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A Novel Bonding Scheme of an Allene System in a Transition Metal Cluster Complex. Molecular Structure of μ_3-η-(1-Methyl-3-ethyl-3-allenyl)-μ-hydrido-*triangulo*-tris(tricarbonylruthenium)(3*Ru–Ru*)

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The molecular structure of μ_3-η-(1-methyl-3-ethyl-3-allenyl)-μ-hydrido-*triangulo*-tris(tricarbonylruthenium), $HRu_3(CO)_9C_6H_9$, has been determined by a single-crystal x-ray analysis. This compound crystallizes in the triclinic system, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 9.569$ (11) Å, $b = 11.231$ (7) Å, $c = 9.379$ (5) Å, $\alpha = 95.09$ (1)°, $\beta = 90.96$ (4)°, and $\gamma = 99.75$ (1)°. A total of 2890 nonzero reflections were collected with an automatic diffractometer; the structure was solved by Patterson and Fourier methods. The hydrogen atom positions were revealed when only low-angle data ($0 < (\sin\theta)/\lambda \leq 0.35$ Å^{-1}) were used to calculate difference maps. The atom parameters were refined by least-squares techniques to $R = 0.035$. The molecule consists of a cluster of three ruthenium atoms each bonded to three carbonyl groups, at the corners of an isosceles triangle, and an allene ligand. The bonding between the two parts of the molecule is attained via two π bonds and one σ bond in a new arrangement found for an allene ligand. The hydridic hydrogen atom symmetrically bridges the longest Ru–Ru bond. A comparison is made with another compound of the same molecular formula obtained by thermal rearrangement of the title compound.

Introduction

Two compounds A and B of molecular formula $HRu_3(CO)_9C_6H_9$ are obtained from the reaction of $Ru_3(CO)_{12}$ with the isomers of hexadiene.[1] Isomer B is easily obtained by thermal rearrangement of isomer A and its molecular structure is already known.[2] The lower homologues $HRu_3(CO)_9C_5H_7$ are also the main products of the reaction of $Ru_3(CO)_{12}$ with pentenes.[3] The importance of the molecular structure of the isomer $HRu_3(CO)_9C_6H_9$-A and the opportunity to make a comparison with $HRu_3(CO)_9C_6H_9$-B has driven us to carry out an x-ray analysis of the former compound.

This study has revealed the new scheme[4] of an allene system bonded to the metal cluster via two π bonds and one σ bond.

Experimental Section

The recrystallization of the compound $HRu_3(CO)_9C_6H_9$-A from *n*-heptane at 0 °C led almost always to yellow tabular (100) polycrystals and the choice of a single crystal suitable for x-ray analysis was very troublesome.

The crystal used (dimensions 0.12 × 0.29 × 0.51 mm) was elongated in the *z* direction with well-developed {010}, {110}, {110}, and {011} faces. Weissenberg and precession photographs indicated triclinic symmetry. The unit cell parameters, obtained by refining via a least-squares procedure the θ angles of 25 reflections measured on a Philips PW 1100 four-circle automatic diffractometer, are given in Table I, together with other relevant crystal data.

Integrated intensities were collected on the same diffractometer up to a 2θ limit of 50° with graphite-monochromatized Mo Kα radiation using an ω-scan technique (scan range 1.80°, scan speed 0.08°/s); 5 s was spent for background measurements on both sides of each peak. A total of 345 reflections, that after a prescan gave $I_{top} - 2I_{top}{}^{1/2} < I_{bck}$, were considered weak and not measured.

Three standard reflections $(2\bar{1}\bar{2})$, $(\bar{1}23)$, and $(13\bar{1})$ were checked every 120 reflections and no significant variations of the intensity were detected. Of the 3113 independent reflections collected, 223 were rejected as being unobserved ($I < 3\sigma(I)$). An absorption correction was applied, using the program GONO9 by Hamilton;[5] no secondary extinction correction was made, as only a few intense reflections were affected. Atomic scattering factors were taken from Cromer and Waber;[6] the effects of anomalous dispersion of ruthenium were included in structure factor calculations using Cromer and Liberman's[7] values for $\Delta f'$ and $\Delta f''$.

Table I. Crystal Data for $HRu_3(CO)_9C_6H_9$-A

$a = 9.569$ (11) Å	Mol wt 637.45
$b = 11.231$ (7) Å	Space group $P1$
$c = 9.379$ (5) Å	$Z = 2$
$\alpha = 95.09$ (1)°	$F(000) = 608$
$\beta = 90.96$ (4)°	$d_{measd} = 2.13$ g cm^{-3} (flotation)
$\gamma = 99.75$ (1)°	$d_{calcd} = 2.14$ g cm^{-3}
$V = 998.95$ Å^3	μ(Mo Kα) = 22.50 cm^{-1}

Solution and Refinement of the Structure

A three-dimensional Patterson map was interpretable in terms of three independent heavy-atom positions in the centric space group $P\bar{1}$. Subsequent difference-Fourier syntheses revealed the positions of all the other nonhydrogen atoms. Least-squares refinement[8] of all positional and anisotropic thermal parameters was considered complete when the shifts of the parameters were smaller than their estimated standard deviations and resulted in the agreement factor $R = 0.038$ for the 2890 reflections.

A difference-Fourier synthesis revealed at this stage many peaks whose heights ranged from 0.4 to 0.7 e Å^{-3}. This map showed promising peaks at likely positions for some hydrogen atoms but was unfortunately marred by a large number of background peaks. With the technique suggested by Ibers and co-workers,[9] some difference Fourier maps with the $(\sin\theta)/\lambda$ cutoff equal to 0.35, 0.40, and 0.45 Å^{-1} were calculated. The first had no background peaks and revealed the hydrogen atom positions quite clearly.

The hydrogen atom parameters were refined first using only the low-angle data (667 reflections; $(\sin\theta)/\lambda$ cutoff 0.35 Å^{-1}) and then using all of the data. Continued refinement by least-squares methods, with all atom parameters allowed to vary, led to slightly satisfying thermal parameters for the hydrogen atoms, but the positional parameters gave a good agreement with that expected.

The final R value for the 2890 reflections is 0.035; the weighted value R' is 0.044. The weighting scheme was ($|F_o| = 1.919$ times the absolute scale)

$$\text{for } |F_o| \leqslant 55\text{: } w = 0.01|F_o| + 0.45$$

$$\text{for } |F_o| > 55\text{: } w = \frac{467}{0.1|F_o|^2 + 2|F_o| + 55}$$

The constants in these expressions were modified during the refinement in order to obtain $\sum w\Delta^2$ satisfactorily constant for the amplitudes batched in various groups.

Table II. Final Fractional Coordinates for $HRu_3(CO)_9C_6H_9$-A[a]

	x/a	*y/b*	*z/c*
Ru1	0.395 09 (5)	0.246 54 (4)	0.250 52 (5)
Ru2	0.135 87 (5)	0.350 76 (4)	0.329 44 (4)
Ru3	0.208 11 (5)	0.305 23 (4)	0.050 83 (4)
C1	0.480 7 (7)	0.180 2 (6)	0.405 5 (8)
C2	0.498 9 (6)	0.407 9 (6)	0.283 0 (8)
C3	0.519 9 (7)	0.202 9 (6)	0.105 1 (9)
C4	−0.033 4 (7)	0.404 3 (6)	0.280 4 (7)
C5	0.076 0 (8)	0.302 4 (7)	0.511 2 (7)
C6	0.231 1 (7)	0.516 0 (7)	0.390 7 (7)
C7	0.041 1 (8)	0.331 7 (6)	−0.044 5 (7)
C8	0.297 0 (8)	0.247 2 (6)	−0.116 5 (7)
C9	0.299 7 (7)	0.470 6 (7)	0.053 2 (7)
C10	−0.149 7 (10)	0.077 6 (10)	0.297 1 (12)
C11	−0.077 3 (6)	0.124 0 (7)	0.164 6 (8)
C12	0.071 3 (6)	0.192 2 (5)	0.200 5 (6)
C13	0.187 6 (6)	0.146 4 (5)	0.154 5 (6)
C14	0.263 2 (7)	0.055 8 (5)	0.174 1 (7)
C15	0.220 3 (10)	−0.036 5 (7)	0.281 0 (10)
O1	0.525 5 (7)	0.139 7 (5)	0.496 6 (7)
O2	0.563 3 (5)	0.501 9 (5)	0.303 5 (7)
O3	0.596 0 (6)	0.174 1 (6)	0.025 5 (7)
O4	−0.136 2 (6)	0.432 9 (6)	0.251 1 (6)
O5	0.040 7 (8)	0.270 1 (7)	0.616 7 (6)
O6	0.281 9 (7)	0.613 3 (5)	0.422 6 (7)
O7	−0.061 5 (6)	0.347 1 (6)	−0.094 7 (6)
O8	0.349 8 (8)	0.212 9 (6)	−0.215 3 (7)
O9	0.357 6 (6)	0.567 1 (5)	0.057 8 (6)
H1	0.290 (8)	0.291 (7)	0.369 (9)
H2	−0.230 (11)	0.019 (9)	0.273 (11)
H3	−0.083 (11)	−0.004 (9)	0.696 (11)
H4	−0.126 (10)	0.113 (9)	0.380 (11)
H5	−0.129 (8)	0.180 (8)	0.104 (9)
H6	−0.081 (9)	0.046 (7)	0.091 (9)
H7	0.321 (6)	0.025 (5)	0.097 (7)
H8	0.306 (15)	−0.083 (13)	0.300 (16)
H9	0.134 (8)	−0.099 (7)	0.239 (8)
H10	0.186 (8)	0.008 (7)	0.363 (9)

[a] Figures in parentheses in this and following tables are estimated standard deviations in the last significant figure.

On a final difference-Fourier map some peaks of height 0.4 e Å^{-3} remain, but they have no chemical evidence.

A table of observed and calculated structure factor amplitudes is available.[10] Final fractional coordinates are listed in Table II; anisotropic thermal parameters are shown in Table III. Least-squares planes were calculated by the method of ref 11.

Description of Structure and Discussion

The molecular geometry of $HRu_3(CO)_9C_6H_9$-A is shown in Figure 1. Interatomic distances are given in Table IV; bond angles, in Table V.

As predicted[1] the molecule consists of an organic ligand and a cluster of three ruthenium atoms at the corners of an isosceles triangle; each ruthenium atom is bonded to three terminal carbonyl groups (two equatorial and one axial).

Two bonds of the cluster are significantly shorter than the Ru–Ru bond of $Ru_3(CO)_{12}$[12] (2.85 Å); one is longer. They are, however, all within the range of Ru–Ru distances previously reported[13] in ruthenium clusters and are closely comparable with those found in $HRu_3(CO)_9C_6H_5CC_6H_4$,[13a] $HRu_3(CO)_9C_{12}H_{15}$,[13b] and $HRu_3(CO)_9C_6H_9$-B,[2] in which an allyl fragment is π and σ bonded to the three ruthenium atoms.

Only three adjacent carbon atoms of the organic ligand, C12, C13, and C14, are bonded to the metal cluster. ^1H NMR data[1] and bond distances and angles are in agreement with a bent allenic configuration[4] $C_2H_5—C{=}C{=}C—CH—CH_3$ and with a double π coordination on the Ru1 and Ru3 atoms. The difference between the Ru3–C12, Ru3–C13 bonds and the Ru1–C13, Ru1–C14 bonds suggests a different strength of π bonds, although this is not confirmed by the difference between the C12–C13 and C13–C14 bonds. The central carbon atom C13 of the allenic system is closer, also in this compound, to the metals than the other complexed carbons;[4]

Table III

(A) Final Temperature Factors[a] for $HRu_3(CO)_9C_6H_9$-A

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru1	78.7 (5)	59.2 (4)	107.1 (6)	16.1 (3)	−6.3 (4)	14.5 (4)
Ru2	90.5 (6)	60.3 (4)	64.4 (5)	12.9 (3)	9.2 (3)	0.9 (3)
Ru3	90.4 (6)	63.3 (4)	64.3 (5)	21.7 (3)	11.5 (4)	12.0 (3)
C1	131 (9)	83 (6)	165 (10)	26 (6)	−39 (8)	25 (6)
C2	93 (7)	86 (6)	151 (9)	19 (6)	−11 (7)	14 (6)
C3	114 (8)	85 (6)	178 (11)	30 (6)	27 (8)	27 (7)
C4	126 (9)	83 (6)	98 (7)	28 (6)	16 (6)	−10 (5)
C5	160 (10)	101 (7)	98 (8)	14 (7)	23 (7)	13 (6)
C6	135 (9)	95 (7)	113 (8)	26 (6)	10 (7)	−3 (6)
C7	136 (9)	105 (7)	83 (7)	36 (6)	7 (6)	9 (5)
C8	155 (10)	95 (6)	111 (9)	34 (6)	17 (7)	9 (6)
C9	113 (8)	95 (7)	120 (8)	29 (6)	22 (6)	30 (6)
C10	165 (13)	173 (12)	252 (18)	−69 (10)	58 (12)	28 (12)
C11	83 (7)	111 (7)	150 (10)	−3 (6)	3 (6)	−9 (7)
C12	94 (6)	65 (5)	70 (6)	0 (4)	7 (5)	6 (4)
C13	95 (7)	57 (5)	81 (6)	6 (4)	−3 (5)	0 (4)
C14	122 (8)	59 (5)	119 (8)	14 (5)	−3 (6)	0 (5)
C15	215 (14)	72 (6)	216 (15)	6 (7)	−17 (11)	52 (8)
O1	253 (11)	123 (6)	226 (10)	33 (7)	−101 (9)	59 (7)
O2	134 (7)	80 (5)	262 (10)	−17 (4)	−22 (6)	10 (5)
O3	164 (8)	150 (7)	250 (11)	65 (6)	82 (8)	11 (7)
O4	143 (7)	162 (7)	192 (9)	78 (6)	12 (6)	14 (6)
O5	322 (13)	190 (8)	100 (7)	10 (8)	74 (7)	39 (6)
O6	241 (10)	78 (5)	251 (11)	−12 (6)	−5 (8)	−39 (6)
O7	157 (7)	179 (7)	133 (7)	67 (6)	−22 (6)	29 (6)
O8	285 (12)	178 (8)	159 (8)	62 (8)	112 (8)	−17 (6)
O9	179 (8)	86 (5)	216 (9)	−4 (5)	31 (7)	47 (5)

	B, Å^2		*B*, Å^2		*B*, Å^2
H1	1.4 (1.6)	H5	4.2 (2.0)	H8	12.2 (4.2)
H2	5.9 (2.5)	H6	3.8 (1.9)	H9	5.3 (1.7)
H3	10.7 (2.6)	H7	2.6 (1.3)	H10	1.3 (1.9)
H4	10.3 (2.6)				

(B) Root-Mean-Square Displacements (in Å) of Atoms along the Principal Axes of Their Vibration Ellipsoids

	$(\bar{U}^2)_{min}{}^{1/2}$	$(\bar{U}^2)_{med}{}^{1/2}$	$(\bar{U}^2)_{max}{}^{1/2}$
Ru1	0.175	0.195	0.222
Ru2	0.164	0.195	0.204
Ru3	0.164	0.185	0.211
C1	0.192	0.237	0.297
C2	0.198	0.229	0.262
C3	0.210	0.228	0.288
C4	0.183	0.240	0.244
C5	0.201	0.248	0.278
C6	0.212	0.246	0.252
C7	0.191	0.229	0.265
C8	0.216	0.236	0.269
C9	0.207	0.216	0.262
C10	0.189	0.337	0.400
C11	0.189	0.245	0.287
C12	0.174	0.189	0.223
C13	0.177	0.198	0.213
C14	0.190	0.228	0.239
C15	0.186	0.293	0.340
O1	0.197	0.294	0.402
O2	0.196	0.275	0.345
O3	0.205	0.312	0.360
O4	0.210	0.291	0.332
O5	0.178	0.340	0.402
O6	0.194	0.339	0.356
O7	0.205	0.273	0.340
O8	0.187	0.342	0.392
O9	0.201	0.298	0.319

[a] Anisotropic thermal parameters are the β_{ij} coefficients of the formula $\exp(-\Sigma_{i=1}{}^3\Sigma_{j=1}{}^3\beta_{ij}h_ih_j)$.

Table IV. Interatomic Distances (A) for $HRu_3(CO)_9C_6H_9$-A

		(a) Ru–Ru Distances			
Ru1–Ru2	2.994 (1)	Ru1–Ru3	2.766 (1)	Ru2–Ru3	2.741 (1)
		(b) Ru–C Distances			
Ru1–C1	1.923 (7)	Ru2–C4	1.885 (7)	Ru3–C7	1.898 (7)
Ru1–C2	1.910 (7)	Ru2–C5	1.903 (7)	Ru3–C8	1.915 (7)
Ru1–C3	1.914 (7)	Ru2–C6	1.956 (7)	Ru3–C9	1.914 (7)
Ru1–C13	2.242 (5)	Ru2–C12	2.058 (5)	Ru3–C12	2.261 (5)
Ru1–C14	2.341 (6)			Ru3–C13	2.089 (5)
		(c) C–O Distances			
C1–O1	1.115 (10)	C4–O4	1.122 (9)	C7–O7	1.128 (9)
C2–O2	1.128 (9)	C5–O5	1.122 (9)	C8–O8	1.132 (10)
C3–O3	1.118 (10)	C6–O6	1.131 (9)	C9–O9	1.127 (9)
		(d) C–C Distances			
C10–C11	1.522 (13)	C12–C13	1.365 (8)	C14–C15	1.511 (10)
C11–C12	1.514 (9)	C13–C14	1.369 (8)		
		(e) Ru–H Distances			
Ru1–H1	1.61 (7)	Ru2–H1	1.77 (7)		
		(f) C–H Distances			
C10–H2	0.9 (1)	C11–H5	1.1 (1)	C15–H8	1.1 (1)
C10–H3	1.2 (1)	C11–H6	1.1 (1)	C15–H9	1.0 (1)
C10–H4	0.9 (1)	C14–H7	1.0 (1)	C15–H10	0.9 (1)

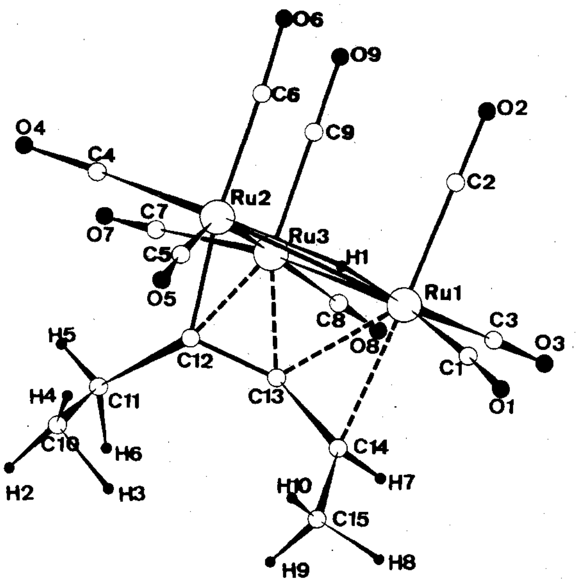

Figure 1. Projection along *c* of one molecule on plane *ab*, showing the atom-labeling system.

the angle of 61° between the coordination planes Ru1–C13–C14 and Ru3–C12–C13 suggests the presence of bent π bonds.

The σ bond Ru2–C12, that completes the coordination between the cluster and the organic ligand, is slightly longer than the Ru–C_{CO} bond (1.913 (7) Å average) and this fact is in agreement with a partial double-bond character as in the compounds $HRu_3(CO)_9C_6H_5CC_6H_4$, $HRu_3(CO)_9C_{12}H_{15}$, and $HRu_3(CO)_9C_6H_9$-B.

The hydridic hydrogen atom lies on the plane of the ruthenium cluster (Table VI), trans to the C3–O3 and C4–O4 carbonyl groups (Table V), and bridges the Ru1–Ru2 bond; this agrees with the lengthening of the Ru1–Ru2 bond and the spreading out of the Ru1–C1–O1 and Ru2–C5–O5 angles (Table V), according to the criteria generally accepted,[13f] though not always valid.[13g] The Ru–H bond lengths are similar to the values found by Sheldrick and Yesinowski,[13g] and the angle Ru–H–Ru is slightly wider.

Table V. Bond Angles (deg) for $HRu_3(CO)_9C_6H_9$-A

	(a) Ru–Ru–Ru Angles		
Ru2–Ru1–Ru3	56.7 (1)	Ru1–Ru3–Ru2	65.9 (1)
Ru1–Ru2–Ru3	57.5 (1)		
	(b) Ru–Ru–C Angles		
Ru2–Ru1–C1	114.1 (2)	Ru3–Ru2–C4	94.3 (2)
Ru2–Ru1–C2	87.0 (2)	Ru3–Ru2–C5	153.1 (2)
Ru2–Ru1–C3	148.5 (2)	Ru3–Ru2–C6	105.9 (2)
Ru2–Ru1–C13	63.3 (1)	Ru3–Ru2–C12	54.0 (2)
Ru2–Ru1–C14	92.9 (2)	Ru1–Ru3–C7	163.1 (2)
Ru3–Ru1–C1	164.9 (2)	Ru1–Ru3–C8	97.1 (2)
Ru3–Ru1–C2	94.2 (2)	Ru1–Ru3–C9	94.5 (2)
Ru3–Ru1–C3	92.1 (2)	Ru1–Ru3–C12	74.7 (1)
Ru3–Ru1–C13	47.9 (1)	Ru1–Ru3–C13	52.8 (2)
Ru3–Ru1–C14	78.4 (2)	Ru2–Ru3–C7	99.7 (2)
Ru1–Ru2–C4	151.6 (2)	Ru2–Ru3–C8	162.6 (2)
Ru1–Ru2–C5	109.1 (2)	Ru2–Ru3–C9	89.2 (2)
Ru1–Ru2–C6	97.5 (2)	Ru2–Ru3–C12	47.4 (1)
Ru1–Ru2–C12	72.3 (2)	Ru2–Ru3–C13	70.0 (1)
	(c) C–Ru–C Angles		
C1–Ru1–C2	97.2 (3)	C5–Ru2–C6	98.7 (3)
C1–Ru1–C3	97.1 (3)	C5–Ru2–C12	101.1 (3)
C1–Ru1–C13	118.3 (3)	C6–Ru2–C12	159.9 (3)
C1–Ru1–C14	90.9 (3)	C7–Ru3–C8	96.5 (3)
C2–Ru1–C3	92.4 (3)	C7–Ru3–C9	93.9 (3)
C2–Ru1–C13	140.2 (2)	C7–Ru3–C12	89.2 (2)
C2–Ru1–C14	171.1 (3)	C7–Ru3–C13	115.4 (3)
C3–Ru1–C13	99.8 (3)	C8–Ru3–C9	96.1 (3)
C3–Ru1–C14	83.0 (3)	C8–Ru3–C12	127.0 (3)
C13–Ru1–C14	34.7 (2)	C8–Ru3–C13	97.3 (3)
C4–Ru2–C5	95.5 (3)	C9–Ru3–C12	136.2 (2)
C4–Ru2–C6	92.2 (3)	C9–Ru3–C13	145.9 (2)
C4–Ru2–C12	89.8 (3)	C12–Ru3–C13	36.3 (2)
	(d) Ru–C–Ru Angles		
Ru2–C12–Ru3	78.6 (2)	Ru1–C13–Ru3	79.3 (2)
	(e) Ru–C–C Angles		
Ru2–C12–C11	129.3 (4)	Ru1–C13–C14	76.6 (4)
Ru2–C12–C13	109.3 (4)	Ru3–C13–C12	78.7 (3)
Ru3–C12–C11	125.2 (4)	Ru3–C13–C14	138.6 (4)
Ru3–C12–C13	65.0 (3)	Ru1–C14–C13	68.7 (3)
Ru1–C13–C12	114.8 (4)	Ru1–C14–C15	120.5 (5)
	(f) Ru–C–O Angles		
Ru1–C1–O1	177.5 (1)	Ru2–C6–O6	177.0 (1)
Ru1–C2–O2	178.1 (1)	Ru3–C7–O7	176.5 (1)
Ru1–C3–O3	176.2 (7)	Ru3–C8–O8	179.9 (1)
Ru2–C4–O4	178.0 (1)	Ru3–C9–O9	177.4 (1)
Ru2–C5–O5	177.8 (1)		
	(g) C–C–C Angles		
C10–C11–C12	111.5 (6)	C12–C13–C14	142.3 (6)
C11–C12–C13	121.2 (5)	C13–C14–C15	121.9 (6)
	(h) Ru–Ru–H Angles		
Ru2–Ru1–H1	29 (3)	Ru1–Ru2–H1	26 (2)
Ru3–Ru1–H1	86 (3)	Ru3–Ru2–H1	84 (2)
	(i) Ru–H–Ru Angles		
Ru1–H1–Ru2	125 (4)		
	(j) Ru–C–H Angles		
Ru1–C14–H7	103 (4)		
	(k) C–Ru–H Angles		
C1–Ru1–H1	86 (3)	C4–Ru2–H1	176 (2)
C2–Ru1–H1	85 (3)	C5–Ru2–H1	85 (2)
C3–Ru1–H1	177 (1)	C6–Ru2–H1	92 (2)
C13–Ru1–H1	80 (3)	C12–Ru2–H1	86 (2)
C14–Ru1–H1	99 (3)		
	(l) C–C–H Angles		
C11–C10–H2	112 (6)	C12–C11–H6	114 (5)
C11–C10–H3	95 (5)	C13–C14–H7	121 (4)
C11–C10–H4	121 (7)	C15–C14–H7	112 (4)
C10–C11–H5	118 (5)	C14–C15–H8	110 (8)
C10–C11–H6	105 (5)	C14–C15–H9	109 (4)
C12–C11–H5	107 (5)	C14–C15–H10	116 (5)

The Ru3 atom achieves a distorted octahedral coordination with two ruthenium atoms, three carbonyl groups, and one π bond; for Ru1 and Ru2, if we include the hydride but ignore the Ru1–Ru2 bond, the coordination is close to octahedral.

A comparison between the A and B isomers (Figure 2)

Table VI. Some Relevant Planes[a] for $HRu_3(CO)_9C_6H_9$-A (a), $HRu_3(CO)_9C_6H_9$-B (b), and $HRu_3(CO)_9C_{12}H_{15}$ (c)

Compd	Atoms and deviations from planes							*A*	*B*	*C*	*D*	χ^2
	Ru1	Ru2	Ru3									
a								3.64	9.51	−0.61	3.63	
b								2.14	2.54	9.39	3.16	
c								6.50	−8.96	4.42	1.44	
	Ru1	Ru2	Ru3	H1								
a	0.01	0.01	−0.01	−3.6				3.64	9.51	−0.61	3.63	0.16
	C11	C12	C13	C14	C15	Ru1	Ru2					
b	−12.5	8.4	−2.6	8.0	2.9	−1.4	0.8	−0.72	8.49	4.22	3.31	9.7
c	0.4	6.2	−2.4	6.3	−7.6	2.8	−0.6	10.34	−5.21	−8.35	1.04	6.0
	C12	C13	Ru1	Ru2								
a	4.5	−4.4	0.2	−0.2				−0.24	−6.66	7.95	0.25	54.3

[a] Equations of weighted planes are in the form $AX + BY + CZ = D$, in fractional coordinates, referred to the cell axes. Distances (Å × 10^2) of relevant atoms from the planes are given below the respective atoms; $\chi^2 = \Sigma(d/\sigma)^2$ and gives the statistical significance of the planarity.[14]

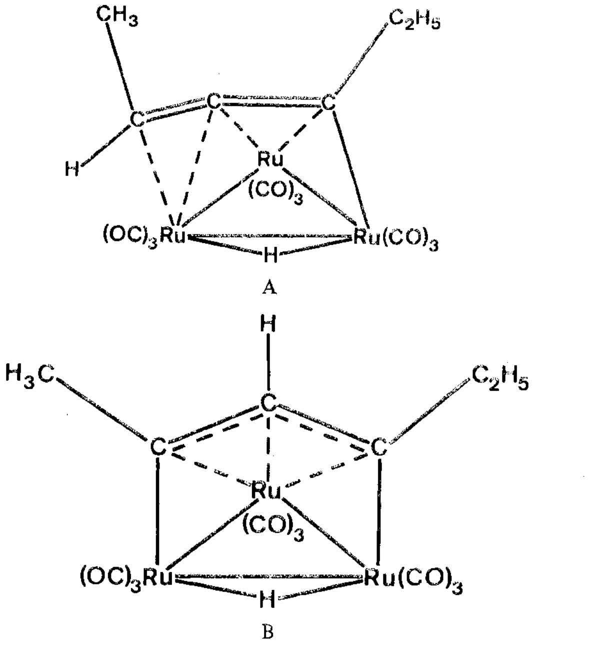

Figure 2. Molecular structures of isomers A and B of $HRu_3(CO)_9C_6H_9$.

allows us to observe that they differ only in the bonding and the arrangement of the organic ligand with respect to the Ru_3 cluster.

In $HRu_3(CO)_9C_6H_9$-B, in $HRu_3(CO)_9C_{12}H_{15}$, and in $HRu_3(CO)_9C_6H_5CC_6H_4$ the atoms Ru1, Ru2, and C11–C15 lie on planes (Table VI) forming angles of 51° with that of Ru_3 cluster, while in $HRu_3(CO)_9C_6H_9$-A only the atoms Ru1, Ru2, C12, and C13 are roughly on a plane (Table VI) inclined at an angle of 57° with respect to the Ru_3 plane.

In the thermal rearrangement from isomer A to isomer B the shift of a hydrogen atom from C14 to C13 is coupled to the closing of the C14–C13–C12 angle (from 142 to 117°) and the opening of the C12–Ru2–Ru1 angle (from 72 to 84°) with subsequent transfer of C14 in the plane mentioned above and the attainment of a more stable allylic system, with a higher electron delocalization.

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Registry No. $HRu_3(CO)_9C_6H_9$-A, 58151-19-2.

Supplementary Material Available: Listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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