

REACTION OF $\text{Ru}_3(\text{CO})_{12}$ WITH STYRENE

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Summary

The reaction of styrene with $\text{Ru}_3(\text{CO})_{12}$ yields the known complex $\text{Ru}_4(\text{CO})_{12}(\text{PhC}=\text{CH})$ and the new cluster $\text{Ru}_4(\text{CO})_9(\text{PhC}=\text{CH})(\text{PhEt})$, in which a second molecule of styrene is hydrogenated and η^6 -bonded.

Introduction

Extensive studies of the reactions of $\text{Ru}_3(\text{CO})_{12}$ with alicyclic unsaturated hydrocarbons have shown that:

(i) Dienes [1] and internal alkynes [2] bearing hydrogen atoms adjacent to a multiple bond give the isomers $\text{HRu}_3(\text{CO})_9(\text{RC}=\text{C}=\text{CR}'\text{R})$ (I) and $\text{HRu}_3(\text{CO})_9(\text{RCCR}'\text{CR}'')$ (II) as the main products.

(ii) Dienes [1] and internal alkynes [3a] without α -H atoms give the isostructural compounds $\text{Ru}_3(\text{CO})_8(\text{LH}_2)$ (L = diene) and $\text{Ru}_3(\text{CO})_8\text{L}'_2$ (L' = alkyne) (III) respectively; furthermore with alkynes the complex $\text{Ru}_4(\text{CO})_{12}\text{L}'$ (IV) is also formed [3]. Complexes III–IV are also obtained as minor products in reactions of type (i).

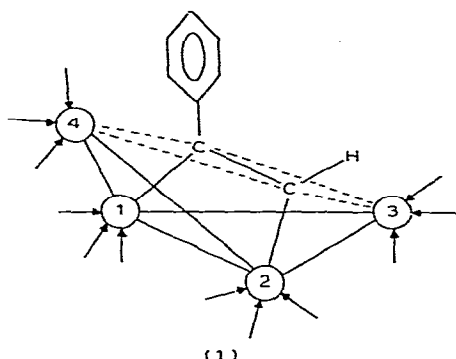
(iii) Terminal and internal olefins [4] give, after isomerization to the equilibrium mixture and dehydrogenation, the isomeric compounds I and II; in addition, as a consequence of the dehydrogenation step, some $\text{Ru}_3(\text{CO})_{12}$ is hydrogenated to $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$.

Recently we have shown [5] that $\text{Os}_3(\text{CO})_{12}$ reacts with ethylene under pressure to give the tetranuclear complexes $\text{Os}_4(\text{CO})_{12}(\text{HC}_2\text{H})$ and $\text{Os}_4(\text{CO})_{12}(\text{HC}_2\text{Et})$, which are isostructural with complex IV containing a "butterfly" metal cluster unit. The former is formed by dehydrogenation of one molecule of the olefin and the latter by the dimerization of two molecules of ethylene followed by a hydrogen shift. These observations prompted us to study the

reaction of $\text{Ru}_3(\text{CO})_{12}$ with styrene, an olefin which is not expected to form compounds of type I and II, unless aromatic carbons are involved on its bonding scheme [6].

Results and discussion

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with an excess of styrene (molecular ratio 1/28) was carried out in a number of solvents. In cyclohexane (b.p. 81°C), methylcyclohexane (101°C) or n-octane (126°C), no evidence for the production of trinuclear complexes was found. The major product of these reactions was the tetranuclear compound **1**, which on the basis of its spectroscopic data (Table 1)



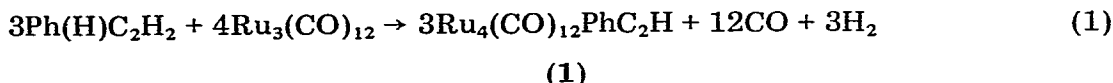
may be formulated as $\text{Ru}_4(\text{CO})_{12}\text{PhC}_2\text{H}$ and is considered isostructural with IV [3a,3b]. Thus, the downfield singlet at δ 10.10 ppm, observed in the ^1H NMR spectrum may be assigned to the hydrogen atom at a δ and η coordinated carbon atom. A similar downfield peak was observed in the spectra of both $\text{Os}_4(\text{CO})_{12}(\text{HC}_2\text{H})$ and $\text{Os}_4(\text{CO})_{12}(\text{HC}_2\text{Et})$. The dehydrogenation of styrene to phenylacetylene is also supported by the appearance, in the proton coupled

TABLE 1
IR AND NMR DATA

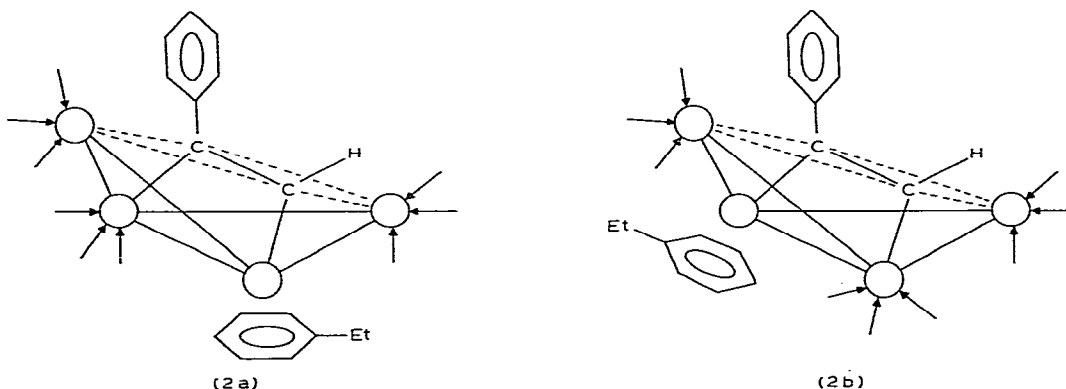
Compound	IR ^a , $\nu(\text{CO})$ (cm^{-1})	^1H NMR ^{b,c} , δ (ppm)	^{13}C NMR ^b , δ (ppm)
$\text{Ru}_2(\text{CO})_6\text{C}_6\text{H}_4\text{C}_2\text{H}_2$	2081ms, 2052vs, 2010s, 1991m, 1983ms	C_2H_2 : 7.85(d,1), 7.00(d,1); C_6H_4 : 7.50–7.15(m,4)	
$\text{Ru}_4(\text{CO})_{12}\text{PhC}_2\text{H}$	2093m, 2067vs, 2044s, 2035vs, 2011ms, 2001w(sh), 1968w	CH: 10.10(s,1); Ph: 7.10(m,5)	PhC: 156.9; HC: 156.1; Ph: 128.0, 125.1, 123.7
$\text{Ru}_4(\text{CO})_9(\text{PhC}_2\text{H})(\text{PhEt})$	2070s, 2028vs, 2016s, 1998m, 1986w, 1968w, 1955m	CH: 10.10(s,1); =CPh: 7.15(m, 5); EtPh: 5.73(mbr,5); CH ₂ : 1.98(q,2); CH ₃ : 1.13(t,3)	PhC: 158.6; HC: 156.1; =CPh: 127.6, 126.4, 123.3; EtPh: 88.9, 86.8, 84.4, 83.7; CH ₂ : 25.6; CH ₃ : 14.4

^a n-Hexane. ^b CDCl_3 . ^c Multiplicity and integrated intensities in parentheses.

^{13}C NMR spectrum, of a doublet centred at δ 156.1 ppm (J 170 Hz) which may be assigned to the $\equiv\text{CH}$ carbon atom.



The ^{13}C NMR spectrum of a ^{13}CO enriched sample of **1** in $\text{CD}_2\text{Cl}_2/\text{CF}_2\text{Cl}_2$ solution shows three resonances at 197.4, 197.2 and 190.3 ppm of relative intensity 1/1/2. The ^1H coupled spectrum shows that only the signal centred at 197.2 ppm is H-coupled ($J^3(\text{CH})$ 1 Hz), which leads us to assign this resonance to the three carbonyls bonded to Ru^2 and which are involved in a fast scrambling process. The remaining two resonances may then be assigned to one



set of exchanging carbonyls bonded to Ru^1 (signal at 197.4 ppm) and to the two equivalent sets of exchanging carbonyls bonded to Ru^3 and Ru^4 . As the temperature is decreased to -80°C the high field signal progressively broadens and eventually collapses at -95°C : unfortunately because of the limited solubility of the sample in CF_2Cl_2 at lower temperatures we are not able to obtain a ground-state spectrum of this complex. These observations are similar to those reported [3b] for $\text{Ru}_4(\text{CO})_{12}(\text{PhC}_2\text{Ph})$.

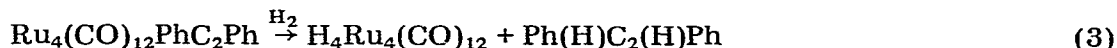
The second product of the reactions, **2**, may be formulated on the basis of its spectroscopic properties as $\text{Ru}_4(\text{CO})_9(\text{PhC}_2\text{H})(\text{PhEt})$. The IR and mass spectra are very similar to those of $\text{Ru}_4(\text{CO})_9(\text{C}_6\text{H}_8)(\text{C}_6\text{H}_6)$, for which the solid state structure has been established as being related to that of **1** but with the three CO groups on Ru, replaced by a benzene molecule [7]. The ^1H and ^{13}C NMR spectra show that the additional organic moiety in **2** is η -coordinated via the aromatic ring and possesses an ethyl group which has been derived from the hydrogenation of one molecule of styrene. The two possible structures for this



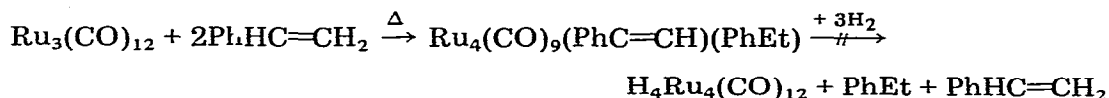
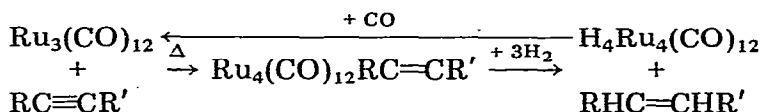
complex are **2a** and **2b**.

The reduction of styrene to ethylbenzene partially accounts for the loss of H_2 in the formation of **1**. In agreement we have established that on reaction of **1** with an excess of styrene compound **2** is not obtained. We have also established that compound **2** does not undergo hydrogenation under the same exper-

imental conditions as $\text{Ru}_4(\text{CO})_{12}(\text{PhC}_2\text{Ph})$ [3a], the latter reacting with H_2 to give $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and stilbene.



It is known that hydrogenation of styrene in the presence of the tetranuclear mixed cluster $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ [8] produces ethylbenzene which then acts as a poison for the catalyst; here the decrease of the hydrogenation rate is associated with the formation of the complex $\text{Co}_2\text{Rh}_2(\text{CO})_9\text{PhEt}$. In our case the η coordination of the ethylbenzene with 1 to form 2 is likely to be a poisoning step to the hydrogenation cycle. A catalytic Ru_3/Ru_4 scheme analogous to that proposed by Kaesz [9] may occur for some alkynes [3a], but it is certainly less accessible for the styrene substrate.



Eventually a binuclear complex 3 is obtained as a product of this reaction. The IR spectrum of this compound is similar to that of $\text{Ru}_2(\text{CO})_6\text{L}'_2$ ($\text{L}' = \text{alkyne}$) [10], however, the mass spectrum shows that the organic moiety corresponds to PhC_2H giving a formula $\text{Ru}_2(\text{CO})_6(\text{PhC}_2\text{H})$. The complexity of the ^1H NMR spectrum in the aromatic region is consistent with the view that a C_4 -ring is coordinated to the $\text{Ru}_2(\text{CO})_6$ moiety; however, because of the small yields of 3 the exact nature of this complex has not been ascertained.

Experimental

$\text{Ru}_3(\text{CO})_{12}$ was prepared by the standard method. All solvents (pure grade commercial products) were dried on molecular sieves and distilled before use. Styrene (C. Erba pure grade) was used without further purification.

The C and H analyses were performed with an F & M Model 185 CHM Analyser, and the Ru analysis with a Perkin—Elmer 303 atomic absorption spectrophotometer. IR spectra were recorded with a Perkin—Elmer 257 spectrophotometer using sodium chloride cells and CO as calibrant. ^1H and ^{13}C NMR spectra were obtained on a Jeol-C 60-HL and a Jeol-Ps 100-FT NMR spectrophotometer respectively. Chemical shifts were reported as downfield positive with respect to SiMe_4 . Mass spectra were measured on an AEI MS 12 spectrometer and calibrated with perfluorotriheptyl/triazine.

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with styrene

(i) In a typical run 1.0 g (1.56 mmol) of $\text{Ru}_3(\text{CO})_{12}$ was suspended in 200 ml of cyclohexane and 5.0 ml (43.64 mmol) of styrene added. The mixture was heated under reflux for 20 h under nitrogen. During the reaction, the solution turned from orange to red-brown. The mixture was filtered hot on SiO_2 column

in order to eliminate any metallic residue. The first elute (colourless) contained the excess styrene (in part polymerized). Further elution with benzene afforded a brown mixture that was dried under vacuum. The residue was dissolved in CH_2Cl_2 and chromatographed (adsorbent Kieselgel PF₂₅₄₊₃₆₆, eluent light petroleum and 15% diethyl ether). Besides unreacted $\text{Ru}_3(\text{CO})_{12}$ (30%), the following derivatives were eluted: $\text{Ru}_4(\text{CO})_{12}(\text{PhC}_2\text{H})$ (**1**), brown crystals (30%). Anal. Found C, 28.82; H, 0.60; Ru, 47.72. $\text{C}_{20}\text{H}_6\text{O}_{12}\text{Ru}_4$ calcd.: C, 28.51; H, 0.71; Ru, 47.98%. Mol. wt. 846, mass spectrum: m/e 846 (M^+) followed by loss of twelve carbonyl groups and by a complicated fragmentation of the organic moiety. An intense peak at m/e 432 corresponding to the ion Ru_4C_2^+ and the doubly charged ion were also observed.

$\text{Ru}_4(\text{CO})_9(\text{PhC}_2\text{H})(\text{PhEt})$ (**2**), violet crystals (15%). Found: C, 34.96; H, 1.73; Ru, 47.01. $\text{C}_{25}\text{H}_{16}\text{O}_9\text{Ru}_4$ calcd.: C, 34.73; H, 1.86; Ru, 46.75%. Mol. wt. 868; mass spectrum: m/e 868 (M^+), followed by loss of nine carbonyl groups and by a complicated fragmentation of the organic moieties. Two intense peaks at m/e 510 and at m/e 432 are assigned respectively to the $\text{Ru}_4\text{HC}_2\text{Ph}^+$ and Ru_4C_2^+ ions. The corresponding doubly charged ions are also observed.

$\text{Ru}_2(\text{CO})_6(\text{C}_8\text{H}_6)$ (**3**), yellow powder (2%). Anal. Found: C, 35.81; H, 1.12; Ru, 42.66. $\text{C}_{14}\text{H}_6\text{O}_6\text{Ru}_2$ calcd.: C, 35.60; H, 1.28; Ru, 42.80%. Mol. wt. 474, mass spectrum m/e 474 (M^+) followed by loss of six carbonyl groups but no fragmentation of the organic moiety. Ultimately the Ru_2^+ ion was observed.

(ii) $\text{Ru}_3(\text{CO})_{12}$ and styrene in the above ratio were refluxed for 20 h in 200 ml of methylcyclohexane under N_2 . The same separation work-up afforded unreacted $\text{Ru}_3(\text{CO})_{12}$ (5%), **1** (20%), **2** (30%) and **3** (2%).

(iii) $\text{Ru}_3(\text{CO})_{12}$ and styrene in the above ratio were heated under reflux for 10 h in 200 ml of n-octane under N_2 . Identical separation procedure gave unreacted $\text{Ru}_3(\text{CO})_{12}$ (trace), **1** (5%), **2** (20%) and **3** (2%).

Reaction of 1 with styrene

0.200 g of **1** were dissolved in 200 ml of cyclohexane and 1.0 ml of styrene added. The mixture was heated under reflux for 20 h under N_2 . The resulting brown solution was filtered and dried under vacuum, the residue dissolved in CH_2Cl_2 and chromatographed (adsorbent and eluent as above). Unreacted **1** (50%) and a dark residue were obtained. No identifiable amount of a complex analogous to **2** was detected.

Enrichment of 1

The ^{13}C enrichment was achieved by stirring a solution of **1** in n-heptane (0.100 g in 100 ml) in a sealed ampoule for four days at $+60^\circ\text{C}$ in the presence of 1 atm. of ^{13}CO (Monsanto Res. Corp.).

Attempted hydrogenation of 2

A slow stream of hydrogen was bubbled through a n-heptane solution of **2** (0.100 g dissolved in 100 ml) for 2 h under reflux. Analyses by TLC and IR spectroscopy of the concentrated solution indicate that **2** was unchanged although some formation of metallic ruthenium occurred.

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