(21)	1·911 (6)	C(21)—O(21)	1·137 (8)
Ru(2)—C(22)	1·985 (6)	C(22)—O(22)	1·120 (7)
Ru(2)—C(23)	1·906 (7)	C(23)—O(23)	1·134 (8)
Ru(3)—C(31)	1·903 (6)	C(31)—O(31)	1·140 (8)
Ru(3)—C(32)	1·984 (6)	C(32)—O(32)	1·129 (8)
Ru(3)—C(33)	1·914 (6)	C(33)—O(33)	1·123 (7)
Ru(1)—H(12)	1·76 (5)	Ru(2)—H(23)	2·02 (8)
Ru(1)—H(13)	1·74 (6)	Ru(3)—H(13)	1·82 (6)
Ru(2)—H(12)	1·76 (6)	Ru(3)—H(23)	1·79 (7)
Ru(2)—Ru(1)—Ru(3)	60·34 (1)	Ru(1)—H(12)—Ru(2)	108 (3)
Ru(1)—Ru(2)—Ru(3)	59·98 (1)	Ru(1)—H(13)—Ru(3)	106 (3)
Ru(1)—Ru(3)—Ru(2)	59·69 (1)	Ru(2)—H(23)—Ru(3)	97 (3)
C(11)—Ru(1)—C(12)	97·5 (2)	Ru(1)—C(11)—O(11)	176·6 (5)
C(11)—Ru(1)—C(13)	95·6 (2)	Ru(1)—C(12)—O(12)	178·3 (5)
C(12)—Ru(1)—C(13)	90·8 (2)	Ru(1)—C(13)—O(13)	177·7 (5)
C(21)—Ru(2)—C(22)	93·4 (3)	Ru(2)—C(21)—O(21)	177·6 (5)
C(21)—Ru(2)—C(23)	91·5 (3)	Ru(2)—C(22)—O(22)	177·5 (5)
C(22)—Ru(2)—C(23)	97·8 (3)	Ru(2)—C(23)—O(23)	179·5 (6)
C(31)—Ru(3)—C(32)	97·6 (2)	Ru(3)—C(31)—O(31)	178·0 (6)
C(31)—Ru(3)—C(33)	93·2 (3)	Ru(3)—C(32)—O(32)	178·0 (6)
C(32)—Ru(3)—C(33)	93·6 (2)	Ru(3)—C(33)—O(33)	177·9 (5)
Ru(2)—Ru(1)—C(11)	115·4 (2)		
Ru(2)—Ru(1)—C(12)	94·4 (2)	Ru(2)—Ru(1)—C(1)	47·5 (1)
Ru(2)—Ru(1)—C(13)	147·5 (2)	Ru(3)—Ru(1)—C(1)	47·7 (1)
Ru(3)—Ru(1)—C(11)	118·1 (2)	Ru(1)—Ru(2)—C(1)	47·7 (1)
Ru(3)—Ru(1)—C(12)	142·2 (2)	Ru(3)—Ru(2)—C(1)	47·6 (1)
Ru(3)—Ru(1)—C(13)	97·4 (2)	Ru(1)—Ru(3)—C(1)	47·5 (1)
Ru(1)—Ru(2)—C(21)	96·1 (2)	Ru(2)—Ru(3)—C(1)	47·1 (1)
Ru(1)—Ru(2)—C(22)	118·4 (2)		
Ru(1)—Ru(2)—C(23)	142·3 (2)	Ru(1)—C(1)—C(2)	129·0 (3)
Ru(3)—Ru(2)—C(21)	148·3 (2)	Ru(2)—C(1)—C(2)	129·2 (3)
Ru(3)—Ru(2)—C(22)	115·8 (2)	Ru(3)—C(1)—C(2)	128·1 (3)
Ru(3)—Ru(2)—C(23)	96·4 (2)		
Ru(1)—Ru(3)—C(31)	141·7 (2)	C(13)—Ru(1)—H(12)	170·4 (18)
Ru(1)—Ru(3)—C(32)	119·1 (2)	C(12)—Ru(1)—H(13)	175·8 (19)
Ru(1)—Ru(3)—C(33)	95·0 (2)	C(23)—Ru(2)—H(12)	173·7 (18)
Ru(2)—Ru(3)—C(31)	94·7 (2)	C(21)—Ru(2)—H(23)	170·1 (20)
Ru(2)—Ru(3)—C(32)	118·2 (2)	C(31)—Ru(3)—H(13)	175·3 (18)
Ru(2)—Ru(3)—C(33)	145·9 (2)	C(33)—Ru(3)—H(23)	167·5 (23)

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Structure of 3,4;3′,4′-Bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene–Dichlorocuprate (BEDT-TTF)$CuCl_2$

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Abstract. $C_{10}H_8S_8.CuCl_2$, $M_r = 519\cdot105$, triclinic, $P\bar{1}$, $a = 6\cdot577\,(2)$, $b = 12\cdot154\,(2)$, $c = 5\cdot781\,(1)$ Å, $\alpha = 100\cdot87\,(1)°$, $\beta = 94\cdot74\,(1)°$, $\gamma = 108\cdot58\,(1)°$, $V = 424\cdot4\,(1)$ Å^3, $Z = 1$, $D_x = 2\cdot031$, $D_m = 2\cdot029$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu = 140\cdot45$ cm^{-1}, $F(000) = 259$, $T = 293$ K, $R = 0\cdot036$ for 1586 observed reflections. BEDT-TTF molecules are stacked to form columns along **c** [interplanar distance 3·39 (3) Å]. Shortest contacts between adjacent BEDT-TTF molecules in a column are S···S 3·712 (1) Å. The central C=C bond in BEDT-TTF is 1·382 (6) Å.

Introduction. A new family of organic conductors has recently been synthesized, namely, the charge-transfer salts of 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF): *e.g.* (BEDT-TTF)$_2ClO_4(C_2H_3Cl_3)_{0.5}$ (Saito, Enoki, Toriumi & Inokuchi, 1982). These include the first sulfur-based organic superconductors, (BEDT-TTF)$_2ReO_4$ ($T_c = 2$ K) at 0·4 GPa pressure (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983) and (BEDT-TTF)I_3 ($T_c = 1\cdot5$ K) at ambient pressure (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984). After these, many BEDT-TTF salts have been synthesized in an attempt to obtain an organic superconductor with high critical temperature. Many known BEDT-TTF salts have a composition (BEDT-TTF)$_2X$ or (BEDT-TTF)$_3X_2$, where X is a univalent anion such as PF_6^- (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1983), AsF_6^- (Leung, Beno, Blackman, Coughlin, Miderski, Joss, Crabtree & Williams, 1984), $InBr_4^-$ (Beno, Cox, Williams & Kwak, 1984), ClO_4^- (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1984), I_3^- (Leung, Emge, Beno, Wang & Williams, 1984; Bender, Hennig, Schweitzer, Dietz, Endres & Keller, 1984; Shibaeva, Kaminskii & Yagubskii, 1985) or other polyhalide series. (BEDT-TTF)X(THF)$_{0.5}$ ($X = ReO_4^-$ and IO_4^-; THF = tetrahydrofuran) salts (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1984) form 4:4 salts which consist of four independent complexes in the unit cell.

In the present paper, we report the crystal structure of the 1:1 salt (BEDT-TTF)$CuCl_2$.

Experimental. Crystal prepared by diffusion of BEDT-TTF and $CuCl_2.2H_2O$ in 1,1,2-trichloroethane; black prism $0\cdot50 \times 0\cdot30 \times 0\cdot30$ mm; D_m by flotation; Rigaku automated four-circle diffractometer AFC-5R; cell dimensions from 20 selected reflections with $25 \le \theta \le 31°$; 1585 measured reflections, $2\theta_{\max} = 126\cdot0°$, $-8 \le h \le 8$, $-14 \le k \le 14$, $0 \le l \le 7$, $R_{\rm int}$

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