Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CHEMISTRY OF DODECACARBONYLTRIRUTHENIUM
I. ACETYLENE DERIVATIVES OF DODECACARBONYLTRIRUTHENIUM*

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(Received August 5th, 1968; in final edited form February 20th, 1969)

SUMMARY

Substitutions of carbonyl groups in $Ru_3(CO)_{12}$ by diphenylacetylene and tetraphenylcyclopentadienone are described. Nine compounds, six of which are trinuclear ruthenium carbonyl acetylenes, were isolated from the reaction with diphenylacetylene in inert solvents. In methyl alcohol two $Ru_3(CO)_8(C_2Ph_2)_2$ isomers were obtained, a violet one having only terminal carbonyls and an orange-yellow one with bridging carbonyl groups. The thermal decomposition of the products and replacements of carbonyl groups with basic ligands (mainly triphenylphosphine) were studied.

A compound $Ru_3(CO)_5(C_2Ph_2)_2(PPh_3)_3$, containing bridging carbonyl groups, is also described.

The greater tendency of the ruthenium carbonyl than of iron carbonyl to retain the trinuclear cluster in these reactions is discussed, with emphasis on the fact that the ruthenium carbonyl can give rise to bridged carbonyl compounds even when such groups are not present in the original structure.

INTRODUCTION

Metal carbonyls are known to react with various acetylenes in inert solvents to give substituted carbonyls as well as cyclic organic products such as ketones, quinones, etc. In recent years, the formation of complexes from acetylenes and metal carbonyls containing metal atom clusters has been studied[1]. This work has been mainly restricted to the first of the three elements, *viz.* Fe, Ru, and Os, able to form triatomic cluster carbonyls. Hubel *et al.*[2] carried out a thorough investigation of the products from the reaction of acetylene with $Fe_3(CO)_{12}$, as well as with $Fe(CO)_5$ and $Fe_2(CO)_9$. We have sought to gain more detailed knowledge of such reactions, and have included the two remaining elements of the Fe triad in our studies.

To set this work in perspective, it should be noted that the only close similarity between the chemistry of ruthenium and iron compounds at low oxidation states is to be found in the sandwich compounds and corresponding carbonyls. In the case of osmium, the similarity to iron and ruthenium compounds is even smaller[3]. As for

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* Presented at the Xth National Congress of Società Chimica Italiana, Padova, 1968.

TABLE 1

DIPHENYLACETYLENE DERIVATIVES OF $Ru_3(CO)_{12}$

Compound	Physical properties		Analysis, found (calcd.) (%)				Mol. wt., found (calcd.)	IR spectra (CCl_4)
		M.p. (°C)	C	H	O	Ru		
$Ru_2(CO)_6[C_2(C_6H_5)_2]$ (I)	Red brown powder	158–159	43.34 (43.79)	1.98 (1.83)		37.37 (36.86)	528.1 (548.5)	2091 m, 2057 vs, 2032 s, 2028 (sh) 2016 (sh); 767, 699, 692, 677, 663
$Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ Violet isomer (II)	Red-violet powder	125–127 dec.	49.15 (48.92)	2.55 (2.28)	14.31 (14.48)	33.87 (34.32)	891 (883.9)	2081 s, 2051 vs, 2028 vs, 1997 m, 1968 m; 757, 730, 703
$Ru_3(CO)_9[C_2(C_6H_5)_2]$ (III)	Brown powder	170 dec.	37.05 (37.65)	2.07 (1.37)		41.75 (41.34)	715.7 (733.6)	2094 m, 2066 vs, 2041 vs, 2018 m, 2010 (sh), 1995 vw, 1970 m; 787, 760, 692
$Ru_2(CO)_6[C_2(C_6H_5)_2]_2$ (IV)	Yellow crystals	192	56.51 (56.19)	3.31 (2.77)		27.16 (27.82)	705.6 (726.7)	2082s, 2043 vs, 2020 s, 1998 vs, 1952 w; 792, 698, 676, 643, 615
$Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ Orange-yellow isomer (V)	Bright-orange powder	170 dec.	48.87 (48.92)	2.48 (2.28)	14.72 (14.48)	34.62 (34.32)	860.6 (883.9)	2071 m, 2031 (sh), 2026 vs, 2016 (sh), 1978 s, 1880 m, 1858 m; 750, 715, 695, 675, 618
$Ru_3(CO)_{10}[C_2(C_6H_5)_2]_2$ (VI)	Deep-red powder	112–114	48.90 (48.55)	2.21 (2.14)	17.95 (17.02)	31.94 (32.27)	921 (939.9)	2102 s, 2074 vs, 2041 (sh), 2027 vs, 2008 (sh), 1997 w, 1982 m, 1953 m; 730, 715, 700, 645, 607
$Ru_2(CO)_7[C_2(C_6H_5)_2]_2$ (VII)	Yellow powder	108–110	54.93 (55.69)	2.99 (2.67)		27.33 (26.79)	729.8 (754.7)	2089 m, 2069 vs, 2031 s, 2026 (sh), 2011 m, 1677 w; 780, 750, 725, 710, 637
$Ru(CO)_4[C_2(C_6H_5)_2]_2$ (VIII)	Yellow powder	135–137 dec.	68.05 (67.47)	3.61 (3.54)		17.97 (17.74)	549.7 (569.6)	2083.5 vs, 2030 s, 2009 s, 1680 w 773, 695
$Ru_3(CO)_9[C_2(C_6H_5)_2]_3$ (IX)	Black-violet powder	..	55.70 (56.20)	2.97 (2.60)	13.43 (13.2)	26.93 (27.60)	1021 (1089)	2011 vs, 1974 m, 1957 m, 1920 m

$M_3(CO)_{12}$ carbonyls, even though all of them have a cluster of three atoms they display quite different chemical behaviour. Indeed, as the strength of the metal-to-metal bond in the series Fe, Ru, and Os increases with increasing atomic weight one might expect an increasing tendency for the triatomic clusters to be conserved.

X-ray structural investigations[4,5], on these carbonyls have shown the presence of bridging carbonyl groups in iron carbonyl, whereas only terminal carbonyl groups are present in the ruthenium and osmium compounds. Even so, no sharp line of distinction in the behaviour between iron, ruthenium and osmium carbonyls* could be recognised in our earlier kinetic studies. Furthermore, the activation energy for M–C bond splitting, which is presumably also involved in the substitution reactions, increased in the order Fe < Ru < Os.

The present paper describes a study of the products of the reaction between $Ru_3(CO)_{12}$ and diphenylacetylene or tetracyclone (tetraphenylcyclopentadienone).

EXPERIMENTAL

The $Ru_3(CO)_{12}$ used in these reactions was made by the method described by Pino *et al.*[7,8]

(*a*) *Reaction with diphenylacetylene in petroleum ether*

In a typical experiment, 2.0 g (3.13 mmoles) of ruthenium carbonyl suspended in 250 ml of 40° to 70° petroleum ether was treated with an equimolecular amount of diphenylacetylene in inert atmosphere. Solvents and gases had been previously purified and dehydrated. The reaction mixture was initially pale yellow, but slowly turned red and then to deep brown. After about 30 h of boiling the residual carbonyl was filtered off and the filtrate was concentrated under vacuum and separated through TLC (adsorbent Kieselgel P.F.; eluent, a mixture of petroleum ether b.p. 40° to 70° and diethyl ether, 5 to 10%). The eluted compounds were recrystallized from hydrocarbon solvents, and were usually obtained as crystalline powders, readily soluble in diethyl ether, carbon disulphide and tetrachloride, toluene and benzene, and moderately or poorly soluble in aliphatic hydrocarbons. They showed fair stability in dry air, but to prevent possible decomposition they were kept under carbon monoxide in sealed containers.

The formulae and characteristics of the nine compounds thus obtained are shown in Table 1, where they are listed in their elution order, starting from the eluent front on the chromatoplates. Molecular weights, in benzene, were measured with a Mechrolab Model 302 osmometer. The C and H analyses were performed with an F and M C, H, N analyzer, and the Ru analysis with a Perkin–Elmer 303 atomic absorption spectrophotometer. IR spectra were obtained with a Beckman IR-12 with KBr optics. Ruthenium compounds resembled iron compounds[9] in the number and relative intensities of absorption bands, though the former show absorption bands displaced by about 10 cm^{-1} towards the upper frequencies.

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* This can only be said with certainty for the temperature ranges at which the kinetic studies were performed; studies at lower temperatures were impracticable because of the low solubility of the carbonyls. The temperatures employed, however, are in the range at which the substitutions with acetylenes take place in these solvents.

TABLE 2

TRIORGANOPHOSPHINE DERIVATIVES OF RUTHENIUM-CARBONYL-DIPHENYLACETYLENE COMPLEXES

Compound	Physical properties		Analysis, found (calcd.) (%)			Mol. wt., found (Calcd.)	IR spectra (CCl_4)
		M.p. (°C)	C	H	But		
$Ru_3(CO)_5[C_2(C_6H_5)_2]_2[P(C_6H_5)_3]_3$ C	Brick-red powder	177–178 dec.	65.93 (65.86)	4.92 (4.13)	18.90 (19.15)	1545 (1586.7)	2055.5 m, 2020 s, 2016 sh, 1997 m, 1966 s, 1957 (sh), 1880 m, 1861 m, 1821 m
$Ru_2(CO)_5[C_2(C_6H_5)_2]_2[P(C_6H_5)_3]$ A	Yellow powder	212–214 dec.	63.60 (63.66)	4.07 (3.67)	20.29 (21.14)	943 (962.2)	2044.5 s, 2018 s, 1984 s, 1970 (sh)
$Ru_2(CO)_5[C_2(C_6H_5)_2]_2[P(But)_3]$ B	Yellow oil		60.40 (60.12)	5.20 (5.04)	21.75 (22.49)	878 (899)	2037 s, 2012 vs, 1973 s, 1948 (sh)

(*b*). *Reactions with diphenylacetylene in solvents other than petroleum ether: Formation of two* $Ru_3(CO)_8(C_2Ph_2)_2$ *isomers*

Boiling n-heptane, ligroin and benzene were also used; reaction times were shorter (15 h in benzene and n-heptane, 10 h ligroin), and increased yields were obtained of some compounds apparently having greater thermal stability (IV, VI, IX)[11].

A mixture of $Ru_3(CO)_{12}$(1.0 g, 1.56 mmoles) and C_2Ph_2(0.309 g) was heated at 55° in methyl alcohol, under nitrogen for 6 h.

A violet terminal-carbonyl complex with the formula $Ru_3(CO)_8(C_2Ph_2)_2$ [compound (II)] was separated by TLC and recrystallized from carbon tetrachloride.

In petroleum ether (b.p. 40–70°) and gasoline (b.p. 65–95°) under nitrogen, the violet compound (II) rearranged in $1\frac{1}{2}$ h to its orange-yellow isomer (V) having a bridging carbonyls. In carbon tetrachloride, it decomposed to compound (IV) on continued boiling.

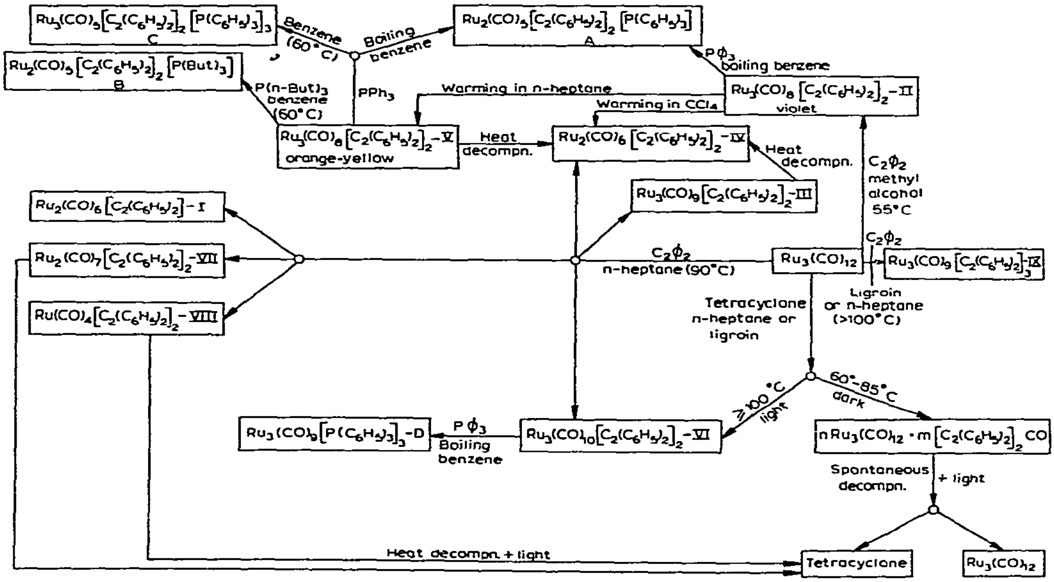

Fig. 1. Reactions of $Ru_3(CO)_{12}$ with diphenylacetylene and tetracyclone.

Compound (II) reacted with an equimolecular amount of triphenylphosphine in benzene at boiling point or at 60°, yielding compound A (Table 2). In benzene, compound (V) reacted with equimolecular amounts of triphenylphosphine to give the same compound A in 1 h at the boiling point, but when the reaction was carried out at 60° a trinuclear compound C with bridging carbonyls was isolated.

Compounds (II) and (V) reacted with tributylphosphine to give compounds B under all reaction conditions; this is in accord with the more basic nature of the ligand.

The IR spectra of the violet and orange-yellow isomers are in good agreement with those of the corresponding iron compounds[10]. There was also good agreement between the X-ray powder patterns of the iron and ruthenium isomers. (Our results, still unpublished.)

*(c). Reactions with tetracyclone in hydrocarbon solvents**

In a typical experiment, 2 g of ruthenium carbonyl in 250 ml of n-heptane or ligroin solvent were treated with an equimolecular amount of tetracyclone for a maximum of 10 h. The products thus obtained were recovered and purified by TLC.

The products varied with the reaction temperature. In n-heptane or ligroin solvents at 90° for 10 h the main product was compound (VI), along with small amounts of other compounds not yet identified.

The analysis indicate that compound (VI) is a trinuclear carbonyl with a triatomic cluster linked to an unidentified organic group. When compound (VI) reacts with an equimolecular amount of triphenylphosphine in boiling benzene under inert atmosphere, it yields mainly the trinuclear compound $Ru_3(CO)_9(PPh_3)_3$, the compound obtained when $Ru_3(CO)_{12}$ is treated with triphenylphosphine[12].

Compound (VI) is remarkably stable in the presence of air, heat and light. No absorption due to ketonic carbonyls could be observed in its IR spectrum (even at solid state investigation in KBr); such absorptions are present in compounds (VII) and (VIII)[13]. The assumption that trinuclear compounds come from a direct reaction between ruthenium carbonyl and tetracyclone is confirmed by experiments under milder conditions; thus reaction at 60° to 85°, with strict exclusion of light, yielded an orange-yellow product. The complete analysis has not yet been carried out for this compound, which shows the following IR bands in carbon tetrachloride: 2100 m, 2033 vs, 2019 s, 2007 s, 1985 m, 1955 m, 1935 m. In carbon disulphide, absorptions corresponding to the presence of phenyl groups were also observed. The data so far obtained suggest it is a molecular addition compound, with ruthenium carbonyl and tetracyclone in 1:1 ratio.

RESULTS AND DISCUSSION

The results indicate that iron and ruthenium carbonyls behave rather similarly in the reaction with diphenylacetylene with respect to formation of several intermediate products. But marked differences in the stability of the triatomic cluster of ruthenium and iron carbonyls show up in reactions in hydrocarbons and methanol. With ruthenium there is a dominant formation of trinuclear intermediate compounds (which were isolated), and only after prolonged heating, are bi- and mononuclear compounds obtained. Even more remarkable is the stability of the compound $Ru_3(CO)_8(C_2Ph)_2$, which possesses bridging carbonyls ("orange-yellow isomer"), in comparison with $Ru_3(CO)_{12}$ which has only terminal carbonyl groups. This supports our assumption of the existence of more than one form of ruthenium carbonyl in equilibrium in the solution[6]. With ruthenium, as with iron, the appearance of com-

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* A similar reaction was carried out by other experimenters[17] but with benzene as solvent, and gave products different from ours. A study of the influence of solvents and reagent concentrations, is under way in our laboratory.

pounds containing heterocyclic five-atom rings of the ruthenium–cyclopentadiene type was observed*.

On the other hand, substantial differences were noted between the iron and ruthenium carbonyls in their behaviour towards the five-atom cyclic compounds. Thus, $Fe_3(CO)_{12}$ when reacting with organic compounds of this type mostly formed mono- or at maximum binuclear organometal derivatives, and there was only a slight tendency to give trinuclear complexes[14]. With ruthenium, however, trinuclear compounds, some of which are highly stable, are formed, which is important in respect of the cyclising properties of such carbonyls. Also of interest would be a detailed study of the organic portions of the metal–carbonyl–acetylene products described so far.

ACKNOWLEDGEMENT

This research was carried out with the financial support of C.N.R. (Council of National Research).

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* Some of our unpublished work has shown that in the case of the iron and ruthenium carbonylacetylenes (I), (IV) and (V), there is no exchange between acetylene groups such as occur with complexes $(RC_2R')Co_2(CO)_6$ studied by us[15,16]. This suggests that the acetylene ligand has lost its identity in the compounds in (I), (IV) and (V), by forming bonds more complex and more stable than the simple bond present in the cobalt acetylenic derivatives.