Fig. 2 shows a stereoscopic view of the unit cell. As can be seen, the packing in the [010] direction is characterized by successive layers of polyanions, centred at 0·25 and 0·75, and cation polyhedra, centred at 0 and 0·5. As analysis has shown, extensive hydrogen bonding within the layers and between them stabilizes the structure.

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References

AHMED, F. R. & PIPPY, M. E. (1970). *NRC Crystallographic Programs for the IBM* 360 *System*. NRC-22, revision June 1970. National Research Council of Canada, Ottawa.

BAUR, W. H. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 129–155.

BAUR, W. H. (1972). *Acta Cryst.* B**28**, 1456–1465.

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

BUCHANAN, D. R. & HARRIS, P. M. (1968). *Acta Cryst.* B**24**, 954–960.

CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* B**38**, 2331–2341.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DEBAERDEMAEKER, T., ARRIETA, J. M. & AMIGO, J. M. (1982). *Acta Cryst.* B**38**, 2465–2468.

DURIF, P. A., AVERBUCH-POUCHOT, M. T. & GUITEL, J. C. (1980). *Acta Cryst.* B**36**, 680–682.

EVANS, H. T. (1966). *Inorg. Chem.* **5**, 967–977.

FANG, J. H. & ROBINSON, P. D. (1976). *Am. Mineral.* **61**, 311–317.

FERRARIS, G., FUESS, H. & JOSWIG, W. (1986). *Acta Cryst.* B**42**, 253–258.

GINDEROW, D. & CESBRON, F. (1979). *Acta Cryst.* B**35**, 2499–2502.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 557. Ithaca, NY: Cornell Univ. Press.

RIGOTTI, G., LAVAT, A. E., ESCOBAR, M. E. & BARAN, E. J. (1983). *Z. Anorg. Allg. Chem.* **501**, 184–190.

RIVERO, B. E., PUNTE, G., RIGOTTI, G. & NAVAZA, A. (1985). *Acta Cryst.* C**41**, 817–820.

RIVERO, B. E., RIGOTTI, G., PUNTE, G. & NAVAZA, A. (1984). *Acta Cryst.* C**40**, 715–718.

SAF'YANOV, YU. N. & BELOV, N. V. (1976). *Dokl. Akad. Nauk SSSR*, **227**, 1112–1115.

SAF'YANOV, YU. N., KUZ'MIN, E. A. & BELOV, N. V. (1978*a*). *Kristallografiya*, **23**, 697–702.

SAF'YANOV, YU. N., KUZ'MIN, E. A. & BELOV, N. V. (1978*b*). *Dokl. Akad. Nauk SSSR*, **242**, 603–605.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SWALLOW, A. G., AHMED, F. R. & BARNES, W. H. (1966). *Acta Cryst.* **21**, 397–405.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., pp. 549–550. Oxford: Clarendon Press.

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Structure of 1,2;1,3;1,4-Tri-μ-carbonyl-1,2,2,2,3,3,3,4,4,4-decacarbonyl-2,3-μ-hydrido-*tetrahedro*-cobalttriruthenium

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Abstract. [CoRu$_3$(μ-H)(μ-CO)$_3$(CO)$_{10}$], $M_r = 727\cdot3$, monoclinic, $P2_1/n$, $a = 8\cdot486\,(1)$, $b = 15\cdot164\,(5)$, $c = 15\cdot688\,(1)$ Å, $\beta = 105\cdot92\,(1)^\circ$, $V = 1941\cdot3\,(7)$ Å^3, $Z = 4$, $D_x = 2\cdot49$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 31\cdot5$ cm^{-1}, $F(000) = 1368$, $T = 298$ K, $R = 0\cdot0179$ for 2782 observed unique reflections. The directly observed hydrido ligand bridges an Ru—Ru edge [Ru—H 1·76 (4), 1·73 (4) Å]. The carbonyl ligand polytope with three bridging carbonyls bonded to cobalt is broadly similar to that found in the precursor anion [CoRu$_3$(μ-CO)$_3$(CO)$_{10}$]$^-$, though the unusual skewed C_3 arrangement is not observed in the title complex.

Introduction. The isolobal relationship between the AuPR_3 unit and the H atom (Evans & Mingos, 1982; Lauher & Wald, 1981) has led to the suggestion that the easily determined position of the former moiety in transition-metal cluster compounds may allow prediction of the H-atom geometry in corresponding hydrido analogues (Lauher & Wald, 1981). This analogy becomes unreliable when more than one AuPR_3 unit is present owing to Au—Au bond formation (Braunstein & Rose, 1985; Hall & Mingos, 1984). From spectroscopic evidence it was proposed that the hydrido ligand in [HCoRu$_3$(CO)$_{13}$] (1) bridged the Ru$_3$ face (Steinhardt, Gladfelter, Harley, Fox & Geoffroy, 1980), while a recent X-ray study on [CoRu$_3$(μ_3-AuPPh$_3$)(μ-CO)$_3$(CO)$_{10}$] (Bruce & Nicholson, 1984) revealed the AuPPh$_3$ unit capping a CoRu$_2$ face. Our interest in the use of monohydrido cluster complexes as precursors for the synthesis of Hg-bridged compounds (Farrugia, 1987) prompted an examination of the structure of (1).

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Experimental. Prepared from modification of literature method (Steinhardt *et al.*, 1980) by treatment of $[\mathrm{N(PPh_3)_2}][\mathrm{CoRu_3(CO)_{13}}]$ with $\mathrm{HBF_4.Et_2O}$. Red prisms from hexane solution: crystal dimensions 0·2 × 0·3 × 0·3 mm; systematic absences: $h+l=2n+1$ in $h0l$; $k=2n+1$ in $0k0$; Enraf–Nonius CAD-4F diffractometer; graphite monochromator; $\theta/2\theta$ scan mode; cell parameters refined by least-squares methods on basis of 25 independent θ values, $11<\theta<13°$; intensities measured to $\theta=25·0°$ over range of hkl 0 to 10, 0 to 18, −18 to 18 and to $\theta=20·0°$ over hkl range 0 to 8, −14 to 0, −14 to 14; $4\bar{2}\bar{7}$, $\bar{1}\bar{1}8$, $3\bar{7}\bar{2}$ measured every 2 h with 0·8% decay over 106 h data collection; 5854 reflections measured, 3397 independent data with 2782 having $I>3·0\sigma(I)$ considered observed and used in structure determination and refinement; R_{int} before absorption correction 0·033, after correction 0·020; corrected for Lorentz–polarization, absorption (*DIFABS*; Walker & Stuart, 1983) and extinction (Larson, 1970); solved by direct methods (*MITHRIL*; Gilmore, 1984) and subsequent full-matrix least squares; anisotropic thermal parameters for all non-H atoms; H atom located as strongest remaining feature (0·57 e Å^{-3}) in difference Fourier map, and subject to unrestricted refinement; $\sum w(F_o-F_c)^2$ minimized with $w=[\sigma^2(F_o)]^{-1}$; max. Δ/σ 0·013, av. 0·001; $(\Delta\rho)_{\max}$ + 0·37, $(\Delta\rho)_{\min}$ − 0·34 e Å^{-3} in vicinity of metal atoms; $R=0·0179$, $wR=0·0224$; R (wR) = 0·0293 (0·0240) for all data; $S=1·49$; atomic scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974); calculations carried out on a Gould-SEL 32/27 minicomputer using the *GX* suite of programs (Mallinson & Muir, 1985).

Table 1. *Final positional parameters (fractional coordinates), with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters,* U_{eq} (Å^2)

$$U_{\mathrm{eq}}=\tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru(1)	0·27393 (3)	0·42657 (2)	0·69783 (2)	0·030
Ru(2)	0·53987 (3)	0·52520 (2)	0·79822 (2)	0·030
Ru(3)	0·53200 (3)	0·33212 (2)	0·81786 (2)	0·033
Co	0·56803 (5)	0·40741 (3)	0·67368 (3)	0·034
C(1)	0·1482 (4)	0·3276 (2)	0·6407 (2)	0·045
C(2)	0·1364 (4)	0·5171 (2)	0·6299 (2)	0·042
C(3)	0·1552 (4)	0·4365 (2)	0·7843 (2)	0·047
C(4)	0·4451 (4)	0·6223 (2)	0·7257 (2)	0·042
C(5)	0·4206 (4)	0·5490 (2)	0·8824 (2)	0·042
C(6)	0·7386 (5)	0·5833 (2)	0·8669 (2)	0·052
C(7)	0·7111 (5)	0·2822 (3)	0·9096 (3)	0·058
C(8)	0·4451 (4)	0·2266 (2)	0·7588 (2)	0·044
C(9)	0·3932 (4)	0·3291 (2)	0·8956 (2)	0·046
C(10)	0·3766 (4)	0·4362 (2)	0·5853 (2)	0·044
C(11)	0·7148 (4)	0·3282 (2)	0·7452 (2)	0·052
C(12)	0·6899 (4)	0·5083 (2)	0·6999 (2)	0·042
C(13)	0·6464 (5)	0·3706 (3)	0·5861 (2)	0·061
O(1)	0·0722 (3)	0·2701 (2)	0·6060 (2)	0·071
O(2)	0·0579 (3)	0·5690 (2)	0·5874 (2)	0·058
O(3)	0·0738 (3)	0·4451 (2)	0·8301 (2)	0·073
O(4)	0·3861 (3)	0·6802 (2)	0·6823 (2)	0·062
O(5)	0·3562 (3)	0·5648 (2)	0·9350 (2)	0·060
O(6)	0·8510 (4)	0·6187 (2)	0·9052 (2)	0·090
O(7)	0·8138 (4)	0·2525 (2)	0·9624 (2)	0·097
O(8)	0·3971 (3)	0·1635 (2)	0·7216 (2)	0·063
O(9)	0·3211 (3)	0·3233 (2)	0·9466 (2)	0·068
O(10)	0·3269 (3)	0·4532 (2)	0·5117 (2)	0·078
O(11)	0·8360 (4)	0·2910 (2)	0·7514 (2)	0·089
O(12)	0·7892 (3)	0·5518 (2)	0·6849 (2)	0·067
O(13)	0·6975 (4)	0·3472 (2)	0·5309 (2)	0·105
H	0·614 (6)	0·431 (3)	0·863 (3)	0·10 (2)

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Ru(1)–Ru(2)	2·8036 (4)	Co–Ru(1)	2·6411 (5)
Ru(1)–Ru(3)	2·8515 (4)	Co–Ru(2)	2·7057 (5)
Ru(2)–Ru(3)	2·9467 (4)	Co–Ru(3)	2·6254 (5)
Ru(1)–C(1)	1·916 (4)	Ru(3)–C(7)	1·938 (4)
Ru(1)–C(2)	1·924 (3)	Ru(3)–C(8)	1·894 (4)
Ru(1)–C(3)	1·905 (4)	Ru(3)–C(9)	1·914 (4)
Ru(2)–C(4)	1·899 (3)	Co–C(10)	1·876 (3)
Ru(2)–C(5)	1·906 (3)	Co–C(11)	1·867 (4)
Ru(2)–C(6)	1·945 (4)	Co–C(12)	1·829 (3)
Ru(2)–H	1·76 (4)	Co–C(13)	1·773 (4)
Ru(3)–H	1·73 (4)		
Ru(1)–C(10)	2·177 (3)	Mean C–O(terminal)	1·130 [1]
Ru(2)–C(12)	2·268 (3)	Mean C–O(bridging)	1·148 [3]
Ru(3)–C(11)	2·163 (4)		
Ru(1)–Co–C(13)	135·7 (2)	C(10)–Co–C(13)	86·2 (2)
Ru(2)–Co–C(13)	153·3 (2)	C(11)–Co–C(13)	86·2 (2)
Ru(3)–Co–C(13)	133·5 (2)	C(12)–Co–C(13)	97·4 (2)

Discussion. Final positional parameters are given in Table 1, with selected bond distances and angles in Table 2.* The atomic labelling scheme is shown in Fig.

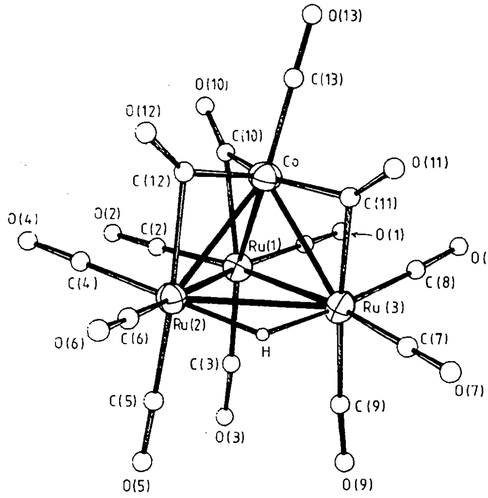

Fig. 1. Molecular structure of complex (1).

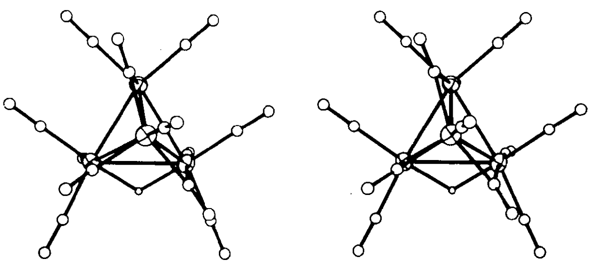

Fig. 2. Stereoview of complex (1).

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* Lists of structure factors, anisotropic thermal parameters for all non-H atoms, a complete listing of bond lengths and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44454 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1. A stereoview in Fig. 2 shows that complex (1) possesses no symmetry element since the Co—C(13) axis is tilted 13·2° from the normal to the Ru_3 plane, away from Ru(2). (1) may be viewed as constructed from the fragments '$Co(CO)_4$' and '$Ru_3(\mu\text{-H})(CO)_9$' each of which possess idealized C_s symmetry. For the '$Co(CO)_4$' fragment this mirror plane comprises Co, C(12), O(12), C(13), O(13), whilst for '$Ru_3(\mu\text{-H})(CO)_9$' the mirror plane contains Ru(1), H, C(3), O(3). Within complex (1), however, these fragment mirror planes are not coincident, but are rotated relative to each other by 57·8°. The bridging carbonyl ligands do not show the skewed C_3 arrangement found in the precursor anion $[CoRu_3(\mu\text{-CO})_3(CO)_{10}]^-$ (Steinhardt *et al.*, 1980), but approximately eclipse the Co—Ru vectors.

The hydride bridges the longest Ru—Ru bond [Ru(2)—Ru(3)] and the Ru—H distances compare favourably with the mean value of 1·79 (1) Å found over a range of structures containing the $\overline{\mathrm{Ru}(\mu\text{-H})\mathrm{Ru}}$ moiety (Teller & Bau, 1981). The μ_2 bonding mode found for the hydride ligand in (1) contrasts with the asymmetric μ_3 geometry of the $AuPPh_3$ unit in $[CoRu_3(\mu_3\text{-}AuPPh_3)(\mu\text{-CO})_3(CO)_{10}]$ (Bruce & Nicholson, 1984), where this ligand bridges a $CoRu_2$ face. These results thus provide further evidence that the isolobal relationship between H and $AuPPh_3$ cannot reliably be used to infer hydride ligand positions from known stereochemistry in phosphineaurio derivatives.

Complex (1) appears to be isomorphous and isostructural to the osmium analogue $[CoOs_3(\mu\text{-H})(\mu\text{-CO})_3(CO)_{10}]$ (Raithby, personal communication).

References

Braunstein, P. & Rose, J. (1985). *Gold Bull.* **18**, 17–30.
Bruce, M. I. & Nicholson, B. K. (1984). *Organometallics*, **3**, 101–108.
Evans, D. G. & Mingos, D. M. P. (1982). *J. Organomet. Chem.* **232**, 171–191.
Farrugia, L. J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 147–149.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
Hall, K. P. & Mingos, D. M. P. (1984). *Prog. Inorg. Chem.* **32**, 237–325.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, p. 291. Copenhagen: Munksgaard.
Lauher, J. W. & Wald, K. (1981). *J. Am. Chem. Soc.* **103**, 7648–7650.
Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Steinhardt, P. C., Gladfelter, W. L., Harley, A. D., Fox, J. R. & Geoffroy, G. L. (1980). *Inorg. Chem.* **19**, 332–339.
Teller, R. G. & Bau, R. (1981). *Struct. Bonding (Berlin)*, **44**, 1–82.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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$ErRh_3Si_2$ and Isotypes with an Orthorhombic Deformation Superstructure of the $CeCo_3B_2$ Type

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Abstract. $M_r = 532{\cdot}1$, $oI24$, $Imma$, $a = 7{\cdot}098\ (8)$, $b = 9{\cdot}519\ (1)$, $c = 5{\cdot}500\ (1)$ Å, $V = 371{\cdot}6\ (5)$ Å^3, $Z = 4$, $D_x = 9{\cdot}51$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 36{\cdot}3$ mm^{-1}, $F(000) = 924$, $T = 293$ K, $R = 0{\cdot}047$ for 291 independent reflections. YRh_3Si_2, $LaRh_3Si_2$ and $NdRh_3Si_2$ are isotypic with $ErRh_3Si_2$. The $ErRh_3Si_2$ structure represents a new deformation superstructure of the hexagonal $CeCo_3B_2$ (ternary $CaCu_5$) structure where $a \simeq 2c[CeCo_3B_2]$, $b \simeq 3^{1/2}a[CeCo_3B_2]$ and $c \simeq a[CeCo_3B_2]$. As compared with the parent type this deformation variant is characterized by zigzag chains of rare-earth atoms and by pairs of Si atoms. The structure of $ErRh_3Si_2$ is further compared with four other deformation variants of the $CeCo_3B_2$ type and a review of structure types related to $CaCu_5$ is presented.

Introduction. $ErRh_3Si_2$ and eight other RRh_3Si_2 compounds with R = Y, La, Nd, Sm, Gd, Tb, Dy and Ho were originally reported to crystallize with the $CeCo_3B_2$-type structure by Chevalier, Cole, Lejay & Etourneau (1981) who also investigated their magnetic properties and superconducting behaviour. However, additional lines were present on all our powder X-ray diffraction films of samples containing $ErRh_3Si_2$. We shall show here that $ErRh_3Si_2$ and at least three other compounds reported by Chevalier *et al.* (and probably

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