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$HRu_3(CO)_{10}(COCH_3)$. A CLUSTER WITH AN OXYGEN-CONTAINING μ_2-CARBYNE LIGAND; PREPARATION, STRUCTURE AND FLUXIONALITY

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Summary

The cluster $HRu_3(CO)_{10}(COCH_3)$ has been prepared from $Na[HRu_3(CO)_{11}]$ and $[(CH_3)_3O]BF_4$ in acetonitrile. The complex crystallises in the monoclinic space group $P2_1/c$, with cell dimensions a 7.937(2), b 16.880(9), c 14.074(3) Å, β 104.16(3)° and Z 4. The structure was solved by a combination of Patterson and Fourier techniques, and refined by full-matrix least-squares to final residues of $R = 0.031$ and $R_w = 0.035$ for the 2529 unique intensities. The three ruthenium atoms define an approximately equilateral triangle with one edge bridged by both a μ_2-H and a μ_2-$COCH_3$ ligand. The fluxional behaviour of $HRu_3(CO)_{10}(COCH_3)$ has been studied by variable temperature ^{13}C NMR spectroscopy. The spectra are indicative of several dynamic processes occurring in solution over the range —100 to +90°C. The μ_2-$COCH_3$ species can be considered as a bridging three-electron donor and thus represents a μ_2-carbyne ligand.

It has been shown recently that the methylation of the anions $[HFe_3(CO)_{11}]^-$ and $[HOs_3(CO)_{11}]^-$ occurs at the oxygen atom of the bridging carbonyl group to form the clusters $HFe_3(CO)_{10}(COCH_3)$ [1] and $HOs_3(CO)_{10}(COCH_3)$ [2]. To complete this series, we have prepared the ruthenium analogue $HRu_3(CO)_{10}(COCH_3)$ from the previously unknown anion $[HRu_3(CO)_{11}]^-$ [3] and trimethyloxoniumtetrafluoroborate, and investigated its structural and fluxional features. The nature of the μ_2-$COCH_3$ species in $HFe_3(CO)_{10}(COCH_3)$ has been described as a "triple metal semibridging unit" [1] or in $HOs_3(CO)_{10}(COCH_3)$ as an "O-alkylated carbonyl group" [2]. We interpret our findings as reconcilable with the assumption that the μ_2-$COCH_3$ unit represents a μ_2-carbyne ligand.

Results and discussion

A solution of $Na[HRu_3(CO)_{11}]$ [3] in acetonitrile reacts with $[(CH_3)_3O]BF_4$ to yield the neutral cluster $HRu_3(CO)_{10}(COCH_3)$, which can be isolated by chromatographic methods. The compound is also accessible by the reaction of $[(CH_3)_3NH][HRu_3(CO)_{11}]$ with CH_3Si_3F in dichloromethane [4].

$$Na[HRu_3(CO)_{11}] + [(CH_3)_3O]BF_4 \xrightarrow{CH_3CN} HRu_3(CO)_{10}(COCH_3) + (CH_3)_2O + NaBF_4$$

The product can be obtained as yellow crystals which decompose rather indistinctly over the range 105 to 125°C. The substance is volatile under high vacuum and is stable in air.

The mass spectrum of $HRu_3(CO)_{10}(COCH_3)$ shows the molecular ion at *m/e* 630 (calculated for ^{102}Ru) and the fragments of the series $HRu_3(CO)_n(COCH_3)$ [with $n = 10—0$] and $HRu_3(CO)_m(CO)$ [with $m = 10—4$], according to a stepwise loss of CO groups and a CH_3 fragmentation. In the ^1H NMR spectrum the resonance of the methoxy protons is observed at δ +4.46 ppm, whereas the hydride signal appears at δ —14.85 ppm ($CDCl_3$). The IR spectrum reveals nine absorptions in the region of terminal carbonyls at 2103w, 2064vs, 2053s, 2029vs, 2015s, 2007s, 2001s, 1995w and 1985vw cm^{-1} (hexane). The solid state full range spectrum (KBr pellet) displays in addition a characteristic band at 1450m cm^{-1} attributed to the μ_2-C—OCH_3 vibration, and an absorption at 1285s cm^{-1} assigned to the μ_2-CO—CH_3 stretching mode.

The X-ray structural determination shows that $HRu_3(CO)_{10}(COCH_3)$ exists as discrete molecules separated by normal van der Waals' distances. As for the iron analogue [1], and the closely related $HOs_3(CO)_9(CBu\text{-}t)(COCH_3)$ complex [2], the three metal atoms define an approximately equilateral triangle one edge of which is symmetrically bridged by the μ_2-carbyne and the hydride ligand. The carbonyl groups are all terminal and linear, with three coordinated to each ruthenium atom involved in bridge bonding, and four to the unique metal. Figure 1 is an ORTEP plot of the molecule including the atom number-

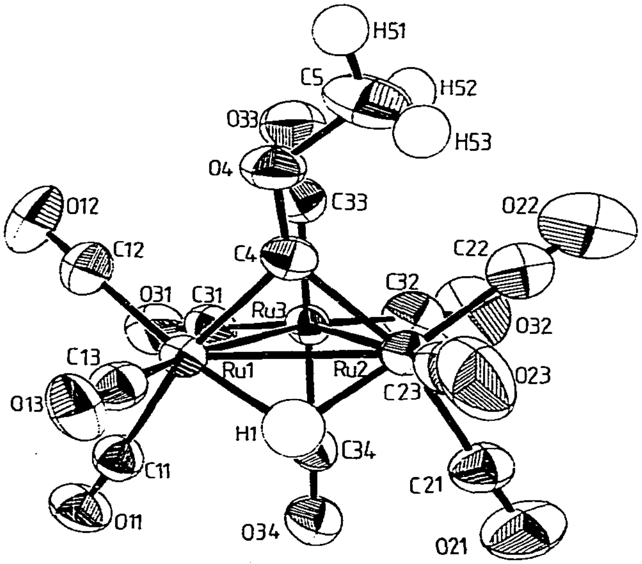


Fig. 1. The molecular structure of $HRu_3(CO)_{10}(COCH_3)$ including the atom numbering scheme adopted.

TABLE 1

BOND LENGTHS (Å)

Ru(2)—Ru(1)	2.803(2)	C(11)—Ru(1)	1.989(7)
Ru(3)—Ru(1)	2.810(2)	C(12)—Ru(1)	1.903(8)
Ru(3)—Ru(2)	2.821(2)	C(13)—Ru(1)	1.910(7)
C(4)—Ru(1)	1.976(6)	C(21)—Ru(2)	1.987(8)
C(4)—Ru(2)	1.978(7)	C(22)—Ru(2)	1.894(8)
H(1)—Ru(1)	1.778(72)	C(23)—Ru(2)	1.906(9)
H(1)—Ru(2)	1.743(72)	C(31)—Ru(3)	1.858(9)
O(11)—C(11)	1.106(8)	C(32)—Ru(3)	1.915(9)
O(12)—C(12)	1.110(9)	C(33)—Ru(3)	1.941(8)
O(13)—C(13)	1.122(8)	C(34)—Ru(3)	1.921(8)
O(21)—C(21)	1.111(9)	O(31)—C(31)	1.155(10)
O(22)—C(22)	1.109(9)	O(32)—C(32)	1.117(10)
O(23)—C(23)	1.098(10)	O(33)—C(33)	1.133(9)
O(4)—C(4)	1.299(8)	O(34)—C(34)	1.152(9)
O(4)—C(5)	1.427(9)	H(51)—C(5)	0.999(9)
H(52)—C(5)	1.012(9)	H(53)—C(5)	0.998(9)

ing scheme adopted, and the final bond lengths and angles are given in Tables 1 and 2, respectively.

The ruthenium—ruthenium distances in this cluster are, on average, 0.05 Å shorter than in the parent carbonyl, $Ru_3(CO)_{12}$ [5], and between 0.012 and 0.035 Å shorter than in the related anion $[HRu_3(CO)_{11}]^-$ [3]. It has been shown that an unsupported μ_2-H bridge on a metal cluster causes lengthening of the bridged metal—metal bond [6]. In the presence of another bridging group spanning the same edge, the metal—metal distance may either increase or decrease depending upon the combined effect of the two ligands. In this cluster the bond lengthening effect of the hydride is counterbalanced by the shortening effect of the carbyne ligand. This results in a bridged Ru—Ru distance which is 0.013 Å shorter than the average of the unbridged distances.

The Ru—C(carbyne) bond lengths are 0.093 Å shorter than the corresponding Ru—C(carbonyl) distances (mean 2.070 Å) in $[HRu_3(CO)_{11}]^-$ [3], while the Ru—C—Ru angle is ca. 5° wider at 90.3(3)°. All this is consistent with increased electron density in the Ru—C(carbyne) bonds. The C(4)—O(4) bond distances is intermediate in length between the formally double bond value of 1.180(12) Å in the anion and the single O(4)—C(5) bond of 1.427(9) Å in this complex. It is very similar in length to the corresponding C—O bond (1.270(32) Å) in $HOs_3(CO)_9(CBu\text{-}t)(COCH_3)$ [2]. The C(4) atom has a planar coordination geometry and may be considered to be formally sp^2 hybridized. The C(4)—O(4)—C(5) angle is also indicative of sp^2 hybridization at the oxygen.

An examination of the Ru—C(carbonyl) bond lengths shows that the carbyne ligand exerts a strong *trans* influence. The two Ru—C distances *trans* to this group are lengthened by ca. 0.07 Å compared to the other metal—carbon bonds. A similar, though less marked, effect has also been observed in $[HRu_3(CO)_{11}]^-$ [3] and $HRu_3(CO)_{10}(CNCH_3)$ [6], suggesting that μ_2-$COCH_3$ is the stronger π-acceptor. The Ru—C(carbonyl) distances *trans* to the hydride are much shorter, and are in close agreement with the mean value of 1.898 Å found for the equivalent bonds in the anion. The four equatorial Ru—C(carbonyl) distances (mean 1.897 Å) are significantly shorter than the two axial bonds on

TABLE 2

BOND ANGLES (deg.)

Ru(3)—Ru(1)—Ru(2)	60.3(1)	C(11)—Ru(1)—Ru(2)	121.2(2)
Ru(3)—Ru(2)—Ru(1)	60.0(1)	C(11)—Ru(1)—Ru(3)	92.1(2)
Ru(2)—Ru(3)—Ru(1)	59.7(1)	C(12)—Ru(1)—Ru(2)	134.6(2)
Ru(2)—H(1)—Ru(1)	105.5(38)	C(12)—Ru(1)—Ru(3)	93.9(2)
Ru(2)—C(4)—Ru(1)	90.3(3)	C(13)—Ru(1)—Ru(2)	105.2(2)
O(4)—C(4)—Ru(1)	128.9(5)	C(13)—Ru(1)—Ru(3)	165.5(2)
O(4)—C(4)—Ru(2)	140.2(5)	C(21)—Ru(2)—Ru(1)	117.5(2)
C(5)—O(4)—C(4)	120.3(6)	C(21)—Ru(2)—Ru(3)	95.1(2)
O(4)—C(5)—H(51)	110.0(13)	C(22)—Ru(2)—Ru(1)	138.6(3)
O(4)—C(5)—H(52)	108.7(13)	C(22)—Ru(2)—Ru(3)	92.4(3)
O(4)—C(5)—H(53)	111.3(13)	C(23)—Ru(2)—Ru(1)	106.2(3)
H(52)—C(5)—H(51)	108.2(14)	C(23)—Ru(2)—Ru(3)	165.5(3)
H(53)—C(5)—H(51)	110.3(14)	C(31)—Ru(3)—Ru(1)	94.5(3)
H(53)—C(5)—H(52)	108.2(14)	C(31)—Ru(3)—Ru(2)	153.5(3)
C(4)—Ru(1)—Ru(2)	44.9(2)	C(32)—Ru(3)—Ru(1)	160.5(3)
C(4)—Ru(1)—Ru(3)	72.5(2)	C(32)—Ru(3)—Ru(2)	101.1(3)
C(4)—Ru(1)—C(11)	163.0(3)	C(33)—Ru(3)—Ru(1)	91.5(2)
C(4)—Ru(1)—C(12)	94.0(3)	C(33)—Ru(3)—Ru(2)	93.4(2)
C(4)—Ru(1)—C(13)	97.9(3)	C(34)—Ru(3)—Ru(1)	81.6(2)
C(4)—Ru(2)—Ru(1)	44.8(2)	C(34)—Ru(3)—Ru(2)	80.2(2)
C(4)—Ru(2)—Ru(3)	72.2(2)	C(12)—Ru(1)—C(11)	94.3(3)
C(4)—Ru(2)—C(21)	161.7(3)	C(13)—Ru(1)—C(11)	95.8(3)
C(4)—Ru(2)—C(22)	100.2(3)	C(13)—Ru(1)—C(12)	97.6(3)
C(4)—Ru(2)—C(23)	95.0(3)	C(22)—Ru(2)—C(21)	93.4(3)
H(1)—Ru(1)—Ru(2)	36.8(23)	C(23)—Ru(2)—C(21)	95.6(4)
H(1)—Ru(1)—Ru(3)	82.0(23)	C(23)—Ru(2)—C(22)	96.7(4)
H(1)—Ru(1)—C(11)	93.6(24)	C(32)—Ru(3)—C(31)	104.1(4)
H(1)—Ru(1)—C(12)	171.2(24)	C(33)—Ru(3)—C(31)	93.3(4)
H(1)—Ru(1)—C(13)	85.3(23)	C(33)—Ru(3)—C(32)	93.4(4)
H(1)—Ru(1)—C(4)	77.4(24)	C(34)—Ru(3)—C(31)	90.8(4)
H(1)—Ru(2)—Ru(1)	37.7(24)	C(34)—Ru(3)—C(32)	92.0(4)
H(1)—Ru(2)—Ru(3)	82.2(24)	C(34)—Ru(3)—C(33)	172.3(3)
H(1)—Ru(2)—C(21)	87.2(24)	O(11)—C(11)—Ru(1)	176.5(7)
H(1)—Ru(2)—C(22)	174.7(24)	O(12)—C(12)—Ru(1)	178.1(7)
H(1)—Ru(2)—C(23)	88.5(24)	O(13)—C(13)—Ru(1)	177.8(6)
H(1)—Ru(2)—C(4)	78.2(24)	O(21)—C(21)—Ru(2)	178.1(8)
O(22)—C(22)—Ru(2)	177.6(8)	O(23)—C(23)—Ru(2)	178.7(9)
O(31)—C(31)—Ru(3)	179.3(9)	O(32)—C(32)—Ru(3)	179.9(3)
O(33)—C(33)—Ru(3)	177.4(7)	O(34)—C(34)—Ru(3)	174.5(7)

Ru(3) (mean 1.931 Å). This is as expected since there is increased competition for the back donation from the metal *d* orbitals in the axial case.

The hydride bridges the Ru(1)—Ru(2) edge symmetrically, to within experimental error. The Ru—H distances and Ru—H—Ru angles are within the range of values reported in a number of hydrido—ruthenium cluster complexes [6,7]. The Ru—H—Ru bridge is best described as a "bent three-centre two-electron" bond.

The differences in the ligand polyhedra between $HRu_3(CO)_{10}(COCH_3)$ and $[HRu_3(CO)_{11}]^-$ are similar, but smaller, than those reported between $HFe_3(CO)_{10}(COCH_3)$ and its corresponding anion [1]. The non-bonded Ru(3)....C(4) distance of 2.90 Å is much shorter than for the corresponding distance in the anion (3.17 Å). In both the neutral complex and the anion the bridging C—O vector is not perpendicular to the Ru—Ru vector, but is bent towards one of the metals. As for the iron analogue the dihedral angle between the M_3 plane and the M_2C plane is smaller for the alkylated complex than for the parent anion ($[HM_3(CO)_{11}]^-$, Fe 102°, Ru 104.4°; $HM_3(CO)_{10}(COCH_3)$, Fe 91°, Ru 94.7°).

The fluxional properties of $HRu_3(CO)_{10}(COCH_3)$ have been studied by variable temperature ^{13}C NMR spectroscopy. The low temperature limiting spectrum, reflecting the rigid structure of the molecule corresponding to the solid state, was obtained at −100°C. Upon increasing the temperature subsequent dynamic processes occurred until at +90°C the high temperature limiting spectrum indicates complete scrambling of the terminal carbonyls (Fig. 2).

A comparison of the spectra of $HRu_3(CO)_{10}(\mu_2\text{-}COCH_3)$ with the ^{13}C NMR spectra of its geometrically similar precursor $[HRu_3(CO)_{10}(\mu_2\text{-}CO)]^-$ [3] reveals

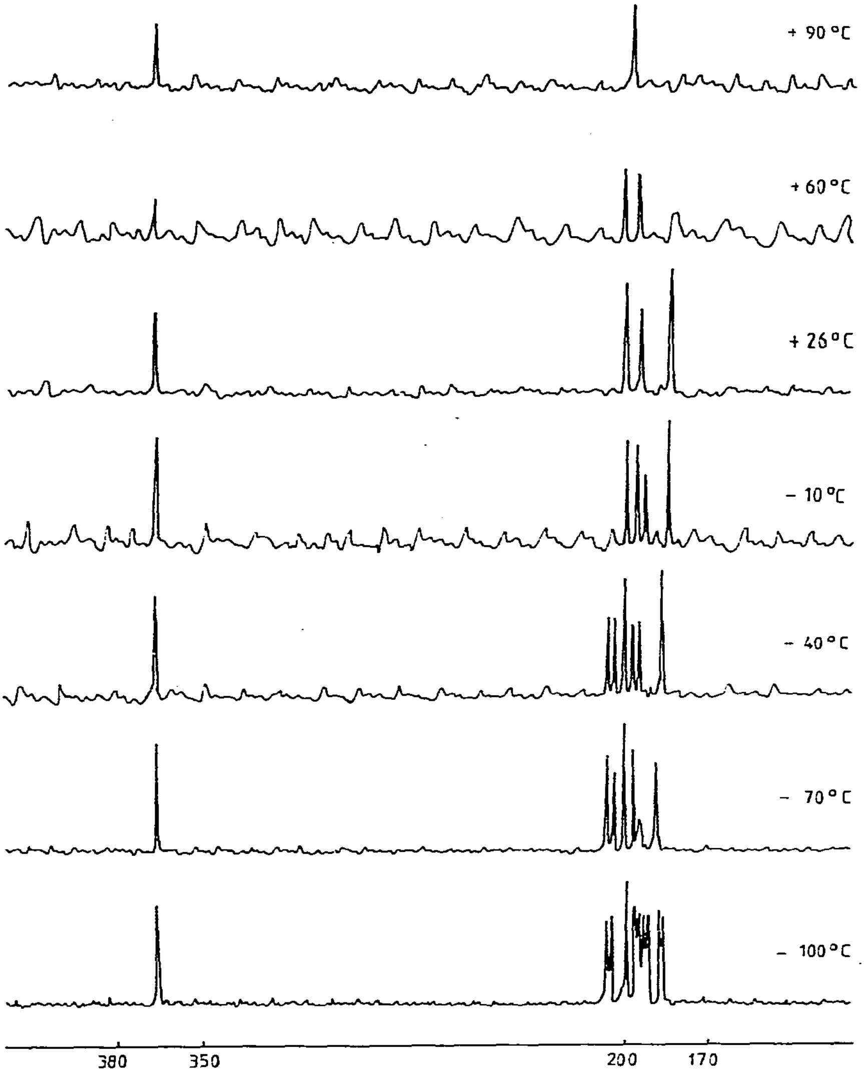


Fig. 2. Variable temperature ^{13}C NMR spectra of $HRu_3(CO)_{10}(COCH_3)$ over the range −100 to +90°C (proton-decoupled).

two major differences. Firstly, the higher number of ^{13}C signals in the low temperature limiting spectrum of $HRu_3(CO)_{10}(COCH_3)$ (Fig. 3) compared to the corresponding spectrum of $[HRu_3(CO)_{11}]^-$ indicates that the introduction of a methyl group into the μ_2-CO ligand of $[HRu_3(CO)_{11}]^-$ causes a further element of asymmetry due to the bent C—O—C system. Secondly, the maintenance of the ^{13}C resonance of the bridging carbon atom in $HRu_3(CO)_{10}$-$(COCH_3)$ over the whole range from —100 to +90°C (Fig. 2) clearly shows that the $COCH_3$ ligand does not take part in fluxional processes involving other carbonyls, whereas in $[HRu_3(CO)_{11}]^-$ it was the opening of the carbonyl bridge which initiated the fluxional processes [3].

On the grounds of chemical shift, proton coupling, and intensity, and in the light of a satisfactory interpretation, an assignment of the ^{13}C resonances to the particular carbonyl groups in $HRu_3(CO)_{10}(COCH_3)$ is proposed (Fig. 4). The fact that the carbonyls 4 and 4', which are assigned to signal d, do not correspond to individual resonances but must be ascribed to an accidental degeneracy. On the basis of this assignment, and in agreement with the findings on $HOs_3(CO)_{10}(COCH_3)$ [3], a possible interpretation of the variable temperature measurements comrpises several dynamic processes over the range —100 to +90°C.

The first process obviously is confined to a rotational movement within the $COCH_3$ ligand and does not involve other ligands. Upon increasing the temperature from —100 to —40°C coalescence between the signals e and e', f and f', g and g' is observed, indicating that the carbonyls 2 and 2', 5 and 5', 3 and 3' in $HRu_3(CO)_{10}(COCH_3)$ become equivalent. This degeneracy, being the consequence of an increase in the degree of symmetry, must arise from a rotation of the methyl group around the C—OCH_3 axis.

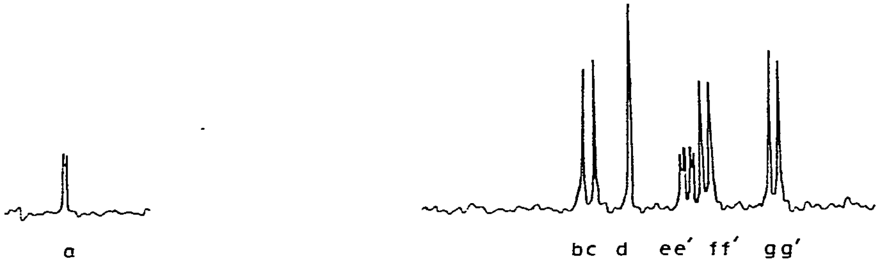


Fig. 3. ^{13}C NMR low-temperature limiting spectrum of $HRu_3(CO)_{10}(COCH_3)$ at —100°C (proton-coupled).

Signal	Rel. int.	[TMS] (ppm)	$J(^{13}C—^1H)$ (Hz)
a	1	366.5	4.9
b	1	203.7	
c	1	202.8	
d	2	198.9	
e	1	195.6	5.2
e'	1	195.3	7.6
f	1	194.7	
f'	1	193.9	
g	1	187.5	
g'	1	187.0	

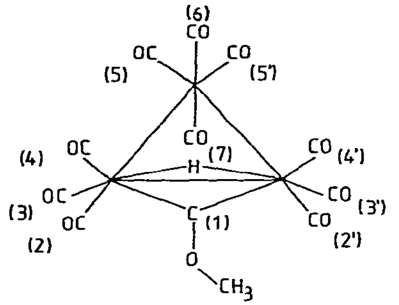


Fig. 4. Assignment of the ^{13}C NMR spectrum of $HRu_3(CO)_{10}(COCH_3)$.

Signal	Carbon atom	Signal	Carbon atom
a	1	e′	2′
b	6	f	5
c	7	f′	5′
d	4, 4′	g	3
e	2	g′	3′

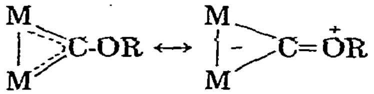
The further dynamic processes involve terminal carbonyls in $HRu_3(CO)_{10}$-$(COCH_3)$. On increasing the temperature from −40 to +26°C the signals b, c and f coalesce, suggesting a polytopal rearrangement of the $Ru(CO)_4$ species with the carbonyls 5, 5′, 6 and 7, as it was analogously proposed for $HOs_3(CO)_{10}$-$(COCH_3)$ [2]. Upon further warming also the $Ru(CO)_3$ units with the carbonyls 2, 3, 4 and 2′, 3′, 4′ seem to undergo a polytopal rearrangement, until at +90°C complete scrambling of the terminal CO groups is observed. Throughout all these processes the signal a, which corresponds to the μ_2-carbyne carbon atom 1, remains unaffected.

The nature of the $COCH_3$ ligand in $HRu_3(CO)_{10}(COCH_3)$ is particularly interesting. In the first compound of this series, $HFe_3(CO)_{10}(COCH_3)$, the $COCH_3$ moiety had been described as a "triple metal semibridging unit" [1], assuming a weak linkage between the bridging carbon atom and the unique iron atom. In the osmium analogue $HOs_{10}(COCH_3)$ the $COCH_3$ ligand was regarded as an "O-alkylated carbonyl group" [2]. A description which considers the bond between the bridging carbon atom and the methoxy group as a conventional C=O double bond is an unsatisfactory approach for the representation of the bonding situation of the μ_2-$COCH_3$ ligand. We interpret our findings on $HRu_3(CO)_{10}(COCH_3)$ as in agreement with the characterisation of the $COCH_3$ unit as a μ_2-carbyne ligand. This would then be similar to the bridging nitrosyl ligand in $HRu_3(CO)_{10}NO$ [8], since both the nitrosyl and this μ_2-carbyne ligand contribute three electrons to the cluster skeleton.

A classical carbyne ligand containing nitrogen as a hetero-atom has been described as a resonance hybrid with the mesomeric limiting structures [9]:

$$\mathrm{M{\equiv}CNR_2} \longleftrightarrow \overset{-}{\mathrm{M}}\mathrm{{=}C{=}}\overset{+}{\mathrm{N}}\mathrm{R_2}$$

Analogously, the bonding situation in $HRu_3(CO)_{10}(COCH_3)$ can be considered as a resonance hybrid of the following mesomeric forms, in which the metal cluster exercises the function of the metal central atom in the mononuclear complex.



This picture, with the ligand representing a three-electron donor, and the carbon—oxygen bond having only partial π character, is favoured by spectroscopic and structural data. In the IR spectrum the C—OCH_3 stretching vibration is observed at 1450 cm^{-1}, which lies between the characteristic regions for organometallic CO double and single bonds. The X-ray structure shows that this C—O bond has a length of 1.299(8) Å which is intermediate between normal double and single bond values. This interpretation is also confirmed by the observation of a hindered rotation of the methyl group around the C—OCH_3 axis, as it is shown by the variable temperature ^{13}C NMR spectra of $HRu_3(CO)_{10}$-($COCH_3$). A partial π character of the C—OCH_3 bond, as it results from the representation of the ligand bonding as a resonance hybrid of the previously mentioned mesomeric forms, is expected to allow a hindered rotation as observed. It should also be pointed out that the recently published compound $HRu_3(CO)_{10}(CN(CH_3)_2)$ [6] can be treated in the same fashion, considering the $CN(CH_3)_2$ unit as a μ_2-carbyne ligand, although the reported results were not interpreted in this way.

Experimental

Although $HRu_3(CO)_{10}(COCH_3)$ is stable in air, strict exclusion of air and water is required for the preparation, as the salt $Na\{HRu_3(CO)_{11}\}$ is very sensitive towards oxygen. Traces of acid, introduced by the extremely hygroscopic trimethyloxoniumtetrafluoroborate, leads to the formation of $H_4Ru_4(CO)_{12}$ as a side-product. All manipulations were therefore carried out under rigorous exclusion of air and moisture by using Schlenk techniques. The solvents were distilled over drying agents such as sodium—potassium alloy or calcium hydride, and saturated with purified nitrogen.

Preparation of $HRu_3(CO)_{10}(COCH_3)$

A suspension of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and $NaBH_4$ (100 mg, 2.5 mmol) in tetrahydrofuran (50 ml) was stirred for 20 min; the solution turned dark red, due to the formation of $Na[HRu_3(CO)_{11}]$. The reaction mixture was filtered through filter floc, and the filtrate evaporated to dryness. The red residue was dissolved in acetonitrile (50 ml) and solid $[(CH_3)_3O]BF_4$ (ca. 1 g) was added. Then the solution, which turned yellow, was stirred for 1 h, and subsequently filtered through filter floc. The filtrate was brought to dryness and the residue taken into hexane (5 ml). This solution was chromatographed on a column of silica gel (length 10 cm, diameter 2 cm), using hexane as eluant. The slowly moving bright yellow zone was collected, the solvent drawn off, and the residue was crystallized from pentane (5 ml) at —78°C. Alternative methods of purification are thin-layer chromatography (silica gel, cyclohexane) or sublimation (high vacuum, 60°C). The fine crystalline product was dried under high vacuum at room temperature. Yield 210 mg (67%).

X-Ray structural analysis of $HRu_3(CO)_{10}(COCH_3)$

Crystal data: $C_{12}H_4O_{11}Ru_3$, mol. wt. 627.45, monoclinic, a 7.937(2), b 16.880(9), c 14.074(3) Å, β 104.16(3)°, U 1828.9 Å^3, d_c 2.278 g cm^{-3}, Z 4. Space group $P2_1/c$ from systematic absences. Graphite-monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 24.2 cm^{-1}. Intensity data was recorded from a crystal of dimensions 0.46 × 0.25 × 0.37 mm at a temperature of 280 K.

Yellow tablets of $HRu_3(CO)_{10}(COCH_3)$ were deposited from pentane solution, and a single crystal mounted on a glass fibre. This was set on a Stoe STADI-2 two-cricle diffractometer, and aligned such that the crystallographic b axis and the instrument ω axis were co-axial. The a and c cell dimensions, and the angle β were determined by a least-squares fit to the ω medians of the zero layer reflections, whilst b was determined from diffractometer μ angle measurements. 3748 intensities (layers h, 0—20, l) were recorded using graphite-monochromated Mo-K_α radiation. Lp corrections, and an empirical absorption correction, based on an azimuthal scan of the 060 reflection, were applied, and equivalent reflections averaged to give 2535 unique observed [$F > 5\sigma(F)$] intensities.

TABLE 3

ATOM COORDINATES (× 10^4) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 × 10^3)

	x/a	y/b	z/c	U
Ru(1)	3259(1)	536(1)	1637(1)	
Ru(2)	1558(1)	1904(1)	2041(1)	
Ru(3)	1456(1)	507(1)	3124(1)	
C(11)	1930(9)	—387(4)	960(5)	
C(12)	5135(10)	—90(4)	2356(5)	
C(13)	4264(9)	823(4)	584(5)	
C(21)	—997(11)	1965(5)	1498(6)	
C(22)	1509(11)	2559(5)	3127(6)	
C(23)	2114(12)	2718(5)	1229(6)	
C(31)	1750(12)	—575(5)	3350(6)	
C(32)	—48(13)	823(5)	3932(6)	
C(33)	3550(10)	774(4)	4111(5)	
C(34)	—476(10)	314(4)	2025(5)	
C(4)	3955(9)	1487(4)	2458(5)	
C(5)	5746(13)	2452(6)	3428(7)	
H(51)	7014(19)	2555(16)	3693(27)	44(11)
H(52)	5177(48)	2435(15)	3998(19)	44(11)
H(53)	5204(48)	2891(9)	2982(18)	44(11)
O(11)	1262(7)	—923(3)	600(4)	
O(12)	6208(8)	—456(4)	2796(5)	
O(13)	4805(8)	1001(2)	—50(4)	
O(21)	—2419(9)	2017(4)	1182(6)	
O(22)	1432(11)	2954(4)	3744(5)	
O(23)	2459(12)	3178(5)	760(5)	
O(31)	1923(10)	—1247(5)	3498(5)	
O(32)	—926(11)	1005(5)	4404(6)	
O(33)	4775(9)	902(4)	4699(4)	
O(34)	—1664(8)	146(4)	1405(5)	
O(4)	5497(7)	1706(3)	2938(4)	
H(1)	1602(94)	1227(34)	1112(52)	65(22)

The three ruthenium atom positions were derived from a Patterson synthesis, and all the remaining non-hydrogen atoms located from a subsequent Fourier difference map. All these atoms were assigned anisotropic thermal parameters, and the structure refined by full-matrix least-squares using complex neutral-atom scattering factors [10]. A difference map calculated using data with a sin $\theta/\lambda < 0.3$ cut-off revealed the positions of the hydridic and the three methyl hydrogen atoms. These were included in further cycles of least-squares, with the hydridic hydrogen assigned an individual isotropic temperature factor, and the methyl hydrogens a common isotropic thermal parameters; the methyl H atoms were constrained to lie at three of the vertices of a regular tetrahedron with the C—H distance fixed at 1.00 Å. A constraint of the form $U_{22} = (U_{11} + U_{33})/2$ was applied to the anisotropic thermal parameters to reduce correlation involving interlayer scale factors, which were also refined. In the last cycles of least-squares six reflections considered to be suffering severely from extinction were zero weighted, and a weighting scheme of the form $w = [\sigma^2(F) + 0.0005|F|^2]^{-1}$ introduced. The refinement converged to $R = 0.031$ and $R' = \Sigma w^{1/2}\Delta / \Sigma w^{1/2}|F_0| = 0.035$ for the remaining 2529 observed intensities. The highest peak in a final difference map was ca. 0.5 eÅ^{-3}. The final atomic coordinates and associated thermal parameters are presented in Tables 3 and 4, respectively.

Calculations were performed with the University of Cambridge IBM 370/165

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS (Å^2 X 10^3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	37(1)	38(1)	36(1)	—4(1)	11(1)	—1(1)
Ru(2)	46(1)	37(1)	39(1)	—3(1)	7(1)	3(1)
Ru(3)	46(1)	44(1)	35(1)	1(1)	12(1)	0(1)
C(11)	47(3)	48(2)	49(3)	—4(3)	12(3)	—4(3)
C(12)	52(4)	55(2)	57(4)	4(3)	21(3)	8(4)
C(13)	41(3)	46(2)	51(3)	—6(3)	8(3)	0(3)
C(21)	54(4)	57(2)	60(4)	—9(4)	4(4)	5(4)
C(22)	62(4)	62(2)	62(4)	—10(4)	17(4)	10(4)
C(23)	82(5)	63(2)	45(4)	1(4)	2(4)	—7(5)
C(31)	77(5)	65(2)	54(4)	6(4)	11(4)	—4(5)
C(32)	85(5)	69(2)	52(4)	—9(4)	19(4)	10(5)
C(33)	62(4)	52(2)	41(3)	4(3)	9(3)	5(4)
C(34)	56(4)	53(2)	50(3)	—1(3)	19(3)	—8(4)
C(4)	47(3)	44(2)	42(3)	—7(3)	8(3)	—1(3)
C(5)	82(6)	86(3)	90(6)	—41(6)	8(6)	—23(6)
O(11)	68(3)	70(2)	72(3)	—22(3)	14(3)	—21(3)
O(12)	63(3)	84(2)	104(4)	33(4)	26(3)	29(3)
O(13)	79(3)	65(2)	50(2)	3(3)	33(3)	—9(3)
O(21)	60(4)	90(2)	120(5)	—25(4)	—8(4)	13(4)
O(22)	127(5)	101(2)	74(4)	—44(4)	21(4)	25(5)
O(23)	148(6)	108(3)	70(4)	29(4)	29(4)	—32(5)
O(31)	107(5)	97(2)	88(4)	17(4)	0(4)	—9(5)
O(32)	130(6)	124(3)	117(5)	—26(5)	80(5)	8(5)
O(33)	76(3)	74(2)	70(3)	—5(3)	1(3)	1(3)
O(34)	65(3)	71(2)	76(3)	—4(3)	11(3)	—15(3)
O(4)	48(3)	56(1)	64(3)	—12(2)	—2(2)	—8(2)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$

using the 'SHELX' program [11]. Figure 1 was drawn using the ORTEP plotting program. Structure factor tables may be obtained from the authors.

Variable temperature ^{13}C NMR study

The measurements were performed with a Varian XL-100-15 spectrometer using solutions of $HRu_3(CO)_{10}(COCH_3)$. The $HRu_3(CO)_{10}(CO)$ moiety of the molecule was ca. 30% ^{13}C enriched. For the temperature range —100 to —40°C a mixture of CD_2Cl_2 and $CHCl_2F$ (1/3) was used as a solvent, for the range —10 to +90°C $C_6D_5CD_3$ was employed. Tris-acetylacetonatochromium(III) was added as a relaxation agent only for the range —40 to +90°C. The chemical shifts were measured relative to the CD_2Cl_2 and $C_6D_5CD_3$ signals, and related to the standard TMS using the solvent signals at 53.9 ppm (CD_2Cl_2) and 137.3 ppm ($C_6D_5CD_3$).

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