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The Reactivity of $HRu_3(CO)_9C_2{\cdot}CMe_3$. The Hydrogenation of Coordinated t-Butyl-acetylene to *neo*-Hexane and the Crystal Structure of the Intermediate Trihydride $H_3Ru_3(CO)_9C{\cdot}CH_2{\cdot}CMe_3$

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The reaction of $Ru_3(CO)_{12}$ *with 3-3-dimethyl-but-1-yne (t-Butylacetylene) gives the mono-hydride* $HRu_3(CO)_9C_2Bu^t$ *in good yields. This complex reacts in hydrocarbon solvents with molecular hydrogen, to give the tri-hydride* $H_3Ru_3(CO)_9C{\cdot}CH_2{\cdot}CMe_3$ *which, upon further hydrogenation, affords* $H_4Ru_4(CO)_{12}$ *and neo-hexane. In this way, a full hydrogenation cycle can be obtained; however, low yields of the hydrogenated product, and some decomposition to metal powder are also observed. The probable intermediate steps of these reactions are discussed.*

The structure of the intermediate $H_3Ru_3(CO)_9C{\cdot}CH_2{\cdot}CMe_3$ *has been studied by X-ray diffraction; the complex crystallizes in the triclinic system, space group* $P\bar{1}$ *with* $a = 8.781(3)$, $b = 9.253(3)$, $c = 14.910(4)$ Å, $\alpha = 86.17(5)$, $\beta = 85.69(5)$, $\gamma = 63.50(4)^\circ$.

The ruthenium atoms were located by the Patterson method and the remaining carbon and oxygen atoms by Fourier-difference maps.

A least-squares anisotropic refinement led to $R = 0.0385$ *for 4028 observed reflections with* $I \geqslant 3\sigma(I)$.

The title compound belongs to the series of methylidine complexes with a 'tetrahedral' Ru_3C *core; each ruthenium atom links three terminal carbonyl groups and a chain–*CH_2*–*$C(CH_3)_3$ *is bonded to the apical carbon atom of the core.*

The presence of the three bridging hydridic atoms is discussed and a comparison with the parent $HRu_3(CO)_9C_2C(CH_3)_3$ *complex is made.*

Introduction

The reaction of $Ru_3(CO)_{12}$ with $HC_2{\cdot}CMe_3$ leads to high yields of mono-hydride $HRu_3(CO)_9C_2{\cdot}CMe_3$ (complex I) [1, 2].

This allowed a detailed study of the chemistry of this complex, which reacts with excess of 3,3-dimethyl-but-1-yne [3, 4], isopropenylacetylene [5] and diphenyl-acetylene [6] to give tri- [3, 5, 6] and tetra-alkyne [4] substituted clusters.

In all the above reactions hydridic hydrogen shift is observed, as deuteration experiments and chemical evidence [6] indicate. The analysis of the complex I reactivity was extended with respect to molecular hydrogen and the reactions were studied with the aid of g.l.c. technique.

The reported [7] reaction of (I) with molecular hydrogen gives as main products $H_4Ru_4(CO)_{12}$ and an hydridic derivative (complex II) formulated as $H_2Ru_3(CO)_9(HC_2Bu^t)$ on the basis of ^1H NMR and mass spectral evidence. An X-ray analysis of complex II has shown that it does not correspond to the previous formula and a reinvestigation of its mass spectral behaviour shows a strong dependence from the operative conditions, with easy de-hydrogenation at temperatures higher than room. Low yield products of the reaction are the 'asymmetric' di-hydridic species $H_2Ru_3(CO)_9(HC_2CMe_3)$ (complex III) and (IIIa) $H_2Ru_3(CO)_9(C_2(H)CMe_3)$.

A further hydrogenation of (II) gives $H_4Ru_4(CO)_{12}$ and $H_3C{\cdot}CH_2{\cdot}CMe_3$ (2,2-dimethyl-butane, neo-hexane) in small yields. Since $H_4Ru_4(CO)_{12}$ yields (I) when reacted with t-butyl-acetylene, a full hydrogenation cycle, from t-butyl-acetylene to neo-hexane is obtained. Complex II is therefore an intermediate in this process; its correct formula corresponds to the $H_3Ru_3(CO)_9C{\cdot}CH_2{\cdot}C(CH_3)_3$ complex and is closely related to $H_3Ru_3(CO)_9CMe$ (complex IIa, X-ray analysis) [8] and $H_3Os_3(CO)_9CMe$ (complex IIb, proposed) [9].

(IIa) was obtained either by reducing $Ru_3(CO)_{12}$ with $NaBH_4$ or by reacting $H_4Ru_4(CO)_{12}$ with ethylene [10].

(IIb) was obtained by treating $H_2Os_3(CO)_{10}$ either with ethylene or acetylene, and by further reversible hydrogenation [10], thus showing a relationship with the alkene and alkyne chemistry of the osmium cluster. The reactions of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ with 3,3-dimethyl-but-1-ene and of $H_4Ru_4(CO)_{12}$ with 3,3-dimethyl-but-1-yne were thus investigated.

Experimental

$Ru_3(CO)_{12}$ [11] and $H_4Ru_4(CO)_{12}$ [12] were obtained by established procedures, as well as (I) [1]. The 3,3-dimethyl-but-1-yne, 3,3-dimethyl-but-1-ene and 2,2-dimethyl-butane were obtained by Farchan Division and Fluka; the latter was used as g.l.c. standard; the former two were checked for purity before use, by g.l.c. methods. The solvents and gases were dried prior of use.

Synthesis of (II)

The reaction of (I) with H_2 has already been reported [7]. When heptane was used as solvent, $H_4Ru_4(CO)_{12}$ was also obtained; the use of octane leads to the completion of the reaction within one hour. However, some metal powder and only trace amounts of $H_4Ru_4(CO)_{12}$ were the side-products. G.l.c. evidence showed the presence of some neo-hexane in the reaction solution.

Synthesis of (III)

This dark-yellow complex is sometimes obtained, in trace amounts, in the above reaction; however, a reproducible synthesis, in reasonable yields, was not obtained by these procedure.

Complex (III) was obtained in a way similar to that used for $H_2Ru_3(CO)_9(C_2Ph_2)$ [13], by treating $Ru_3(CO)_{12}$ (300 mg *ca.*, 0.5 m*M*) with 50 ml of 1 *N* KOH in 120 ml CH_3OH, at room temperature, under nitrogen, stirring for about 15 hours; then 3,3-dimethyl-but-1-yne (1 ml) was added, and the solution was warmed to 50 °C for 6 hours. The resultant mixture, acidified with 2 *N* sulphuric acid, was extracted with CCl_4 and purified by t.l.c. Yields of about 5% of (III) and a mixture of $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$, (II), (I) (these latter two in trace amounts) and unknown derivatives, were obtained.

Prolonged storage of (III) resulted in partial decomposition to $H_4Ru_4(CO)_{12}$, (I), (II) and metal powder.

The same reaction in presence of 2,2-dimethyl-but-1-ene yielded only $H_4Ru_4(CO)_{12}$ (20%) and $H_2Ru_4(CO)_{13}$ (10%), that is the same product obtained in hydrocarbon solution.

Reactions of (I) and (II) with Hydrogen

The reactions of (I) leading to (II) have already been discussed. In the present study, however, the reaction mixtures were checked for the presence of free alkyne, alkene or alkane in solution, by means of g.l.c. By treating (I) in refluxing octane, for 1 hour, as reported above, some 2,2-dimethyl-butane is found in the reaction mixture. By refluxing in octane for 1 hour 40 min. (II) in presence of a slow hydrogen flow, a dark solution is obtained, which contains metal powder (about half of (II) can be considered decomposed) and trace amounts of $H_4Ru_4(CO)_{12}$. In the solution, some neo-hexane and lower amount of 3,3-dimethyl-but-1-ene are found. By treating $H_4Ru_4(CO)_{12}$ with 3,3-dimethyl-but-1-yne, besides of the already reported complexes, some 3,3-dimethyl-but-1-ene can be detected in solution.

Reaction of (II) with Hydrogen and Carbon Monoxide

By treating (II) with a slow flow of hydrogen and of CO (50%) in refluxing octane for 1 hour, an orange solution is obtained, with a metallic mirror appearance on the glass inlet of the gases; some $H_4Ru_4(CO)_{12}$ and a good yield of $Ru_3(CO)_{12}$ is obtained, whereas the solution appears free of hydrocarbons other than solvent.

Reactions of $Ru_3(CO)_{12}$ with 3,3-Dimethyl-but-1-ene

By treating the ruthenium carbonyl with a 5:1 molar excess of alkene, in 40–70° light petroleum, a 40% of unreacted ruthenium carbonyl is recovered after 8 hours, and decomposition is observed, together with trace amounts of $H_4Ru_4(CO)_{12}$ and (IIIa). Better yields of the same products, and a 30% of $H_2Ru_4(CO)_{13}$ are recovered in heptane (same reaction time); only a 15% of ruthenium carbonyl remains unreacted.

In sealed vials, under vacuum (solvent heptane, 150 °C, 15 hours), some (IIIa) and a 10% of (I) is obtained, together with traces of (II). No organic reduction products were detected.

Reaction of $H_4Ru_4(CO)_{12}$ with 3,3-Dimethyl-but-1-yne

A 3:1 molar excess of alkyne was refluxed in heptane for 135 min, under nitrogen, with $H_4Ru_4(CO)_{12}$. A 20% *ca.* of the hydride was recovered unreacted, together with (I) (15% yield) and trace amounts of (II) and (III). Longer reaction times lead to the products of the reaction of (I) with excess of alkyne [3, 4, 7]. No 2,2-dimethylbutane was found in the reaction solution.

Reaction of $H_4Ru_4(CO)_{12}$ with 3,3-Dimethyl-but-1-ene

The ruthenium hydride was treated with a 5:1 molar excess of alkene in sealed vials (heptane, under vacuum, 150 °C, 12 hours): traces of (IIIa) and about a 20% of (I) were obtained.

Analyses of the Products

The elemental analyses were performed with an F & M C, H, N Analyzer and a Perkin-Elmer 303 Atomic Absorption Spectrophotometer; as expected, the values for (I), (II), (III) and (IIIa) do not show significant differences, and are not reported.

The IR spectra were registered on a Beckman IR-12, and the ^1H NMR on a Jeol C 60 HL instrument.

G.l.c. Runs

These were performed on a Carlo Erba model B/F Fractovap, using a 4 m column filled with 20% silicone oil 702 on chromosorb P (J. Manville) 60/80 mesh. The column was operated at 60 °C using He as carrier gas at a flow rate of 6 l/h.

Mass Spectra

The mass spectra were obtained on a Varian CH-5 and on a Hitachi Perkin-Elmer RMU 6H; both were equipped with electron impact ion sources, and were operated with the inlet system at room temperature. Perfluoroalkanes were used as standards, and the peak at 643 m/e has been found particularly useful for counting the parent ions of (II) (644 m/e), (III) and (IIIa) (642) m/e); the presence of this signal, however, strongly modifies the isotopic pattern of the parent ions.

X-ray Data Collection and Structure Determination

Crystallization of (II): this green-yellow complex is poorly soluble in heptane. Crystals of II suitable for the X-ray analysis were obtained together with some $H_2Ru_4(CO)_{13}$ crystals from an heptane-$CHCl_3$ (1:1) solution cooled at −10 °C, under nitrogen, after standing for some days. Storage of the solution for long time at 0 °C yielded some (III). Neither (III) nor (IIIa) could be obtained in crystals suitable for X-rays. Crystal data: a = 8.781(3), b = 9.253(3), c = 14.910(4) Å, α = 86.17(5), β = 85.68(5), γ = 63.50(4)°, V = 1080.4 Å^3, M = 641.48, Z = 2, D_c = 1.97 g cm^{-3}, MoKα radiation (0.7107 Å), μ-MoKα = 19.12 cm^{-1}, triclinic space group $P\bar{1}$ from structure determination. Unit cell parameters were determined from least-squares refinement of the θ angles of 15 reflections accurately centered on a Nonius four-circle automatic diffractometer.

A total of 6297 unique reflections were collected on the same diffractometer; 4028 of these with $I \geqslant 3\sigma(I)$ were considered observed and used in the analysis.

The intensity data were corrected for Lorentz and polarization factors, but no correction for absorption was applied. The three ruthenium atoms were located from a three-dimensional Patterson map, and the subsequent C and O atoms by Fourier-difference maps. The refinement was carried out by least-squares full matrix cycles using the SHELX 70 system of computer programs with isotropic thermal parameters for the initial cycles and anisotropic for the last ones.

At this stage (R = 0.0437) the difference map showed a wide set of peaks 0.5 ÷ 1.2 e Å^{-3} high. Some of them are near the carbon atoms of the organic ligand but have no chemical significance. Three of the lowest ones fit satisfyingly the expected hydrogen atoms bridging the Ru–Ru bonds and were introduced in the refinement and were kept fixed.

TABLE I. Fractional Coordinates of $H_3Ru_3(CO)_9[(CH_2\text{-}C(CH_3)_3]$ with the Estimated Standard Deviation in Parentheses.

Atom	x/a	y/b	z/c
Ru(1)	0.22688(5)	0.09049(5)	0.12492(3)
Ru(2)	−0.06829(5)	0.35460(4)	0.19363(3)
Ru(3)	0.06179(5)	0.05460(5)	0.28986(3)
C(1)	0.4455(8)	−0.0726(8)	0.1544(4)
C(2)	0.3217(8)	0.2195(9)	0.0646(4)
C(3)	0.2108(9)	−0.0072(9)	0.0143(5)
C(4)	−0.1794(8)	0.4818(7)	0.2946(4)
C(5)	−0.0102(10)	0.5183(8)	0.1380(4)
C(6)	−0.2911(10)	0.4219(8)	0.1347(5)
C(7)	0.2602(8)	−0.1073(8)	0.3422(4)
C(8)	−0.0347(9)	0.1427(8)	0.4033(4)
C(9)	−0.0643(11)	−0.0766(9)	0.2891(6)
C(10)	0.1691(7)	0.2107(6)	0.2477(3)
C(11)	0.3156(10)	0.2359(10)	0.2805(5)
C(12)	0.3202(9)	0.3060(10)	0.3654(5)
C(13)	0.4649(17)	0.3375(23)	0.3780(9)
C(14)	0.2831(29)	0.2225(24)	0.4499(7)
C(15)	0.1611(22)	0.4724(22)	0.3794(19)
O(1)	0.5745(7)	−0.1693(7)	0.1709(4)
O(2)	0.3739(9)	0.2998(9)	0.0283(4)
O(3)	0.1989(8)	−0.0573(9)	−0.0487(4)
O(4)	−0.2485(7)	0.5545(7)	0.3543(4)
O(5)	0.0154(10)	0.6166(7)	0.1050(4)
O(6)	−0.4117(8)	0.4553(8)	0.1044(5)
O(7)	0.3802(7)	−0.2037(7)	0.3727(4)
O(8)	−0.1011(8)	0.1933(8)	0.4700(3)
O(9)	−0.1371(11)	−0.1514(9)	0.2874(6)
H(12)	0.0139	0.2411	0.0993
H(13)	0.1304	−0.0262	0.1794
H(23)	0.8942	0.1912	0.2275

It was impossible to locate the hydrogen atoms of the organic ligand, and they were calculated and kept fixed during the last cycles. The final R's are R = 0.0385 and R_w = 0.0439 with w = $1/(\sigma(F)^2 + 0.001\,F^2)$. The atomic fractional coordinates are listed in Table I and the thermal parameters in Table II. A list of F_o and F_c is available from the authors (G.G.).

Results and Discussion

Spectroscopic Results. IR Spectra

All the spectra were registered in heptane solution; those of (I) and (II) have been already reported [1, 7] and are shown here for comparison. In the CO stretching region, the following absorptions were

TABLE II. Thermal Parameters ($\times 10^4$ for Ru and $\times 10^3$ for C and O) with their e.s.d. s in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	519(2)	564(2)	511(2)	–47(2)	–38(2)	–215(2)
Ru(2)	634(2)	402(2)	461(2)	–9(1)	–56(2)	–199(2)
Ru(3)	577(2)	456(2)	530(2)	60(2)	–68(2)	–217(2)
C(1)	67(4)	68(3)	70(4)	–8(2)	–5(3)	–24(3)
C(2)	71(4)	79(4)	61(3)	–5(2)	2(2)	–37(3)
C(3)	69(4)	83(4)	66(4)	–27(3)	6(3)	–23(3)
C(4)	69(3)	52(3)	64(3)	–11(2)	3(3)	–21(2)
C(5)	97(5)	58(3)	66(3)	3(3)	1(3)	–34(3)
C(6)	92(5)	58(3)	83(4)	10(3)	–24(4)	–26(3)
C(7)	67(3)	60(3)	69(4)	10(3)	–9(3)	–20(3)
C(8)	79(4)	73(4)	58(3)	10(3)	–5(3)	–32(3)
C(9)	97(5)	66(4)	110(6)	13(4)	–6(4)	–41(4)
C(10)	64(3)	58(3)	45(2)	4(2)	–11(2)	–35(2)
C(11)	89(5)	96(5)	83(5)	–19(4)	–16(4)	–42(4)
C(12)	83(4)	98(5)	81(5)	–17(4)	–18(3)	–50(4)
C(13)	161(11)	315(21)	139(10)	–52(12)	–27(9)	–169(14)
C(14)	398(26)	296(21)	62(5)	–2(8)	–35(10)	–281(22)
C(15)	193(15)	175(16)	521(41)	–210(23)	–203(22)	72(13)
O(1)	72(3)	89(3)	113(4)	–17(3)	–18(3)	–1(3)
O(2)	115(4)	127(5)	104(4)	10(4)	15(4)	–71(4)
O(3)	112(4)	158(6)	90(4)	–59(4)	5(3)	–62(4)
O(4)	91(4)	83(3)	92(4)	–29(3)	13(3)	–13(3)
O(5)	166(6)	86(4)	108(4)	20(3)	6(4)	–74(4)
O(6)	99(4)	105(4)	153(6)	30(4)	–64(4)	–45(3)
O(7)	81(3)	83(3)	114(4)	32(3)	–22(3)	–8(3)
O(8)	111(4)	110(4)	60(3)	–3(3)	22(3)	–32(3)
O(9)	154(6)	125(5)	194(8)	12(5)	–26(6)	–107(5)

observed: (I): 2097 m, 2070 vs, 2054 vs, 2022 vs, 1992 m, cm^{-1}. (II): 2080 vs, 2038 vs, 2018 vs, 2000 s (sh), cm^{-1}. (III): 2108 s, 2080 vs, 2072 s (sh), 2057 vs, 2044 s (sh) 2018 vs, 1995 s (sh), cm^{-1}. (IIIa): 2100 m, 2087 s, 2074 m, 2057 vs, 2014 vs, 1998 s (sh), 1987 s (sh), cm^{-1}.

The latter two compounds show the same number of signals. The spectrum of (III) is well comparable with the spectra of $H_2Ru_3(CO)_9X$ ($X = C_2Ph_2$ [13], X = S, Se, Te [14]).

^1H NMR Spectra

In the already reported spectrum of (II) [7] the intensities ratio must be modified as follows: 4.4 (s, 2H), 1.2 (s, 9H), –17.5 (s, 3H) δ.

The spectrum of (III) shows signals at 8.35 (s, 1 H), 1.10 (s, 9 H) and –18.7 (broad, 2 H) δ. Finally, (IIIa) shows signals at 0.5 (s, 3 H), 1.2 (s, 6 H), 6.0 (m, broad, 1 H), and –19.5 (broad, 2 H) δ.

All the spectra were registered in CCl_4.

Mass Spectra

(II) was formulated as di-hydride also on the basis of accurate counting of the mass spectra, registered with the inlet system at 50 °C. However, when the inlet system is maintained at room temperature, P^+ 644 m/e is observed (standard perfluoroalkanes). Examples of dependence of the mass spectra from the geometry of the instrument and from the operating conditions have been already reported [15, 16]. Thus, evidence of easy dehydrogenation of (II) to complexes like (III) or (IIIa) is obtained, in these conditions.

The mass spectra of (III) and (IIIa) are similar each other, and to that obtained from (II) at 50 °C; P^+ 642 m/e (internal standard perfluoroalkane) is observed, together with release of 9 COs and competitive loss of hydrogen (H_2).

In all the above spectra, intense $Ru_3C_2^+$ ions are observed; this is found also for (I) [1] and for other $H_nRu_3(CO)_9L$ derivatives [17]. On the contrary, we could not detect Ru_3C^+ ions, whereas Co_3C^+ ions are typical for the $Co_3(CO)_9CR$ complexes [18]. This could be an indirect evidence for a rearrangement of (II) in the mass spectrometer.

From the above results we propose for (III) a structure similar to those of the di-hydrides $H_2Ru_3(CO)_9X$ [13, 14], and for the isomeric (IIIa) a structure comparable with that of $H_2Os_3(CO)_9$ ($C = CH_2$) [19].

TABLE III. Interatomic Distances (Å) for $H_3Ru_3(CO)_9$-$[CCH_2C(CH_3)_3]$.

Ru(1)–Ru(2)	2.832(1)	Ru(3)–C(10)	2.091(5)
Ru(1)–Ru(3)	2.836(1)	Ru(3)–H(13)	1.80
Ru(2)–Ru(3)	2.820(1)	Ru(3)–H(23)	1.74
Ru(1)–C(1)	1.899(6)	C(10)–C(11)	1.525(9)
Ru(1)–C(2)	1.886(7)	C(11)–C(12)	1.471(9)
Ru(1)–C(3)	1.976(6)	C(12)–C(13)	1.453(11)
Ru(1)–C(10)	2.116(5)	C(12)–C(14)	1.524(14)
Ru(1)–H(12)	1.82	C(12)–C(15)	1.564(14)
Ru(1)–H(13)	1.77	C(1)–O(1)	1.119(8)
Ru(2)–C(4)	1.897(6)	C(2)–O(2)	1.127(8)
Ru(2)–C(5)	1.924(7)	C(3)–O(3)	1.107(8)
Ru(2)–C(6)	2.022(7)	C(4)–O(4)	1.116(7)
Ru(2)–C(10)	2.098(5)	C(5)–O(5)	1.107(8)
Ru(2)–H(12)	1.72	C(6)–O(6)	1.087(8)
Ru(2)–H(23)	1.72	C(7)–O(7)	1.137(8)
Ru(3)–C(7)	1.900(6)	C(8)–O(8)	1.131(8)
Ru(3)–C(8)	1.896(7)	C(9)–O(9)	1.136(9)
Ru(3)–C(9)	1.975(8)		

X-ray Structure of (II)

The bond distances and angles are listed in Tables III and IV respectively.

The complex (Fig. 1) is formed by a triruthenium cluster capped by a trihapto $C \cdot CH_2 \cdot CMe_3$ ligand. Each ruthenium atom is bonded to two equatorial and one axial carbonyl group; three hydrogen atoms bridge the three Ru–Ru bonds.

The Ru_3 cluster is slightly isosceles (Table III); this feature differentiates it from the $H_3Ru_3(CO)_9$-CCH_3 complex, which has an equilateral cluster (Table V).

The Ru–Ru distances are between the values of the parent compound (I) and of (IIa) (Table V); the greatest difference is between (I) and (II) owing to the rearrangement following the hydrogenation of the ligand and of the cluster. In the organic ligand $C \cdot CH_2CMe_3$ some not good values of angles or distances can be attributed to the great thermal motion of the methyls. The C10–C11 distance (1.525(9) Å), very close to a single bond, could explain the

TABLE IV. Bond Angles (°) for $H_3Ru_3(CO)_9[CCH_2C(CH_3)_3]$.

Ru(2)–Ru(1)–Ru(3)	59.7(0)	Ru(3)–Ru(2)–C(4)	96.0(2)
Ru(2)–Ru(1)–C(1)	143.9(2)	Ru(3)–Ru(2)–C(5)	144.0(2)
Ru(2)–Ru(1)–C(2)	94.9(2)	Ru(3)–Ru(2)–C(6)	116.5(2)
Ru(2)–Ru(1)–C(3)	118.4(2)	Ru(3)–Ru(2)–C(10)	47.6(1)
Ru(2)–Ru(1)–C(10)	47.5(1)	Ru(3)–Ru(2)–H(12)	85.2(0)
Ru(2)–Ru(1)–H(12)	35.7(0)	Ru(3)–Ru(2)–H(23)	35.6(0)
Ru(2)–Ru(1)–H(13)	83.7(0)		
		C(4)–Ru(2)–C(5)	92.3(3)
Ru(3)–Ru(1)–C(1)	94.9(2)	C(4)–Ru(2)–C(6)	92.2(3)
Ru(3)–Ru(1)–C(2)	142.5(2)	C(4)–Ru(2)–C(10)	98.7(2)
Ru(3)–Ru(1)–C(3)	121.2(2)	C(4)–Ru(2)–H(12)	174.5(2)
Ru(3)–Ru(1)–C(10)	47.2(1)	C(4)–Ru(2)–H(23)	97.0(2)
Ru(3)–Ru(1)–H(12)	83.1(0)		
Ru(3)–Ru(1)–H(13)	37.9(0)	C(5)–Ru(2)–C(6)	98.0(3)
		C(5)–Ru(2)–C(10)	96.6(3)
C(1)–Ru(1)–C(2)	91.8(3)	C(5)–Ru(2)–H(12)	89.9(2)
C(1)–Ru(1)–C(3)	96.3(3)	C(5)–Ru(2)–H(23)	170.6(2)
C(1)–Ru(1)–C(10)	96.6(2)		
C(1)–Ru(1)–H(12)	177.5(2)	C(6)–Ru(2)–C(10)	161.4(2)
C(1)–Ru(1)–H(13)	90.3(2)	C(6)–Ru(2)–H(12)	82.6(2)
		C(6)–Ru(2)–H(23)	81.0(2)
C(2)–Ru(1)–C(3)	94.5(3)		
C(2)–Ru(1)–C(10)	95.3(2)	C(10)–Ru(2)–H(12)	86.0(1)
C(2)–Ru(1)–H(12)	90.7(2)	C(10)–Ru(2)–H(23)	82.7(2)
C(2)–Ru(1)–H(13)	177.8(2)		
		H(12)–Ru(2)–H(23)	80.8(0)
C(3)–Ru(1)–C(10)	163.5(2)		
C(3)–Ru(1)–H(12)	83.5(2)	Ru(1)–Ru(3)–Ru(2)	60.1(0)
C(3)–Ru(1)–H(13)	84.6(2)	Ru(1)–Ru(3)–C(7)	96.1(2)
		Ru(1)–Ru(3)–C(8)	146.2(2)
C(10)–Ru(1)–H(12)	83.2(1)	Ru(1)–Ru(3)–C(9)	116.8(3)
C(10)–Ru(1)–H(13)	85.1(1)	Ru(1)–Ru(3)–C(10)	48.0(1)
		Ru(1)–Ru(3)–H(13)	37.1(0)
H(12)–Ru(1)–H(13)	87.2(0)	Ru(1)–Ru(3)–H(23)	76.9(0)

(continued overleaf)

TABLE IV. *(continued)*

Ru(1)–Ru(2)–Ru(3)	60.2(0)	Ru(2)–Ru(3)–C(7)	143.6(2)
Ru(1)–Ru(2)–C(4)	146.5(2)	Ru(2)–Ru(3)–C(8)	95.1(2)
Ru(1)–Ru(2)–C(5)	95.3(2)	Ru(2)–Ru(3)–C(9)	117.9(2)
Ru(1)–Ru(2)–C(6)	118.8(2)	Ru(2)–Ru(3)–C(10)	47.8(1)
Ru(1)–Ru(2)–C(10)	48.0(1)	Ru(2)–Ru(3)–H(13)	83.6(0)
Ru(1)–Ru(2)–H(12)	38.0(0)	Ru(2)–Ru(3)–H(23)	35.2(0)
Ru(1)–Ru(2)–H(23)	77.2(0)		
		Ru(3)–C(7)–O(7)	179.1(7)
C(7)–Ru(3)–C(8)	92.1(3)	Ru(3)–C(8)–O(8)	175.5(7)
C(7)–Ru(3)–C(9)	96.9(3)	Ru(3)–C(9)–O(9)	179.0(9)
C(7)–Ru(3)–C(10)	95.9(2)		
C(7)–Ru(3)–H(13)	92.6(2)	Ru(1)–C(10)–Ru(2)	84.5(2)
C(7)–Ru(3)–H(23)	171.9(2)	Ru(1)–C(10)–Ru(3)	84.8(2)
C(8)–Ru(3)–C(9)	94.5(3)	Ru(2)–C(10)–Ru(3)	84.6(2)
C(8)–Ru(3)–C(10)	98.7(3)		
C(8)–Ru(3)–H(13)	173.7(2)	Ru(1)–C(10)–C(11)	113.9(4)
C(8)–Ru(3)–H(23)	96.0(2)		
		Ru(2)–C(10)–C(11)	137.1(4)
C(9)–Ru(3)–C(10)	161.3(3)		
C(9)–Ru(3)–H(13)	80.7(3)	Ru(3)–C(10)–C(11)	133.1(4)
C(9)–Ru(3)–H(23)	82.8(2)		
		C(10)–C(11)–C(12)	127.4(7)
C(10)–Ru(3)–H(13)	85.1(1)		
C(10)–Ru(3)–H(23)	82.6(1)	C(11)–C(12)–C(13)	118.1(8)
		C(11)–C(12)–C(14)	114.6(7)
H(1)–Ru(3)–H(23)	79.4(0)	C(11)–C(12)–C(15)	111.4(9)
Ru(1)–C(1)–O(1)	179.3(6)	C(13)–C(12)–C(14)	109.8(9)
Ru(1)–C(2)–O(2)	178.1(7)	C(13)–C(12)–C(15)	104.6(1.1)
Ru(1)–C(3)–O(3)	177.8(7)		
		C(14)–C(12)–C(15)	95.6(1.6)
Ru(2)–C(4)–O(4)	177.7(6)		
Ru(2)–C(5)–O(5)	176.7(8)	Ru(1)–H(12)–Ru(2)	106.3(0)
Ru(2)–C(6)–O(6)	178.2(7)	Ru(1)–H(13)–Ru(3)	105.0(0)
		Ru(2)–H(23)–Ru(3)	109.2(0)

TABLE V. Some Relevant Distances and Angles of the (I), (II) and (IIa) Complexes.

Complex	Ru–Ru	Ru–C_{ap}	Ru–C_{ap}–Ru	Ru–C_{ap}–C	Ref.
$HRu_3(CO)_9(C_2CMe_3)$ (I)	2.795(3) Å	1.947(3) Å		153.7(2)°	2
	2.799(3)	2.207(3)		75.5(1)	
	2.792(3)	2.214(3)		75.3(1)	
$H_3Ru_3(CO)_9(CCH_2CMe_3)$ (II)	2.832(1)	2.116(5)	84.5(2)°	113.9(4)	this work
	2.836(1)	2.098(5)	84.8(2)	137.1(4)	
	2.820(1)	2.091(5)	84.6(2)	133.1(4)	
$H_3Ru_3(CO)_9(CCH_3)$ (IIa)	2.841(6)	2.086(10)	86.0(4)	127.8(5)	8
	2.844(6)	2.078(12)		128.5(10)	
	2.841(6)	2.086(10)			

relatively easy release of alkane; values ranging from 1.36 to 1.54 Å were found in structurally related complexes [20, 21]. The linkage of the organic ligand to the cluster gives rise to a 'tetrahedral' Ru_3C cluster, belonging to the wide set of M_3C clusters with M = Co [22], Fe [23].

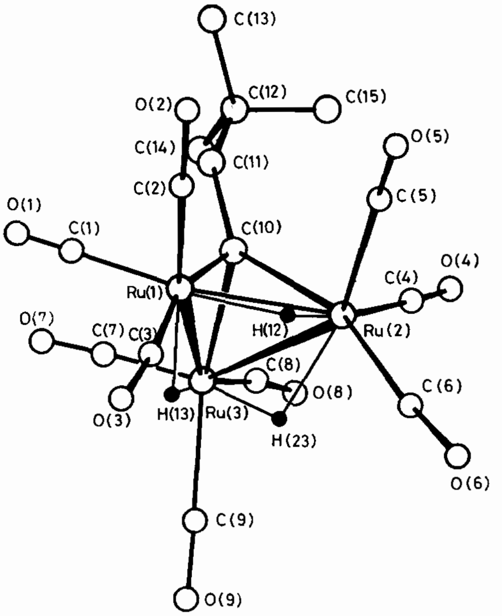

Fig. 1. The molecular structure of $H_3Ru_3(CO)_9C \cdot CH_2 \cdot CMe_3$ with the atom labelling scheme.

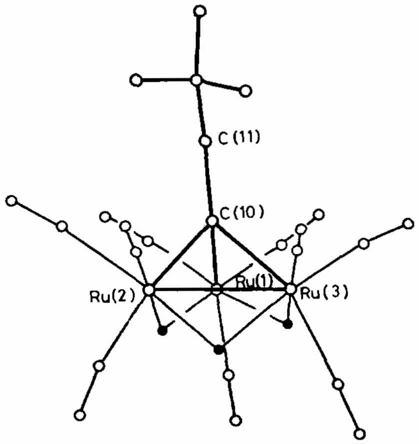

Fig. 2. View of the $H_3Ru_3(CO)_9C \cdot CH_2 \cdot CMe_3$ molecule normally to the Ru(2)–Ru(3) bond.

A very slight difference (Table V) exists between the Ru–C_{ap} distances of (II) and (IIa), so the shortening of the cluster Ru–Ru distances of (II) with respect to (IIa) causes smaller Ru–C–Ru angles.

The feature that markedly differentiates the two $C-CH_3$ and $C-CH_2-CMe_3$ ligands lies in the disposition of the C_{ap}–C bond with respect to the Ru_3 plane. While in the ethylidine complex the C_{ap}–C bond is practically perpendicular to the Ru_3 plane (Ru–C–C av. 128°) in the complex (II) it is inclined toward Ru1 (Ru1–C10–C11 113.9, Ru2–C10–C11 137.1, Ru3–C10–C11 133.1°). The projection of the molecule down the direction of the bisector of the Ru2–Ru1–Ru3 angle (Fig. 2) shows that Ru1, C10, C11, C12, C3, O3 lie roughly on a plane (Table VI). The Fig. 2 shows also that this plane can be considered as a pseudo symmetry plane of the molecule nearly perpendicular to the Ru_3 plane. This distortion can be attributed to the great hindrance of the CMe_3 group that causes probably a distortion around C10 and C11 (C10–C11–C12 127.4°) to avoid the interference of the methyl groups with the $Ru_3(CO)_9$ moiety. The bridging hydrides lie in the expected position between the axial and equatorial carbonyl groups below the plane of the cluster, on the opposite side of the organic ligand. The arrangement is close to that found in (I) and (IIa): the hydrogen atoms are nearly *trans* to equatorial CO and the values of angles and distances are near that of literature [2], but a discussion about them is impossible owing to the uncertainty of the hydrogen atoms positions.

The terminal CO groups are closely similar in their position with respect to the cluster to the compound IIa, but a great difference arises going from (I) to (II). A comparison of I and II, evidences, beside a small but significant closing of CO among them, a different orientation of the $(CO)_3$ groups

TABLE VI. Equation of Least-squares Planes in the Form AX + BY + CZ = D, in Fractional Coordinates, Referred to the Cell Axes. $\chi^2 = \Sigma(d/\sigma)^2$ gives the statistical significance of the planarity. Distances (A × 10^2) for the atoms from the planes are given below the respective atoms with the e.s.d's in parentheses.

Atoms				A	B	C	D	χ^2
Ru(1)	Ru(2)	Ru(3)		7.17	5.82	8.44	3.21	
Ru(1)	C(10)	C(11)	C(12)	−0.08	7.26	−6.54	−0.17	224
−0.9(1)	6(1)	2(1)	−2(1)					
C(3)	O(3)	H(23)						
O(1)	5(1)	O(0)						

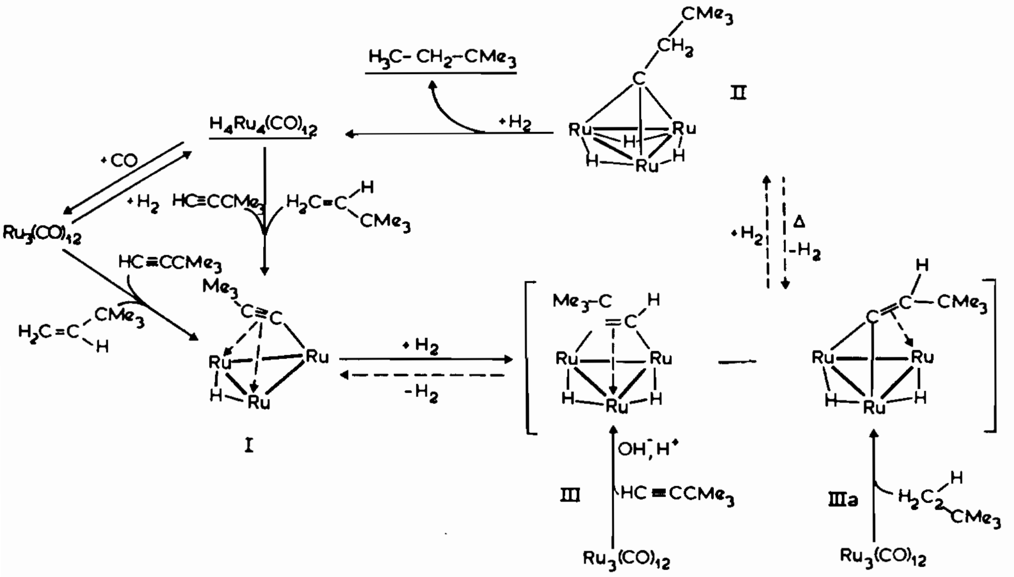

Fig. 3. Proposed reaction scheme. Dotted lines indicate indirect evidence.

with respect to the Ru_3 plane due to the different and asymmetric type of coordination of the organic ligand in (I).

The Hydrogenation of 3,3-Dimethyl-but-1-yne

The evidence reported above indicates that (I) reacts with excess of hydrogen to give (II); probable intermediates could be (III) or (IIIa). The easy dehydrogenation of (II) in the mass spectrometer could indicate a partial reversibility of the reaction. In the presence of hydrogen, (II) gives neo-hexane and $H_4Ru_4(CO)_{12}$, which has been shown to give (I) when treated with 3,3-dimethyl-but-1-yne. This step of the reaction, however, is sided by the formation of considerable quantity of metal powder. The use of a mixture of CO and H_2 strongly reduces the formation of metal powder and the yield in neo-hexane is reduced to zero; some $Ru_3(CO)_{12}$ is obtained instead of $H_4Ru_4(CO)_{12}$.

Thus, probably, either the metal powder is effective in promoting the hydrogenation to neo-hexane, or this latter is obtained by partial decomposition of (II).

Both $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ can dehydrogenate 3,3-dimethyl-but-1-ene, to give (I). Thus, a reversible hydrogenation process occurs for this alkene; its chemistry is related to the one of the alkyne in a way comparable to that discussed for ethylene and acetylene [10].

On the basis of the discussed evidence, we propose the reaction scheme shown in Fig. 3. The same structures are involved, which were found for the formation of (IIb) [10]; however, in the reactions with osmium, (IIb) was a side product of the hydrogenation of ethylene, and its reaction with hydrogen did not give ethane.

Indirect evidence for the scheme proposed can be found in the hydrogenation of acetonitrile on iron clusters [24] and in the reactions of $Ru_3(CO)_{12}$ with nitrobenzene and aniline [25]; intermediates with 'apical' organic ligands were found or proposed in both cases.

Finally, the equilibrium between structures like (I) and (III) or (IIIa) has been considered in order to explain the fluxionality of alkynes on trimetallic clusters [26].

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