

## PRELIMINARY COMMUNICATION

THE CHEMISTRY OF DODECACARBONYL TRIRUTHENIUM  
II. REACTIONS OF  $\text{Ru}_3(\text{CO})_{12}$  WITH SOME SULPHUR CONTAINING ORGANIC  
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Our studies on the reactivity of  $\text{Ru}_3(\text{CO})_{12}$  have included the investigation of reactions between this carbonyl and sulphur-containing compounds such as diethyl and diphenyl disulphide; in particular we were interested to the identification of the products and intermediates obtained, in order to explain the mechanism of these reactions.

Several polynuclear compounds containing sulphur atoms have been obtained from reactions between  $\text{Fe}_3(\text{CO})_{12}$  and various reagents<sup>1</sup> whereas the only example involving ruthenium carbonyl is to be found in a brief note<sup>2,3</sup> reporting the obtaining of  $\text{Ru}_2(\text{CO})_6\text{S}_2\text{Ph}_2$  and  $[\text{Ru}(\text{CO})_2\text{S}_2\text{Ph}_2]_n$  from reactions between ruthenium carbonyl and thiols and thiophenol. IR spectra were given for these compounds, but no analytical data. The second was described as a "polymer" with the carbonyl groups in *cis*-position by analogy with  $[\text{Ru}(\text{CO})_2\text{X}_2]_n$  compounds, where X is a halogen atom.

A polymer with a similar formula can also be obtained from iron<sup>4</sup>; if  $\text{Fe}(\text{CO})_5$  is heated at 120–130° with  $\text{S}_2(\text{CH}_3)_2$  in an autoclave, under CO at 65 atm for about 20 h, the first product obtained is  $[\text{CH}_3\text{SFe}(\text{CO})_3]_2$  in two isomeric forms ("*syn*" and "*anti*"): if CO is omitted, a second compound -  $[(\text{CH}_3\text{S})_2\text{Fe}(\text{CO})_2]_n$  - is also obtained; the latter cannot be prepared, however, by treating  $[\text{CH}_3\text{SFe}(\text{CO})_3]_2$  with dimethyl disulphide in excess. The molecular weight of this iron "polymer", is not given; the context of the report however, indicates that the product is a tetramer with *cis*-carbonyls and the IR spectral data confirm this view.

The present preliminary note is concerned with the behaviour of trinuclear carbonyls of the series Fe, Ru and Os in reactions with organic disulphides, in particular diphenyl disulphide. In the case of iron, these reactions have already been fully studied<sup>1,5</sup>

The same experimental conditions were used in all cases: benzene and n-heptane were used as solvents under nitrogen atmosphere, and diphenyldisulphide was slightly in excess with respect to the carbonyl (molar ratio 1.2/1). No substantial differences could be attributed to the use of one solvent as opposed to the other. Reactions were followed by means of TLC and continued until the inspection of the plates in ultra-violet light showed total disappearance of the carbonyl.

TABLE 1

Analytical data

Compound		m.p. (°C)	Molecular Weight		IR spectra (CCl <sub>4</sub> ) (cm <sup>-1</sup> )
			Found.	Calcd.	
[Ru(CO) <sub>3</sub> SPh] <sub>2</sub>	I yellow-brown powder	85–86° (sharp)	601	588.6	2086 m, 2058 vs, 2014 s, 1973 vw
[Ru(CO) <sub>3</sub> SPh] <sub>n</sub>	II yellow powder	158–162° (dec.)	—	294.3	2083 s, 2032 (sh), 2027 vs, 2016 (sh), 1970 s
[Ru(CO) <sub>3</sub> S <sub>2</sub> Ph <sub>2</sub> ] <sub>n</sub>	III yellow powder	200° (dec.)	1500	403.48	2073 s, 2051 vs, 2020 vs, 2008 (sh), 1995 vw, 1973 m, 1966 m
[Ru(CO) <sub>2</sub> S <sub>2</sub> Ph <sub>2</sub> ] <sub>n</sub>	IV orange needle-crystals	100° (dec.)	—	375.47	2112 vs, 2052 vs, 1996 s
[Ru(CO) <sub>2</sub> S <sub>2</sub> Ph <sub>2</sub> ] <sub>n</sub>	V orange tablets	150–155° (dec.)	2490	375.47	2106 m, 2046 s, 1991 m, 1945 (sh)
[Ru(CO) <sub>3</sub> SEt] <sub>2</sub>	Ia brown powder	67–68°	510.5	492.5	2084 s, 2061 vs, 2025 (sh), 2017 vs, 1998 vw, 1933 m
[Ru(CO) <sub>2</sub> S <sub>2</sub> Et <sub>2</sub> ] <sub>n</sub>	IVa yellow-orange powder	59–60° (sharp)	—	247.3	2110 w, 2041 vs, 1986 s
[Os(CO) <sub>3</sub> SPh] <sub>2</sub>	Ib pale-yellow powder	—	—	766.81	2110 m, 2070 vs, 2061 (sh), 2028 vs, 2004 (sh), 1991 w
[Os(CO) <sub>2</sub> S <sub>2</sub> Ph <sub>2</sub> ] <sub>n</sub>	IIIb orange-yellow insoluble powder	—	—	464.6	2112 (sh), 2099 vs, 2041 s, 2032 (sh), 2016 s, 1949 m

In boiling n-heptane, iron carbonyl disappeared after 2 h and ruthenium carbonyl after 45 min; some osmium carbonyl was still present after 7 h. These data were observed in reactions with diphenyl disulphide; when diethyl disulphide was used, reactions with ruthenium carbonyl were virtually 100% complete in only 10 min.

Particular attention was given to the ruthenium carbonyl reactions: five sulphur-containing compounds were isolated in the case of diphenyl disulphide and four in that of diethyl disulphide; only two of the latter have been certainly identified as yet. The analytical data so far obtained are set out in Table 1, where they are listed in their elution order, starting from the eluent front on the TLC plate: the missing numbers represent the compounds not yet identified. The compounds already identified by Johnston *et al.*<sup>2</sup>, but not yet described, are also reported. The table also gives our preliminary data for the osmium compounds, whose identification is, however, still uncertain.

The compounds were separated and purified by means of TLC. The substrate was Kieselgel P.F. and the eluent a mixture of 90% petroleum ether and 10% ethyl ether; the quantities obtained were, in some cases, too small to permit the determination of molecular weight (osmometry in benzene). Satisfactory analyses were obtained in all cases for carbon, hydrogen, the ruthenium or osmium, and sulphur or oxygen.

Compounds I, V and Ia, IVa gave the best yields, V and IVa being the principal products of their respective reactions their mobility on the TLC plates was poor owing to their insolubility in aliphatic hydrocarbons; they could be eluted from silica substrates since they were soluble in benzene, toluene and, very easily, in ethyl ether.

The results obtained so far, indicate that compounds II and III (whose yield is extremely low) are intermediate products of the "polymerization" of Ru<sub>3</sub>(CO)<sub>12</sub> derivatives; they are characterized by a gradual increase in molecular weight and a reduction in the number of CO groups in their formula-unit.

The relatively high yield and good stability of compound I point to its being a stable reaction product: this view is supported by the behaviour of  $[\text{CH}_3\text{SFe}(\text{CO})_3]_2$  which, in the presence of an excess of dimethyl disulphide, does not give rise to "polymerization".

It is, moreover, likely that products IV and V, with their analogous formulae and very similar spectra, differ in the number of their formula-units or as a result of one of the several cases of isomerism that may occur in these compounds.

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