direct methods (*NRCVAX*). In the final least-squares refinement (*NRCVAX*), the phenyl and methyl H atoms were constrained to idealized (C—H = 0.95 Å) positions (the orientation of the methyl group had been shown previously by a difference map), and the amide H atoms were fixed at difference-map positions. All H atoms were assigned isotropic *U* values of 0.01 plus the *U* value of the attached N or C atom.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# A Redetermination of the X-ray Structure of the Hexanuclear Mixed-Metal Cluster $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$

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## Abstract

The X-ray structure analysis shows that the octahedral hexanuclear mixed-metal cluster $\mu_6$-carbido-$\mu$-carbonyl-4:5$\kappa^2C$-tridecacarbonyl-1$\kappa^3C$,2$\kappa^3C$,3$\kappa^3C$,4$\kappa^2C$,5$\kappa^2C$-[6($\eta^5$)-pentamethylcyclopentadienyl]-*octahedro*-pentarutheniumrhodium(4 *Rh*—*Ru*)(8 *Ru*—*Ru*) $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$, encapsulating a C atom, has Ru—Ru bond lengths in the range 2.813 (1)–2.959 (1) and Ru—Rh bond lengths of 2.825 (1)–2.895 (1) Å. The pentamethylcyclopentadienyl ligand is bound in a terminal fashion to the Rh atom. Of the fourteen carbonyl groups, one is bridging, two semi-bridging and 11 adopt essentially terminal positions.

## Comment

A recent report has shown that treatment of the salt $[N(PPh_3)_2][Ru_5C(CO)_{14}]$ with an equivalent amount of $[Rh(C_5Me_5)(NCMe)_3][BF_4]_2$, under ambient conditions, affords the compound $[Ru_5Rh(\mu_6\text{-}C)(CO)_{13}(\mu\text{-}CO)(\eta^5\text{-}C_{10}H_{15})]$, (1), in *ca* 60% yield. X-ray analysis on the only available crystals of this cluster has established the overall structure, but as a result of poor diffraction the e.s.d.'s assigned to all parameters are relatively high, limiting detailed discussion of the cluster geometry (Bailey *et al.*, 1993). In our recent investigations of the reactivity of cluster (1), we have been able to synthesize this compound in *ca* 75% yield by reacting the carbonylate ion with the rhodium salt $[Rh(C_5Me_5)(NCMe)_3][SbF_6]_2$ (Adatia *et al.*, 1993). Excellent crystals were obtained for the hexanuclear cluster (1) and this allowed the redetermination of its solid-state structure to be carried out with greater precision.

The overall molecular geometry established for the mixed-metal cluster (1) is shown in Fig. 1 and is similar to that reported by Bailey *et al.* (1993). The metal-core geometry established for (1) may be compared with the metal frameworks in the homonuclear analogue $[Ru_6C(CO)_{16}]^{2-}$ (Johnson *et al.*, 1980) and the arene derivatives $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ (arene $= C_6H_3Me_3$ and $C_6H_5Me$) (Mason & Robinson, 1968; Farrugia, 1988). The Ru—Ru distances in (1) [2.813 (1)–2.959 (1) Å] are similar in range to those attained from the previous X-ray study [2.815 (5)–2.957 (5) Å], but the mean Ru—Ru bond length of 2.899 (1) Å obtained from the current study is 0.012 (2) Å shorter than that obtained earlier (Bailey *et al.*, 1993). Interestingly, the mean Ru—Ru distance in (1) closely resembles that in the homonuclear analogue $[Ru_6C(CO)_{16}]^{2-}$ [2.891 (3) Å (Johnson *et al.*, 1980)]. The shortest Ru—Ru bond length of 2.813 (1) Å in (1) is that assigned to Ru(3)—Ru(5), the metal–metal vector asymmetrically bridged by the carbonyl group CO(35), (Fig. 1). Similar shortening of Ru—Ru bonds bridged by CO ligands is also a structural feature present in the carbido dianion $[Ru_6C(CO)_{16}]^{2-}$, where the four Ru—Ru edges of the metal octahedron bridged by carbonyl groups are notably shorter than unbridged bonds.

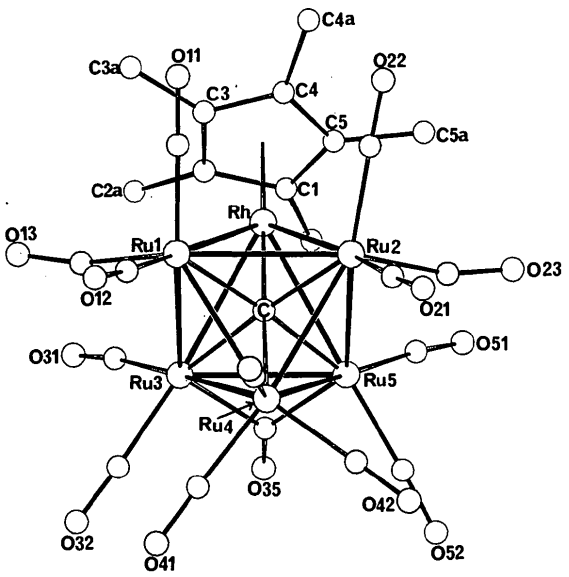

Fig. 1. The molecular structure of the hexanuclear cluster (1) showing the crystallographic numbering scheme. The C atom of each carbonyl group has the same numbering as the O atom.

In the title compound the longest Ru—Rh bond length is 2.895 (1) Å, compared to 2.903 (5) Å reported previously (Bailey *et al.*, 1993). The two longest Ru—Rh bonds in (1) are from atoms Ru(3) and Ru(5) bridged by the carbonyl ligand CO(35). The overall range of Ru—Rh distances [2.825 (1)–2.895 (1) Å] is significantly longer than that observed in the tetranuclear clusters [$Ru_3RhH_3(CO)_{12}$] [2.757 (3)–2.762 (3) Å] and [$Ru_2Rh_2H_2(CO)_{12}$] [2.756 (3)–2.768 (3) Å] (Pursianinen & Pakkanen, 1989).

The range of metal–carbide distances in (1) shows a reasonable similarity in both structure determinations [1.944 (7)–2.080 (7) Å with mean of 2.042 (7) Å, and 1.93 (3)–2.09 (3) Å with mean of 2.04 (3) Å]. Although the octahedral metal core in the title compound includes an Rh atom, the mean Ru—C distance is only slightly shorter than that observed in the homonuclear analogue [$Ru_6C(CO)_{16}]^{2-}$ [2.05 (3) Å (Johnson *et al.*, 1980)] and the arene derivatives [$Ru_6C(CO)_{14}(\eta^6\text{-arene})$] [2.05 (4) Å (Mason & Robinson, 1968; Farrugia, 1988)].

The pentamethylcyclopentadienyl ligand coordinates asymmetrically in an $\eta^5$ mode to the Rh atom [Rh—C(Cp) 2.217 (9)–2.277 (9) Å] with the centroid of the ring being 1.888 (9) Å from the Rh atom. This mode of bonding for the $\eta^5$-$C_5Me_5$ ligand is observed in the mixed-metal cluster [$Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$], in which the $C_5Me_5$ ligand is bound solely to the Rh atom and the two $C_5H_5$ groups coordinate to two Ru atoms of the octahedral metal core (Bailey *et al.*, 1993). In (1), the mean Rh—C(Cp) [2.244 (9) Å], C—C [1.427 (13) Å] and C—C(Me) [1.509 (14) Å] distances associated with $\eta^5$-$C_5Me_5$ show no significant variation from those found in the previous X-ray study and closely resemble the averages reported for the octahedral carbido cluster [$Ru_5Rh(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$] (Bailey *et al.*, 1993).

The carbonyl distribution in (1) consists of thirteen of the fourteen carbonyl groups adopting terminal positions [Ru—C—O 163 (1)–177 (1)°], with the ligand CO(35) asymmetrically bridging the Ru(3)—Ru(5) bond [Ru(3)—C—O(35) 134 (1), Ru(5)—C—O(35) 138 (1)°]. Among the terminal carbonyl groups, the greatest deviation from linearity is found for CO(13) and CO(23), which exhibit short contacts to Ru(3) and Ru(5), respectively [C(13)···Ru(3) 2.759 (12), C(23)···Ru(5) 2.70 (11) Å]. Since Ru(3) and Ru(5) do not strictly obey the 18-electron rule, some degree of bonding interaction of these CO groups may account for these observations. Similar distribution of carbonyl ligands is also a structural feature characterized for the arene derivatives [$Ru_6C(CO)_{14}(\eta^6\text{-arene})$] (Mason & Robinson, 1968; Farrugia, 1988).

## Experimental

An alternative synthesis for the hexanuclear cluster, (1), has been reported elsewhere (Adatia *et al.*, 1994). Suitable crystals were grown from slow diffusion of *n*-pentane/dichloromethane at room temperature.

### *Crystal data*

[$Ru_5Rh(C)(CO)_{14}(C_{10}H_{15})$]
$M_r = 1147.79$
Triclinic
$P\bar{1}$
$a = 17.051$ (3) Å
$b = 10.996$ (2) Å
$c = 9.329$ (2) Å
$\alpha = 115.39$ (3)°
$\beta = 100.40$ (3)°
$\gamma = 78.57$ (2)°
$V = 1539.79$ Å$^3$
$Z = 2$
$D_x = 2.476$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 4$–15°
$\mu = 0.79$ mm$^{-1}$
$T = 298$ K
Rectangular block
0.25 × 0.22 × 0.15 mm
Dark red

### *Data collection*

Philips PW1100 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{\min} = 0.933$, $T_{\max} = 1.069$
5234 measured reflections
4332 independent reflections

4193 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.012$
$\theta_{\max} = 30°$
$h = -20 \rightarrow 19$
$k = -12 \rightarrow 11$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 180 min
intensity variation: < 5%

*Refinement*

Refinement on $F$
$R = 0.0328$
$wR = 0.0374$
$S = 1.53$
4054 reflections
217 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.51$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976) except for Ru and Rh (Cromer & Mann, 1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Ru(1) | 0.33625 (4) | 0.17168 (7) | −0.05603 (8) | 0.0299 (4) |
| Ru(2) | 0.15885 (4) | 0.22163 (7) | −0.08766 (8) | 0.0309 (4) |
| Ru(3) | 0.33218 (4) | 0.11464 (7) | 0.22277 (9) | 0.0323 (4) |
| Ru(4) | 0.24105 (4) | −0.02813 (7) | −0.08885 (8) | 0.0306 (4) |
| Ru(5) | 0.16299 (4) | 0.16376 (7) | 0.19215 (9) | 0.0327 (4) |
| Rh | 0.25267 (4) | 0.36521 (6) | 0.20147 (7) | 0.0249 (3) |
| C | 0.2480 (5) | 0.1738 (7) | 0.0666 (9) | 0.026 (2) |
| C(11) | 0.3379 (7) | 0.3104 (10) | −0.1178 (13) | 0.050 (2) |
| O(11) | 0.3396 (6) | 0.3938 (9) | −0.1624 (11) | 0.079 (2) |
| C(12) | 0.3841 (6) | 0.0465 (10) | −0.2394 (12) | 0.048 (2) |
| O(12) | 0.4149 (6) | −0.0258 (9) | −0.3518 (11) | 0.083 (3) |
| C(13) | 0.4339 (7) | 0.1822 (11) | 0.0778 (14) | 0.059 (3) |
| O(13) | 0.4988 (6) | 0.1984 (9) | 0.1372 (11) | 0.083 (3) |
| C(21) | 0.1139 (7) | 0.1141 (12) | −0.2895 (15) | 0.062 (3) |
| O(21) | 0.0816 (6) | 0.0515 (10) | −0.4152 (13) | 0.096 (3) |
| C(22) | 0.1423 (7) | 0.3647 (11) | −0.1525 (13) | 0.052 (3) |
| O(22) | 0.1304 (6) | 0.4473 (9) | −0.2007 (11) | 0.084 (3) |
| C(23) | 0.0613 (7) | 0.2691 (10) | 0.0035 (13) | 0.052 (3) |
| O(23) | −0.0044 (6) | 0.3138 (8) | 0.0348 (10) | 0.073 (2) |
| C(31) | 0.4001 (6) | 0.1958 (10) | 0.4023 (12) | 0.046 (2) |
| O(31) | 0.4435 (5) | 0.2368 (8) | 0.5176 (11) | 0.074 (2) |
| C(32) | 0.3918 (7) | −0.0430 (11) | 0.2306 (13) | 0.053 (3) |
| O(32) | 0.4325 (6) | −0.1382 (9) | 0.2376 (11) | 0.082 (3) |
| C(41) | 0.3079 (6) | −0.1782 (10) | −0.0708 (12) | 0.043 (2) |
| O(41) | 0.3477 (5) | −0.2791 (8) | −0.0719 (9) | 0.063 (2) |
| C(42) | 0.1473 (7) | −0.1101 (11) | −0.1359 (13) | 0.054 (3) |
| O(42) | 0.0920 (6) | −0.1655 (9) | −0.1729 (11) | 0.086 (3) |
| C(43) | 0.2523 (6) | −0.0952 (10) | −0.3050 (12) | 0.047 (2) |
| O(43) | 0.2552 (5) | −0.1464 (8) | −0.4431 (10) | 0.069 (2) |
| C(51) | 0.0944 (6) | 0.2887 (10) | 0.3371 (12) | 0.046 (2) |
| O(51) | 0.0486 (5) | 0.3593 (8) | 0.4264 (10) | 0.072 (2) |
| C(52) | 0.1029 (7) | 0.0366 (11) | 0.1831 (13) | 0.052 (3) |
| O(52) | 0.0675 (6) | −0.0425 (9) | 0.1880 (11) | 0.080 (3) |
| C(35) | 0.2463 (7) | 0.1254 (11) | 0.3568 (15) | 0.058 (3) |
| O(35) | 0.2479 (6) | 0.1210 (10) | 0.4831 (13) | 0.097 (3) |
| C(1) | 0.2328 (6) | 0.5321 (9) | 0.4394 (11) | 0.038 (2) |
| C(2) | 0.3159 (5) | 0.5205 (8) | 0.4200 (10) | 0.034 (2) |
| C(3) | 0.3167 (6) | 0.5483 (9) | 0.2831 (11) | 0.036 (2) |
| C(4) | 0.2361 (6) | 0.5807 (9) | 0.2243 (11) | 0.037 (2) |
| C(5) | 0.1841 (6) | 0.5690 (9) | 0.3203 (11) | 0.037 (2) |
| C(1*a*) | 0.2068 (7) | 0.5268 (11) | 0.5833 (13) | 0.054 (3) |
| C(2*a*) | 0.3867 (7) | 0.5154 (10) | 0.5355 (13) | 0.053 (3) |
| C(3*a*) | 0.3917 (7) | 0.5663 (10) | 0.2334 (13) | 0.052 (3) |
| C(4*a*) | 0.2115 (7) | 0.6471 (11) | 0.1077 (13) | 0.055 (3) |
| C(5*a*) | 0.0927 (7) | 0.6111 (10) | 0.3094 (13) | 0.055 (3) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Ru(1)—Ru(2) | 2.949 (1) | Ru(1)—Ru(3) | 2.940 (1) |
| Ru(1)—Ru(4) | 2.866 (1) | Ru(1)—Rh | 2.825 (1) |
| Ru(2)—Ru(4) | 2.821 (1) | Ru(2)—Ru(5) | 2.926 (1) |
| Ru(2)—Rh | 2.849 (1) | Ru(3)—Ru(4) | 2.959 (1) |
| Ru(3)—Ru(5) | 2.813 (1) | Ru(3)—Rh | 2.892 (1) |
| Ru(4)—Ru(5) | 2.915 (1) | Ru(5)—Rh | 2.895 (1) |
| Ru(1)—C | 2.039 (8) | Ru(2)—C | 2.050 (8) |
| Ru(3)—C | 2.072 (8) | Ru(4)—C | 2.080 (7) |
| Ru(5)—C | 2.067 (8) | Rh—C | 1.944 (7) |
| Ru—CO(terminal) | 1.836 (10)–1.884 (11) | | |
| Ru—CO(bridging) | 2.021 (12)–2.046 (12) | | |
| Rh—C(Cp) | 2.217 (9)–2.277 (9) | | |
| Ru(3)—Ru(1)—Ru(2) | 88.7 (1) | Ru(4)—Ru(1)—Ru(2) | 58.0 (1) |
| Ru(4)—Ru(1)—Ru(3) | 61.3 (1) | Rh—Ru(1)—Ru(2) | 59.1 (1) |
| Rh—Ru(1)—Ru(3) | 60.2 (1) | Rh—Ru(1)—Ru(4) | 90.0 (1) |
| Ru(4)—Ru(2)—Ru(1) | 59.5 (1) | Ru(5)—Ru(2)—Ru(1) | 88.6 (1) |
| Ru(5)—Ru(2)—Ru(4) | 60.9 (1) | Rh—Ru(2)—Ru(1) | 58.3 (1) |
| Rh—Ru(2)—Ru(4) | 90.4 (1) | Rh—Ru(2)—Ru(5) | 60.2 (1) |
| Ru(4)—Ru(3)—Ru(1) | 58.1 (1) | Ru(5)—Ru(3)—Ru(1) | 91.0 (1) |
| Ru(5)—Ru(3)—Ru(4) | 60.6 (1) | Rh—Ru(3)—Ru(1) | 57.9 (1) |
| Rh—Ru(3)—Ru(4) | 86.9 (1) | Rh—Ru(3)—Ru(5) | 61.0 (1) |
| Ru(2)—Ru(4)—Ru(1) | 62.5 (1) | Ru(3)—Ru(4)—Ru(1) | 60.6 (1) |
| Ru(3)—Ru(4)—Ru(2) | 90.8 (1) | Ru(5)—Ru(4)—Ru(1) | 90.4 (1) |
| Ru(5)—Ru(4)—Ru(2) | 61.3 (1) | Ru(5)—Ru(4)—Ru(3) | 57.2 (1) |
| Ru(3)—Ru(5)—Ru(2) | 91.7 (1) | Ru(4)—Ru(5)—Ru(2) | 57.8 (1) |
| Ru(4)—Ru(5)—Ru(3) | 62.2 (1) | Rh—Ru(5)—Ru(2) | 58.6 (1) |
| Rh—Ru(5)—Ru(3) | 60.8 (1) | Rh—Ru(5)—Ru(4) | 87.6 (1) |
| Ru(2)—Rh—Ru(1) | 62.6 (1) | Ru(3)—Rh—Ru(1) | 61.9 (1) |
| Ru(3)—Rh—Ru(2) | 91.7 (1) | Ru(5)—Rh—Ru(1) | 91.7 (1) |
| Ru(5)—Rh—Ru(2) | 61.2 (1) | Ru(5)—Rh—Ru(3) | 58.2 (1) |
| Ru—C—O(terminal) | 163 (1)–177 (1) | | |
| Ru—C—O(bridging) | 134 (1)–138 (1) | | |

The methods of data collection and data processing used were similar to those described previously (Adams *et al.*, 1980). The positions of the metal atoms were deduced from a calculated Patterson function. The remaining non-H atoms were located from subsequent $\Delta\rho$ maps. In the final stages of structure refinement, anisotropic displacement factors were assigned to all the metal atoms. The H atoms associated with each Me substituent on the pentamethylcyclopentadienyl ligand were geometrically calculated to ride at distances of 1.08 Å from the respective C atom with fixed displacement parameters of 0.08 Å$^2$. Refinement was by full-matrix least squares on the atomic positions and displacement parameters of all the non-H atoms. Crystallographic calculations were performed using *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: AB1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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