

ACETYLENIC DERIVATIVES OF METAL CARBONYLS OF THE TRIAD
Fe, Ru, Os
X. REACTIONS OF DODECACARBONYLTRIRUTHENIUM WITH
TETRAPHENYLCYCLOPENTADIENONE

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(Received August 5th, 1969)

SUMMARY

Following a report of different results obtained by other workers, our previous studies of the reaction between $\text{Ru}_3(\text{CO})_{12}$ and tetraphenylcyclopentadienone have been extended to cover a wider range of concentrations and solvents. The results provided explanations of the differing reports, and permit a general reaction scheme to be drawn up.

Preliminary studies of the reaction between $\text{Os}_3(\text{CO})_{12}$ and tetraphenylcyclopentadienone are also reported.

INTRODUCTION

We previously reported the reaction of $\text{Ru}_3(\text{CO})_{12}$ with tetraphenylcyclopentadienone (tetracyclone) in *n*-heptane¹ but Bruce and Knight, using an excess of tetracyclone and with benzene as solvent obtained different results². Thus, while the products we obtained were still trinuclear, Bruce and Knight reported that the mononuclear compound $\text{Ru}(\text{CO})_4(\text{C}_2\text{Ph}_2)_2$ is the principal product. We have thus now studied this reaction over a wide range of concentrations and in different solvents.

An important feature of the reaction between $\text{Ru}_3(\text{CO})_{12}$ and tetracyclone is that some of the compounds obtained are also produced by reaction of this carbonyl with diphenylacetylene; this is not the case when $\text{Fe}_3(\text{CO})_{12}$ is employed. We have carried out some tests with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ to illustrate the differing reactivities of these three metal carbonyls towards the same reagent.

EXPERIMENTAL

The reactions were carried out under dry nitrogen or argon, in solvents purified by literature methods. The reported reaction times are those required at the b.p. of the solvent for complete removal of the reagent present in deficiency as indicated by TLC.

The pressure reactors used in some of the reactions were of stainless steel, electrically heated, and shaken. High purity $\text{Ru}_3(\text{CO})_{12}$ was obtained from Strem Chemicals: tetracyclone and diphenylacetylene were pure reagents (Alfa Chemicals).

The iron and osmium carbonyls were made by us and purified according to methods described in the literature^{3,4}.

The methods of separation, purification and analysis of products have already been described¹. The Roman numerals assigned to some of the products are, for convenience, those used for the same compounds in earlier papers.

(a). *Reactions between $Ru_3(CO)_{12}$ and tetracyclone*

In methanol, with the reagents in 1/1 molar ratio, the reaction was complete after $7\frac{1}{2}$ h: with an excess of tetracyclone (3/1) only $1\frac{1}{2}$ h was required. In both cases, the main product was $Ru(CO)_4(C_2Ph_2)_2$ (VIII), described by Bruce and Knight²; in the first experiment a small quantity of unreacted tetracyclone was present.

In benzene, with the reagents in 1/1 molar ratio, the reaction required about 13 h and no residual tetracyclone was observed. The main product was (VIII); there were also considerable quantities of $Ru_3(CO)_{10}(C_2Ph_2)_2$ (VI), and an intensely violet compound (XI), formed in too small a quantity to permit analysis, and traces of an orange compound (X): this was first thought to be a molecular addition compound between $Ru_3(CO)_{12}$ and tetracyclone, but was shown on analysis to be $Ru_3(CO)_{10}(C_2Ph_2)_2$: (Found: C, 48.75; H, 2.10; O, 18.30; Ru, 31.79. $C_{38}H_{20}O_{10}Ru_3$ calcd.: C, 48.55; H, 2.14; O, 17.02; Ru, 32.27%.) IR Spectrum (CCl_4): 2104 s, 2036 vs, 2026 s (sh), 2012 m (sh), 1986 m, 1962 m, 1942 m, cm^{-1} . The spectrum is remarkably similar to that of the blue compound⁵ $Os_3(CO)_{10}(C_2Ph_2)_2$.

With a 3/1 excess of tetracyclone only compound (VIII) was obtained.

In n-heptane, with a 3/1 excess of tetracyclone, a 60% yield of compound (VIII), and traces of compound (VI) were obtained, after 14 h. Residual tetracyclone and carbonyl were present.

With a 1/1 molar ratio of reactants, a different reaction pattern was displayed, with good reproducibility (the reaction was carried out 15 times, with times varying from 14 to 26 h). Only very slight quantities of compound (VIII) were obtained, together with considerable amounts (30–40%) of compound (VI), and quite large amounts of compound (X). There were also traces of compound (XI) and residual red-black needle-shaped crystals (20–30%) virtually insoluble in n-heptane. The latter were purified by repeated washings with n-heptane to give pure $Ru_3(CO)_9(C_2Ph_2)_3$. (Found: C, 56.05; H, 2.94; O, 12.99; Ru, 28.15. $C_{51}H_{30}O_9Ru_3$ calcd.: C, 56.20; H, 2.60; O, 13.20; Ru, 27.60 %.)

In each case the reaction mixture, which was initially dark-red, became orange after 2–3 h and turned dark again, as the boiling continued. It was found that the orange solution contained almost entirely compound (X) and the reagents: as the latter gradually disappeared, the other products began to appear and the yield of compound (X) decreased.

With a 3/1 excess of the carbonyl, the solution was pale-red at first and darkened to a deep red: after 12–14 h, it contained, in addition to a considerable amount of $Ru_3(CO)_{12}$, compound (VI) (50% with respect to the tetracyclone), and small quantities of (X) and (XI).

Reactions were also carried out in n-heptane under CO (50 atm of gas, for 16 h, at 120°); with the reagents in 1/1 molar ratio, the main compound was (VIII) together with some unchanged reagents. With a 3/1 excess of tetracyclone a high yield of compound (VIII) was obtained.

(b). *Reaction between $Fe_3(CO)_{12}$ and tetracyclone*

This was carried out in *n*-heptane, with the reagents in 1/1 molar ratio. After 100 min a large quantity of black residue was formed, which did not contain carbonyl groups. Very small quantities of $Fe(CO)_4(C_2Ph_2)_2$ ⁶ were also obtained.

(c). *Reactions between $Os_3(CO)_{12}$ and tetracyclone*

Under CO at 15 atm. pressure no reaction occurred during 8 h at 150° with a reagent ratio of 1/1. When the CO was replaced by N₂ and the pressure lowered to 10 atm, and also when operating under vacuum, many products were obtained, one of which was yellow and displayed an IR spectrum similar to that of compound (VIII): in CCl₄, 2082 vs, 2035 m, 2019 vs, 2000 s, 1675 m, cm⁻¹.

In *n*-heptane, with the reagents in 1/1 ratios, 30 h boiling gave 7 products, all in small quantity, and a considerable amount of residual carbonyl. Two of these products show interesting IR spectra; in CCl₄: 2083 s, 2043 vs, 2021 s, 1997 s, cm⁻¹, and: 2070 vs, 2035 s (sh), 2026 vs, 2016 s (sh), 2003 s (sh), 1977 s, 1880 m, 1857 m, cm⁻¹. The first is similar to those of the M₂(CO)₆(CPh₂)₂ compounds, and the second resembles the M₃(CO)₈(C₂Ph₂)₂ compounds, with bridging carbonyls.

(d). *Reactions of compound (VI) and (IX)*

When heated in *n*-heptane in the presence of light for very long periods, compound (VI) gave only low yields of (VIII), and unidentified products. In presence of an excess of tetracyclone in *n*-heptane, 16 h boiling also produced small quantities of compound (VIII). In presence of an excess of diphenylacetylene in *n*-heptane 8 h of boiling gave compound (IX) along with unidentified compounds: treatment with I₂ in boiling *n*-heptane, for 30 min gave small quantities of tetracyclone and a yellow unidentified carbonyl. The NMR spectrum of compound (VI) showed the existence of protons belonging to phenyl groups, only. Mass spectra with good resolution have not yet been obtained because the compound decomposes partially under the experimental conditions, but the data so far obtained, indicate that the organic part of the compound is composed of a 4-atom carbon ring stabilised by 4 phenyl groups: the presence of the tetracyclone ring (perhaps arising from decomposition) is also evident.

Compound (IX) dissolves in CCl₄ and CS₂ on heating with change of colour and decomposition: the IR spectra obtained in these solvents, are markedly different from those in paraffin, *e.g.*: (in paraffin): 2010 vs, 1975 s, 1950 vs, 1920 s; (in CS₂): 2068 m, 2056 m, 2036 vs, 1995 s, cm⁻¹.

Compound (IX) is also obtained by treating with an excess of diphenylacetylene in *n*-heptane, the following trinuclear compounds: Ru₃(CO)₉C₂Ph₂, both isomers of Ru₃(CO)₈(C₂Ph₂)₂ and compound (VI)⁶. It does not react, however, with either tetracyclone or diphenylacetylene, during 24 h, in *n*-heptane. Under CO (50 atm, for 5 h at 120°) in *n*-heptane, it forms small quantities of Ru₃(CO)₁₂ and good yields of compound (VIII).

RESULTS AND DISCUSSION

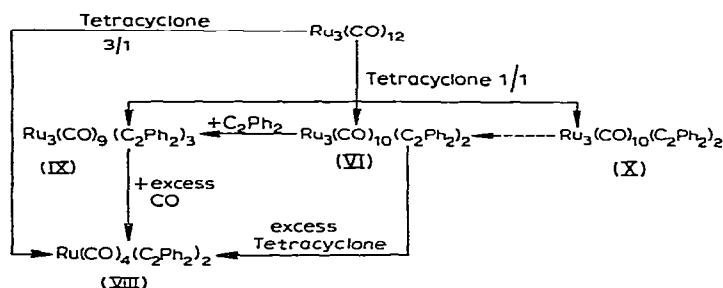
The following points emerge from the above results:

(i). Both the yield and the type of product obtained from the reaction between

$\text{Ru}_3(\text{CO})_{12}$ and tetracyclone are very dependent on the concentration of the latter and the nature of the solvent. [The use of a more polar solvent, such as methanol, favours the formation of the mononuclear compound (VIII).] In presence of an excess of carbon monoxide, CO, compound (VIII) is formed readily.

(ii). Compounds (X) and (VI) have the same empirical formulae. Compound (X) has an IR spectrum closely similar to that of $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)_2$ but is of low stability, whereas product (VI) is more stable. It is possible that (X) and (VI) are structural isomers, but so far it has not been possible to obtain compound (VI) by dissolving and heating compound (X).

(iii). During the reaction of $\text{Ru}_3(\text{CO})_{12}$ with tetracyclone, with the reagents in 1/1 molar ratio, compound (X) is formed first. Other products appear later, and their yields increase until an equilibrium between reagents and products is apparently reached. This would explain the small influence of reaction times in the 14 to 26 h region on the final products.



The course of the reaction is dependent on the ratio of carbon monoxide to tetracyclone, both of which act as Lewis bases on the metal atom cluster. Thus, when both carbon monoxide and tetracyclone are in excess, the mononuclear compound (VIII) is obtained under all conditions. When there is an excess of carbon monoxide the cluster is readily broken, and the fragments are stabilized by tetracyclone. When tetracyclone is in excess, it may behave as both a breaking and a stabilizing agent. Finally, when there is no excess of tetracyclone, and the carbon monoxide is released only by $\text{Ru}_3(\text{CO})_{12}$ in the course of the reaction, it is possible to observe the trinuclear intermediates (X) and (VI). These show no IR absorption bands corresponding to the ketonic carbonyl of the tetracyclone, and this, together with the fact that compounds (X) and (VI) are also produced from the reaction of diphenylacetylene with $\text{Ru}_3(\text{CO})_{12}$ [as is compound (IX)], supports the view that an interaction takes place between the ketonic CO of the organic molecule and the metal carbonyl cluster. Evidence in support of this is supplied by Bruce and Knight's observation of detachment of 4 CO groups, including the ketonic CO, in the mass spectrum of compound (VIII).

REFERENCES

- 1 G. CETINI, O. GAMBINO, E. SAPPA AND M. VALLE, *J. Organometal. Chem.*, 17 (1969) 437.
- 2 M. I. BRUCE AND J. R. KNIGHT, *J. Organometal. Chem.*, 12 (1968) 411.
- 3 C. W. BRADFORD AND R. S. NYHOLM, *Chem. Commun.*, (1967) 384.
- 4 R. B. KING AND F. G. A. STONE, *Inorg. Syn.*, 7 (1963) 193.
- 5 G. CETINI, O. GAMBINO, G. A. VAGLIO AND R. P. FERRARI, to be published.
- 6 O. GAMBINO, G. CETINI, E. SAPPA AND M. VALLE, unpublished results.