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Reactivity of the Ruthenium Carbonyl Hydride $HRu_3(CO)_9C_2C(CH_3)_3$

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In the products of the reaction of $Ru_3(CO)_{12}$ and 3,3-dimethyl-1-butyne, hydrogen transfer and alkyne oligomerization are observed. The behaviour of the main product, $HRu_3(CO)_9C_2C(CH_3)_3$, towards electrophilic reagents has been investigated. By deuterium labelling some insight has been gained into the mechanism of the reaction.

Introduction

We have previously reported that, by reacting dodecacarbonyltriruthenium and 3,3-dimethyl-1-butyne, $HRu_3(CO)_9C_2C(CH_3)_3$ (I) is obtained as the major product [1]. An X-ray and a neutron analysis of I showed that the triple bond of the ligand participates in the bonding with the metallic moiety, forming two η bonds with two $Ru(CO)_3$ moieties; one σ bond is formed between the third $Ru(CO)_3$ and the carbon without substituent [2, 3] (Fig. 1). Thus the acetylene is coordinated μ_3-η^2 on the cluster [4]. The overall electronic requirement of the cluster is fulfilled by a bridging hydride [3, 5]. These unusual features prompted us to investigate the behaviour of I towards electrophilic agents. Dihydridic species $H_2Ru_3(CO)_9[HC_2C(CH_3)_3]$ have been obtained and their structures have been assigned on the basis of their ^1H and ^{13}C n.m.r. spectra.

Minor products of the reaction of $Ru_3(CO)_{12}$ and 3,3-dimethyl-1-butyne are the acetylenic complexes $Ru_3(CO)_6[HC_2C(CH_3)_3CO\text{-}HC_2C(CH_3)_3][HC_2C\text{-}CH_3)_3]_2$ [6]. We have now established that I is an intermediate in their formation. Reaction of the D-homologue of I with alkyne gives some insight into the mechanism of formation of the non-hydridic complexes.

Results and Discussion

Recently several studies on the reactions of $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ with terminal alkynes have shown that $HOs_3(CO)_9C_2R$ (R = H, Me, Et, Bu^t, Ph) [7–9], which is isostructural with I, is obtained by isomerization of the non-hydridic species $Os_3(CO)_9(HC_2R)$, which in turn is obtained by heating $Os_3(CO)_{10}(HC_2R)$. However in our case such intermediates, if ever formed, are not enough thermodynamically stable to be isolated, since they were not detected even in the reactions carried out in low boiling solvents.

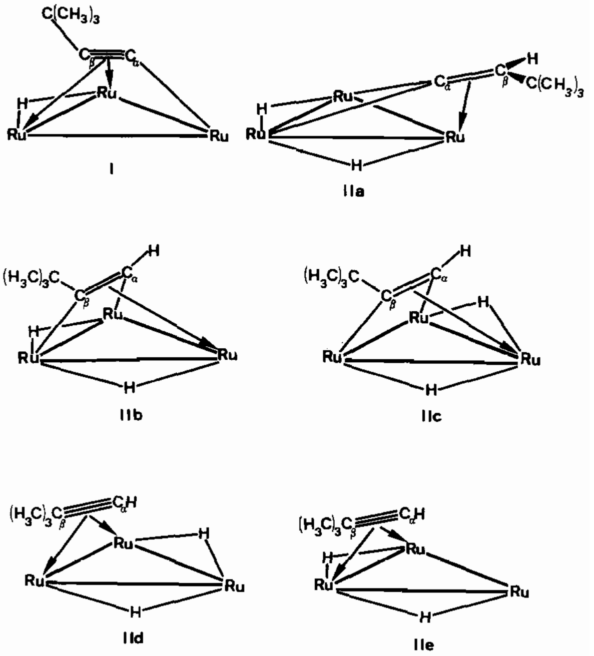

Figure 1. Molecular structures of I and II (carbonyls omitted for clarity).

The reaction of $Ru_3(CO)_{12}$ and $DC_2C(CH_3)_3$ confirms that in the formation of I the source of the bridging hydride is the acidic hydrogen of the ligand, since no high field signal is observed in the product of the reaction, *i.e.*, $DRu_3(CO)_9C_2C(CH_3)_3$ (Ia). Thus hydrogen transfer from the ligand to the cluster occurs with consequent formation of the σ bond between one metal and C_α. This carbon undergoes electrophilic attack both by reacting I with hydrogen and by treating I with acid. In the former case the dihydridic species $H_2Ru_3(CO)_9[HC_2C(CH_3)_3]$ (II) is obtained. Several structures for II are summarized (Fig. 1) and some of them, namely IIa and IIb, have been reported for $H_2M_3(CO)_9(HC_2R)$ (M = Ru, Os) obtained by reacting $M_3(CO)_{12}$ with alkenes (1, 2) [10].

On the basis of its ^1H n.m.r. spectra, we propose a structure in which the $HC_2C(CH_3)_3$ moiety is η bonded to the metal atoms. The resonance of intensity 1 at 4.4 ppm from TMS rules out structures IIb and IIc in which a hydrogen bonded to a carbon which is σ bonded to one metal and η bonded to a second ($C(\sigma, \eta)$) is present. The resonances of such hydrogens have been shown to be at lower fields in a variety of complexes [11]. Structure IIa is also ruled out since a low-field signal has been reported for the complexes with M = Os and R = Me [12]. Additionally the position of this signal is in the range normally observed for the alkynes η bonded to a metal unit [13]. The invariance with the temperature, in the range -80 °C $+26$ °C, of the sharp signal of intensity 2 in the high field region gives further support to the ruling out of the structures IIa–IIc and IIe, suggesting that the structure of II is the symmetric one IId.

A dihydridic species $[H_2Ru_3(CO)_9HC_2C(CH_3)_3]^{2+}$ (III) is also obtained by dissolving I in $ClSO_3H$ (or H_2SO_4) but its ^1H and ^{13}C n.m.r. spectra show that it is not isostructural with II. The lowfield absorptions at δ 9.2 (^1H n.m.r.) and at δ 222.5 and 149.9 ppm (^{13}C n.m.r.) are consistent with the presence in the molecule of two ($C(\sigma, \eta)$). The observation of a signal for C_β which is at lower field than that of C_α, is consistent with our earlier observations on systems having ($C(\sigma, \eta)$): it has been shown that as the electron donating properties of R increase, the resonances of ($C(\sigma, \eta)$) shift to lower field [14, 15]. III differs from II also in the high field region of the ^1H n.m.r. spectrum: two broad signals with equal intensity appear in the room temperature spectrum. These signals further broaden, collapse and merge into a new peak as the temperature is raised. The overall features of the n.m.r. spectra are then in accord with the unsymmetrical structure IIb. Reaction of I with D_2SO_4 gives the dideuterated species $[HDRu_3(CO)_9DC_2C(CH_3)_3]^{2+}$ (IIIa). The observation of two signals in the high field region which behave with the temperature as those of III giving a sharp signal at high temperature whose intensity is 1/9 of that of the methyl resonance indicates the intramolecularity of the interchange of the hydrides.

We have previously reported that minor products of the reaction of $Ru_3(CO)_{12}$ and 3,3-dimethyl-1-butyne are the non hydridic species $Ru_3(CO)_6[HC_2C(CH_3)_3COHC_2C(CH_3)_3][HC_2C(CH_3)_3]_2$ (IV and V) [6]. The same complexes are obtained by reacting I with an excess of alkyne. IV and V consist of an isosceles triangle of ruthenium with two terminal carbonyls on each metal [16]. The organic ligand is formed by two halves, the first originated by the linkage of two molecules of alkyne *via* a –C–O– bridge, and the second by direct linkage of two further molecules of alkyne. IV and V differ in the way the molecules of ligand are joined in the second half (Fig. 2).

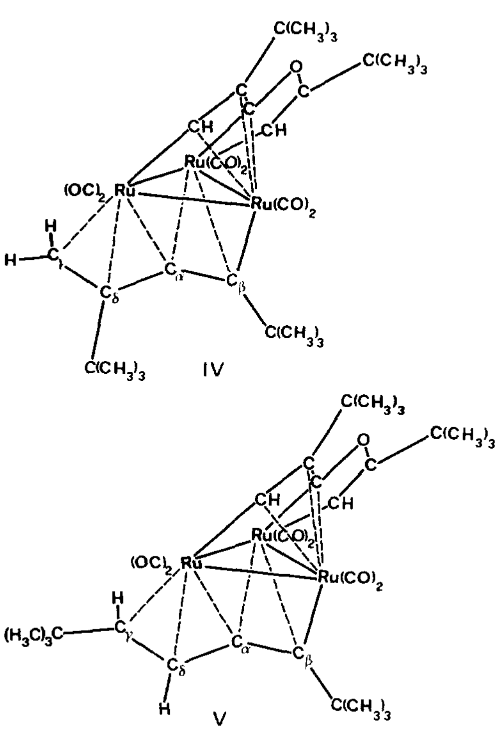

Figure 2. Molecular structures of IV and V.

Noteworthy are the carbon n.m.r. resonances at 235.7 (IV) and 234.6 (V) assigned to the carbon of the C–O bridge, which are in the range found for carbene carbon atoms [17]. Additionally the pattern of the terminal carbonyls shows that these molecules are stereochemically rigid at room temperature whereas facile CO scrambling has been observed in many olefin derivatives of $Ru_3(CO)_{12}$ [18].

The complexity of the molecule does not allow any certain deduction on the fate of the hydride in the formation of IV and V. However, this indication has been gained by reacting $DRu_3(CO)_9C_2C(CH_3)_3$ with $HC_2C(CH_3)_3$. The monodeuterated species IV and V have been obtained. The ^1H n.m.r. spectrum of the most abundant isomer V is equal to that of the non deuterated species, but for the absence of the resonance at 2.4 ppm from TMS, which has to be ascribed to the hydrogen bonded to C_γ [16]. This means that in the formation of V from I the net hydrogen transfer occurs from the bridging hydride to C_γ, thus supporting that insertion of a molecule of alkyne takes place at the ruthenium–C_α bond of compound I. In the isomer IV the same mechanism should be operative, the only difference being the head-to-tail linking of the alkyne molecules. Thus the overall course of the reaction of $Ru_3(CO)_{12}$ with 3,3-dimethyl-1-butyne provides an interesting sequence of hydrogen transfer from the ligand to the cluster with the formation of 1 and from the cluster to the ligand in the next step.

Experimental

Preparation and Identification of the Compounds

3,3-dimethyl-1-butyne was obtained from K & K and used without further purification. $Ru_3(CO)_{12}$ and $HRu_3(CO)_9C_2C(CH_3)_3$ were prepared by literature methods. Solvents and gases were dehydrated prior of use. The reaction mixtures were purified by preparative tlc plates and the compounds further crystallized from n-heptane.

The products were analyzed by means of an F & M 187 Model C, H. N Analyzer and a Perkin Elmer Atomic Absorption Spectrophotometer 303; the i.r. spectra were registered in CCl_4 solutions with a Beckmann 4230 and a Beckmann IR-12. The mass spectra were registered with and without perfluoroalkanes as internal standard on an Hitachi–Perkin Elmer RMU-6H single focusing instrument operating at an ionization potential of 70 eV. The ^1H and ^{13}C n.m.r. spectra were registered respectively on a JEOL C 60 HL and a JEOL PS 100 FT operating at 25.1 MHz in the Fourier transform mode.

$DRu_3(CO)_9C_2C(CH_3)_3$ (Compound Ia)

$DC_2C(CH_3)_3$ was obtained 90% deuterated by reacting ethyl bromide and Mg "*pro Grignard*" in ethyl ether (dried and distilled over sodium and $LiAlH_4$), then adding to the limpid solution $HC_2C(CH_3)_3$, refluxing for 1 hour and finally hydrolyzing the resulting mixture with D_2O. The ethyl ether was distilled off in a Claisen apparatus. $Ru_3(CO)_{12}$ was reacted in refluxing n-heptane under nitrogen, with $DC_2C(CH_3)_3$ and *Ia* was obtained together with the usual minor products from the reaction; trace amounts of ethyl ether were possibly responsible of the formation of some $H_4Ru_4(CO)_{12}$ which forced us to purify the products by tlc rather than the usual methods [1] thus reducing the overall yield. The i.r. spectrum of *Ia* in the carbonyl stretching region is as follows: 2091 m, 2065 vs, 2071 s(sh), 2049 vs, 2019 vs, 2014 vs(sh), 1986 m cm^{-1}. *Ia* shows a mass spectrum comparable with the one reported for I. Proton n.m.r. spectrum in CCl_4: resonance at δ 1.4 (s).

$H_2Ru_3(CO)_9[HC_2C(CH_3)_3]$, Compound II

II is obtained together with $H_4Ru_4(CO)_{12}$, both in 5% yields, by reacting *I* in refluxing n-heptane under slow hydrogen flow. *II* is also obtained by refluxing $Ru_3(CO)_{12}$ with excess 3,3-dimethyl-1-butyne under slow hydrogen flow.

The compounds analyzes as follows. Found C% 29.01, H% 1.97, O% 22.19, Ru% 46.83. Calcd. for $C_{15}H_{12}O_9Ru_3$: C% 28.17, H% 1.89, C% 22.52, Ru% 47.42. *M* = 639.47. The i.r. spectrum in the CO stretching region is as follows: 2080 vs, 2038 vs, 2018 vs, 2000 s(sh) cm^{-1}.

II shows a mass spectrum with P^+ at 642 m/e (^{102}Ru isotope) and a stepwise loss of nine CO groups, competitive with hydrogen loss; the fragmentation after the loss of the CO groups was difficult to interprete because of the superposition of the isotopic patterns of the fragments.

Proton n.m.r. spectrum in CCl_4: resonances at δ 4.4 (s), 1.2 (s), −17.5 (s) in the intensity ratio 1:9:2.

$[H_2Ru_3(CO)_9CH_2C(CH_3)_3]^{2+}$, Compound III

III was obtained by dissolving *I* in $ClSO_3H$ or in H_2SO_4 98%; the resulting yellow solution was air stable for days. Proton n.m.r. spectrum in $ClSO_3H$: resonances at δ 9.2 (s), 1.1 (s), −14.3 (broad doublet) −15.2 (broad doublet) in the intensity ratio 1:9:1:1.

Carbon n.m.r. spectrum in H_2SO_4 ($CDCl_3$ external reference): resonances at δ 222.5 (s), 188.1–181.2 (CO region), 149.9 (d, J = 151 Hz), 49.4 (s), 34.6 (q, J = 127).

$Ru_3(CO)_6[HC_2C(CH_3)_3CO{-}HC_2C(CH_3)_3][HC_2C(CH_3)_3]_2$, Compounds IV and V

These compounds were obtained in 3% yield each, either by reacting $Ru_3(CO)_{12}$ and 3,3-dimethyl-1-butyne under nitrogen atomsphere in refluxing n-heptane (1 hour), or by refluxing *I* or *Ia* with 3,3-dimethyl-1-butyne in n-heptane (1 hour); the same products were also obtained by refluxing $Ru_3(CO)_{12}$ and 3,3-dimethyl-1-butyne under hydrogen current for 2 hours. In all these reactions, excess of acetylene was employed.

The compounds analyze as follows. Found (for *IV*): C% 45.12, H% 4.99, O% 12.88, Ru% 37.01. Found (for *V*): C% 45.06, H% 5.10, O% 13.29, Ru% 36.55. Calcd for $C_{31}H_{40}O_7Ru_3$: C% 44.97, H% 4.87, O% 13.53, Ru% 36.62. *M* = 827.87.

The i.r. spectra, in the CO stretching region are as follows: *IV*: 2045 s(sh), 2043 vs, 2018 vs, 1983 s, 1872 vw cm^{-1}. *V*: 2047 s, 2023 vs, 1992 s, 1865 vw cm^{-1}.

Compounds *IV* and *V* show identical mass spectra with P^+ at 830 m/e and stepwise loss of 6 CO groups; a further loss of a fragment of 28 m/e is considered due to the release of the seventh CO, but no evidence for this fragmentation instead of a C_2H_4 loss was obtained. In this case, also the fragmentations of the organic moieties were difficult to interprete because of the superposition of the isotopic patterns of the fragments.

Proton n.m.r. spectrum of *IV* in CCl_4: resonances at δ 9.4(s), 6.5(s), 3.7(s), 2.1(s), 1.4(s), 1.2(s), 0.7(s) in the intensity ratio 1:1:1:18:9:9:1.

Proton n.m.r. spectrum of *V* in CCl_4: resonances at δ 9.6(s), 6.4(s), 4.6(d, J = 11 Hz), 2.4(d), 2.1(s), 1.5(s), 1.3(s) in the intensity ratio 1:1:1:1:18:9:9.

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