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ACETYLENIC DERIVATIVES OF METAL CARBONYLS OF THE TRIAD Fe, Ru, Os

IX. REACTIONS OF CARBONYLACETYLENIC DERIVATIVES OF RUTHENIUM AND IRON WITH DIPHENYLACETYLENE AND CARBON MONOXIDE

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SUMMARY

The reactions between trinuclear acetylenic carbonyls of ruthenium or iron and an excess of diphenylacetylene or carbon monoxide have been studied in an attempt to determine the order in which the trinuclear intermediates are formed in the reaction between $Ru_3(CO)_{12}$ and diphenylacetylene. The differences in the behaviour of the two carbonyls are discussed.

INTRODUCTION

The reactions between $M_3(CO)_{12}$ carbonyls, where M=Fe or Ru, and diphenylacetylene have already been described[1,2]: Hübel *et al.*, however, were unable to establish the course of the $Fe_3(CO)_{12}$ reaction; in their opinion it is "multicentric", and thus impossible to follow kinetically. Similar difficulties appear in the case of $Ru_3(CO)_{12}$, but we have attempted to establish the reaction sequence for reaction of this carbonyl with diphenylacetylene, and to account for the number and types of intermediates and final products obtained.

Previously we have observed that the $Ru_3(CO)_{12}$ cluster is destroyed to a lesser extent in these reactions than is the case with $Fe_3(CO)_{12}$, and thus a greater number of trinuclear acetylene-substituted intermediates are produced. These intermediates, which we believe to be the first compounds formed in reactions between the carbonyls and diphenylacetylene, have been treated with diphenylacetylene or carbon monoxide in excess. Similar reactions have been carried out on trinuclear iron compounds and on the only trinuclear osmium carbonyl acetylene so far identified.

We have also treated $Ru_3(CO)_{12}$ with diphenylacetylene in various concentrations and in different solvents, in order to provide support for our interpretations of the results of the above reactions.

EXPERIMENTAL

Carbonyl acetylene reactions, involving an excess of diphenylacetylene (molar ratio of the reagents 1/2), were carried out in n-heptane under nitrogen. Reagents and products were checked for purity; the gases were dried, and free of oxygen. Reactions under CO pressure were conducted in 135 ml, stainless steel pressure reactors: 50 ml of n-heptane were used in each experiment. The reactors were stirred, and heated in a mineral oil bath.

The products obtained were purified and identified by means of previously described methods[2]. In each case, reference is made only to the products obtained in significant amounts.

(*a*) *Reactions with an excess of diphenylacetylene*

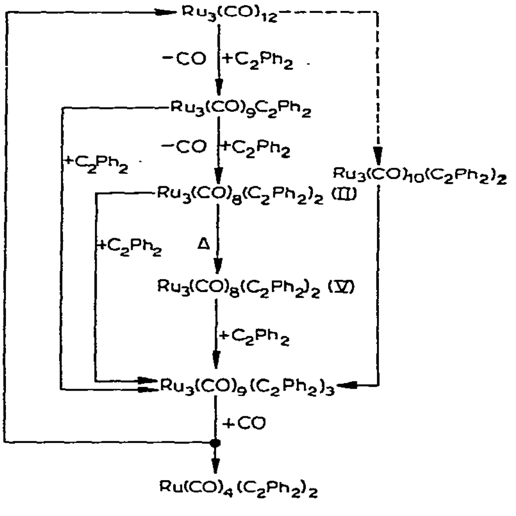
(*i*) $Ru_3(CO)_9C_2Ph_2$. After 3 h numerous products are obtained, including $Ru_2(CO)_6(C_2Ph_2)_2$ (IV), the orange isomer $Ru_3(CO)_8(C_2Ph_2)_2$ (V), and $Ru_3(CO)_9(C_2Ph_2)_3$ (IX). After 7 h, in 40–70° petroleum ether, the same compounds are produced, and a small quantity of the violet isomer $Ru_3(CO)_8(C_2Ph_2)_2$ (II).

(*ii*) $Ru_3(CO)_8(C_2Ph_2)_2$ (*violet*). After $5\frac{1}{2}$ h good yields were obtained of compounds (IV), (IX) and $Ru_3(CO)_{10}(C_2Ph_2)_2$ (VI): the orange isomer (V) was not observed.

(*iii*) $Ru_3(CO)_8(C_2Ph_2)_2$ (*orange*). After 16 h a considerable quantity of starting materials was recovered, together with small quantities of compound (IX).

(*iv*) $Ru_3(CO)_{10}(C_2Ph_2)_2$. After 6 h or longer, unidentified products and small quantities of compound (IX) were obtained.

All these experiments were carried out in boiling n-heptane.



(*b*) *Reactions with an excess of CO*

(*i*) $Fe_3(CO)_9C_2Ph_2$. (90 atm CO, 3 h at 80°). Eleven products were obtained, the only ones isolated in significant yield being $Fe_2(CO)_6(C_2Ph_2)_2$ and the black isomer $Fe_3(CO)_8(C_2Ph_2)_2$; a small quantity of $Fe_3(CO)_{12}$ was also obtained. The same result was obtained after 48 h at 25° under 50 atm CO.

(*ii*) $Ru_3(CO)_9C_2Ph_2$. (80 atm CO, 3 h at 80°). A relatively greater yield of carbonyl was obtained than in the previous experiment; lesser quantities of mono- and bi-nuclear products were found.

(*iii*) *$Fe_3(CO)_8(C_2Ph_2)_2$ (violet)*. (50 atm CO, $1\frac{1}{4}$ h at 180°). Only two products were obtained, namely $Fe_2(CO)_6(C_2Ph_2)_2$ and $Fe(CO)_4(C_2Ph_2)_2$.

(*iv*) *$Ru_3(CO)_8(C_2Ph_2)_2$ (violet)*. Under the same reaction conditions, compounds (IV) and $Ru(CO)_4(C_2Ph_2)_2$ (VIII) are obtained.

(*v*) *$Os_3(CO)_8(C_2Ph_2)_2$ (yellow: without bridged CO-groups)*. Carbon monoxide at 1 atm and a temperature around 0° are sufficient to lead to the quantitative transformation of this compound into a blue, trinuclear product, containing a greater number of CO groups^3.

(*vi*) *$Fe_3(CO)_8(C_2Ph_2)_2$ (black)*. (75 atm CO, 3 h at 160°). Only two compounds, $Fe_2(CO)_6(C_2Ph_2)_2$ and $Fe(CO)_4(C_2Ph_2)_2$, were obtained in good yield.

(*vii*) *$Ru_3(CO)_8(C_2Ph_2)_2$ (orange)*. Under the same conditions as the previous experiment a considerable yield of $Ru_3(CO)_{12}$ and small quantities of compounds (IV) and (IX) were obtained.

TABLE 1

REACTIONS OF $M_3(CO)_{12}$ WITH DIPHENYLACETYLENE

(I) = $M_2(CO)_6C_2Ph_2$; (II) = $M_3(CO)_8(C_2Ph_2)_2$ without bridged CO groups; (III) = $M_3(CO)_9C_2Ph_2$; (IV) = $M_2(CO)_6(C_2Ph_2)_2$; (V) = $M_3(CO)_8(C_2Ph_2)_2$ with bridged CO groups; (VI) = $M_3(CO)_{10}(C_2Ph_2)_2$; (VII) = $M_2(CO)_7(C_2Ph_2)_2$; (VIII) = $M(CO)_4(C_2Ph_2)_2$; (IX) = $M_3(CO)_9(C_2Ph_2)_3$. The Roman numerals assigned to the products are, for convenience, those used for the same compounds in earlier papers.

$M_3(CO)_{12}$	Molar ratio $M_3(CO)_{12}/C_2Ph_2$	Conditions of reaction	Main products obtained
$Fe_3(CO)_{12}$	1.5/1	Boiling n-heptane, under N_2 3–6 h	(I)′, (III)′, (V)′, (IV)′, tetracyclone
	1/2	Same conditions, for $1\frac{1}{2}$ h	(V)′, (IV)′, (VII)′, tetracyclone
	1/2	Boiling benzene, under N_2 for 7 h	(III)′, (V)′, (IV)′, (VII)′, (VIII)′, tetracyclone
	1/1.5	Methanol (48–54°), under N_2, $1\frac{1}{2}$ h	(II)′, (V)′.
$Ru_3(CO)_{12}$	1/1.5	Boiling 40–70° petr. ether, under N_2, 15 h	(III), (V)
	1/1.5	Same conditions, 58 h	(III), (V), (VI), (VII)
	1/1.5	Boiling n-heptane, under N_2, 4 h	(III), (V), (VI)
	1/1.5	Same conditions, 7 h	(III), (V), (VI), (IV), (IX)
	1/10	Same conditions, 6 h	(V), (VIII), (IX)
	1/10	Same conditions, 16 h	(V), (VIII), brown insoluble precipitate
	1/10	n-Heptane (120°), under 20 atm CO, 15 h	(IV), (VIII), hexaphenylbenzene
	1/10	n-Heptane (120°), under 100 atm CO, 15 h	(IV), (VIII), hexaphenylbenzene
	1/1	Boiling methanol, under N_2, $1\frac{1}{2}$ h	(II), (V), (VIII).
$Os_3(CO)_{12}$	1/100	Boiling n-heptane, under N_2, 8 h	(II)″
	1/100	Same conditions, 50 h	(II)″, products not yet identified
	1/10	n-Heptane (150°), under 20 atm CO, 6 h	Hexaphenylbenzene

(*viii*) *$Ru_3(CO)_9(C_2Ph_2)_3$*. (50 atm CO, 6 h at 120°). A high yield of compound (VIII) and small quantities of $Ru_3(CO)_{12}$ were obtained[4].

(*c*) *Reactions between $Ru_3(CO)_{12}$ and diphenylacetylene*

In Table 1 are listed the reactions carried out in this and in previous work. In some reactions an excess of diphenylacetylene was used, and this sometimes gave rise to a dark precipitate, poorly soluble in n-heptane, soluble in benzene and CS_2. (Found: C, 71.98; H, 4.39; O, 6.24; Ru, 17.40%; mol.wt. osmom. in benzene, 848. It decomposed without melting, at 200–300°. The IR data (in CS_2) are: 2033 m, 2027 m, 1978 vs, 1906 s, and 698 s, 731 m cm^{-1}.

RESULTS AND CONCLUSIONS

The following points emerge from the results set out above:

(*a*) As already reported, solvents such as benzene, n-heptane, 40–70° petroleum ether and 80–120° ligroin have no significant effect on the reaction between $Ru_3(CO)_{12}$ and C_2Ph_2. Use of methanol, however, gives very different results.

(*b*) As can be seen from Table 1, experiments carried out in inert, low-boiling solvents, or in inert solvent for short periods of time, produce higher yields of trinuclear compounds, as required by our proposed reaction sequence. Longer reaction times or higher temperatures give increasing quantities of mono- and bi-nuclear products.

(*c*) In the reaction with $Ru_3(CO)_{12}$, tetracyclone is not observed, but in some cases hexaphenylbenzene is obtained: yields of this product are greater when $Os_3(CO)_{12}$ was employed.

(*d*) In the presence of excess CO, some of the compounds gave small quantities of the unsubtituted carbonyl: this behaviour was more marked in the case of ruthenium and osmium, than in that of iron. Destruction of clusters by CO attack was much more evident in the case of $Fe_3(CO)_{12}$.

Our results suggest that stability under such attack increases in the order $Fe < Ru < Os$. This agrees with our previous finding that reactivity towards acetylenes (these being considered as ligands comparable to CO) varies in the order $Fe > Ru > Os$. Similar conclusions have been reached by Johnson *et al.*[5] following mass spectrometric comparison of ruthenium and osmium compounds.

In the early stages, therefore, there seems to be little difference between the reactions of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ with diphenylacetylene, though the former produces two additional trinuclear compounds, (VI) and (IX). It should be noted that these contain a high number of CO groups, as well as two or three diphenylacetylene molecules and we thus suggest that they are directly derived from $Ru_3(CO)_{12}$ rather than through the compounds sequence (III)–(IV)–(V).

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