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REACTIONS OF $Ru_3(CO)_{12}$ WITH CHALCOGEN COMPOUNDS

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SUMMARY

Attempts to synthesize the compounds $Ru_3(CO)_9X_2$ ($X = S, Se, Te$) by treating $Ru_3(CO)_{12}$ in alkaline solution with chalcogen compounds gave the substituted hydrides of the series $H_2Ru_3(CO)_9X$ ($X = S, Se, Te$), which were isolated and characterised. The same products were obtained under other conditions also.

The NMR and mass spectra are discussed, and possible structures for these paramagnetic complexes are suggested.

INTRODUCTION

Many complexes are known which were made from reactions of metal carbonyls—particularly those of Fe and Co—with sulphur or sulphur- or chalcogen compounds, but few reactions between $Ru_3(CO)_{12}$ and these compounds have been previously studied.

Preliminary studies of the reaction between $Ru_3(CO)_{12}$ and thiols[1] or organic disulphides[2] led to the isolation and partial characterisation of binuclear and polymeric substituted products. More recently, however, compounds of the type $HOs_3(CO)_{10}$-OR were obtained by treating $Os_3(CO)_{12}$ with aliphatic alcohols[3,4]. Consequently a more thorough investigation was carried out on the reactions between $Ru_3(CO)_{12}$, alcohols and thiols, the compounds $HRu_3(CO)_{10}SR$ being obtained[5]. These are the initial complexes formed in the reaction of the carbonyl with thiols, the final products being the binuclear and "polymeric" complexes mentioned above.

The behaviour of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ towards chalcogens showed a striking difference, the former very readily giving the $Fe_3(CO)_9X_2$ complexes ($X =$ S, Se, Te)[6], the analogues of which are not known for ruthenium.

We have now attempted to synthesize the compounds $Ru_3(CO)_9X_2$ by using experimental conditions similar to those employed by Hieber and Gruber[6] (*i.e.* in alkaline solutions of the carbonyls, or under high pressures of CO), or by King[7] (*i.e.* in benzene solution, with cyclohexene sulphide). We have also examined the reactions with a number of chalcogen compounds, in order to establish the reactivity of $Ru_3(CO)_{12}$ towards these ligands.

EXPERIMENTAL

$Ru_3(CO)_{12}$ was obtained from Strem Chemicals and the other highpurity reagents from C. Erba. All were used without further purification. Glass reaction vessels of conventional type were used, equipped with reflux condenser and gas inlet; pure, dry nitrogen was used to provide an inert atmosphere.

Electrically heated stainless steel high-pressure reactors were employed, when necessary; no $Fe(CO)_5$ or $Fe_3(CO)_9X_2$ were detected among the reaction products although these products can be formed from reactions under high pressures of CO at high temperature in presence of finely divided iron.

The following reactions were carried out:

(*a*). *Reaction between* $Ru_3(CO)_{12}$ *and* XO_3^- *ions, in alkaline solution.* In a typical experiment, a solution of 200 mg (0.31 mmoles) of $Ru_3(CO)_{12}$ in 50 ml CH_3OH was treated with 20 ml of 1 *M* solution of KOH under nitrogen, as described by Johnson and his coworkers[8]. The mixture was stirred at room temperature, until the carbonyl had completely dissolved. To this solution were successively added either 120 mg (0.9 mmoles) of Na_2SO_3, 400 mg (3.6 mmoles) of SeO_2, or 1.00 g (6.3 mmoles) of TeO_2, dissolved or suspended in a 20 ml solution of 1 *M* KOH, and 40 ml of distilled water. When Na_2SO_3 or SeO_2 was added, the solutions were warmed for 15 and 24 h, respectively, at 50°, but when TeO_2 was added, the reaction was allowed to proceed for 30 min at room temperature.

Finally, the solution was acidified with 2 *N* H_2SO_4, and the precipitate was dried under nitrogen and extracted with CCl_4. The CCl_4 solutions were subjected to TLC and gave, in addition to unchanged $Ru_3(CO)_{12}$, 5%, 1% and 0.5%, respectively, of $H_2Ru_3(CO)_9X$ (X = S, Se, Te). The solids remaining after the extraction with CCl_4, are poorly-defined "polymeric" substances, containing ruthenium and chalcogens, and characterised by absorptions in the IR due to terminal CO groups; the yield increases in the order $S < Se < Te$.

The use of $Na_2S_2O_5$ or S_2Cl_2 instead of Na_2SO_3 gave only yellow, rubbery solids, containing much sulphur. In the case of S_2Cl_2 the reaction was carried out by dissolving $Ru_3(CO)_{12}$ and solid KOH in anhydrous CH_3OH in order to avoid hydrolysis of the S_2Cl_2.

(*b*). *Reactions between* $Ru_3(CO)_{12}$ *and elemental S or Se, under CO pressure.* In a typical experiment, 200 mg (0.31 mmoles) of $Ru_3(CO)_{12}$ were mixed with 200 mg (6.24 mmoles) of sulphur, or 300 mg (3.79 mmoles) of selenium, and heated, in absence of solvent, under 110 atm. of CO, for 26 h at 200° when sulphur was used, and for 36 h at 300° when selenium was used.

The solid product recovered from the inner wall of the reactor was extracted with CCl_4, leaving elemental sulphur or selenium as a residue. The solutions were subjected to TLC to give some uncharged $Ru_3(CO)_{12}$ and very small amounts of $H_2Ru_3(CO)_9X$.

(*c*). *Other reactions.* Refluxing $Ru_3(CO)_{12}$ with CS_2 for 3 h gave a deep-red powder of formula $[Ru(CO)_3CS]_n$. (Found: C, 20.1; O, 21.3; Ru, 43.7; S, 14.5; calcd.: C, 20.90; O, 20.89; Ru, 44.26; S, 13.95%). IR Spectrum (paraffin): 2100 s, 2052 vs, 1990 w cm^{-1}.

The reaction of $Ru_3(CO)_{12}$ with a 5/1 (molar) excess of cyclohexene sulphide in boiling benzene (10 h), or in n-heptane under 20 atm. of CO (20 h, 150°) yielded a yellow complex of formula $[Ru(CO)_3(C_6H_{10})S]_n$. (Found: C, 37.15; H, 3.51; O, 16.2; Ru, 24.1; S, 9.98; calcd.: C, 36.06; H, 3.36; O, 16.01; Ru, 33.77; S, 10.71%.) IR Spectrum (CCl_4): 2104 m, 2040 vs, 1985 s cm^{-1}.

(*d*). *Analysis of the products.* The products were analysed by means of an F & M 186-Model CHN Analyzer, and a Perkin–Elmer 303-Model Atomic Absorption Spectrophotometer. IR Spectra were recorded on a Beckman IR-12 (KBr optics), the NMR spectra on a 60-megacycle JEOL instrument, and the mass spectra on a Hitachi–Perkin–Elmer RMU-6H.

The physical properties and IR spectra of the compounds $H_2Ru_3(CO)_9X$ are listed in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND IR SPECTRA OF THE COMPOUNDS $H_2Ru_3(CO)_9X$

Compound	Physical form	M.p. (°C)	Mol. wt. found[a] (calcd.)	IR (CCl_4) (cm^{-1})
$H_2Ru_3(CO)_9S$	Yellow solid Air sensitive	118	592 (591.3)	2120 s, 2084 vs, 2062 vs, 2050 s(sh), 2018 vs, 2010 s(sh)
$H_2Ru_3(CO)_9Se$	Orange-yellow solid	110 (dec.)	640 (638.2)	2117 s, 2083 vs, 2060 vs, 2048 s(sh), 2016 vs, 2009 s(sh)
$H_2Ru_3(CO)_9Te$	Yellow solid	135 (dec.)	690 (686.8)	2112 s, 2079 vs, 2061 s(sh), 2058 vs, 2047 s(sh), 2014 vs, 2011 s(sh)

[a] By mass spectrometry.

RESULTS

Mass spectra

The mass spectra of the series $H_2Ru_3(CO)_9X$ are all quite similar. The parent molecular ion is observed in all the cases, in high abundance. Although the envelope of isotope peaks associated with the parent ion is complex, an accurate measurement has been possible in presence of an internal standard, and the precise molecular formula has been confirmed in every case. The fundamentation pattern is obtained as follows; after two CO molecules have been ejected, simultaneous loss of H and CO occurs twice, the ions $Ru_3(CO)_nX^+$ (n=4–0) are then detected, the Ru_3X^+ ion is more abundant than the Ru_3^+ ion, except in the case X=Te. The corresponding doubly-charged ions are observed in good abundance, indicating the existence of a trimetallic cluster[3]. On the other hand, no bi- or mono-nuclear ions are observed in high abun-

TABLE 2

PERCENTAGE ABUNDANCES OF FRAGMENTS IN THE MASS SPECTRA OF $H_2Ru_3(CO)_9X$ AND $Fe_3(CO)_9X_2$[a]

Type of fragments	$Fe_3(CO)_9X_2$			$H_2Ru_3(CO)_9X$		
	X=S	Se	Te	X=S	Se	Te
Trinuclear	50	47.5	31.8	68.9	48.4	43.8
Doubly charged trinuclear				9.4	15.6	25.4
Binuclear	32.3	31	22	9.8	4.3	25.1
Mononuclear	17.7	21.5	46.2	11.9	31.7	5.8

[a] For a comparison with the spectra of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ see Ref. 9.

dance. The percentage abundance of the tri-nuclear fragments decreases in the order S > Se > Te (see Table 2).

This behaviour agrees with that reported for the hydrides $H_2Ru_4(CO)_{13}$ and $H_2Os_3(CO)_{10}$[3,8]. In the mass spectra of $HRu_3(CO)_{10}SR$[5], however, no loss of hydrogen was observed.

The percentage abundances of the fragments in the mass spectra of $H_2Ru_3(CO)_9X$ and $Fe_3(CO)_9X_2$ are shown in Table 2. Although there is a marked difference in structure and in the coordinating metal in the two series, it is possible to compare the mass spectra. In those of $Fe_3(CO)_9X_2$ the parent molecular ions are always observed, and there is loss of CO groups to give the ions $Fe_3(CO)_nX_2^+$ ($n=9$–0); moreover, the ions $Fe_3X_2^+$ are always more abundant than Fe_3^+. The percentage abundance of trimetallic fragments still decreases in the order S > Se > Te. Doubly-charged trimetallic fragments are observed in very small quantities.

NMR spectra (CCl_4)

The NMR spectra provide good evidence for the presence of hydrido ligands.

In all cases a single proton resonance (apparently formed by two non-resoluble peaks) is observed at τ 29.45, 29.55 and 29.70 ppm, respectively for X = S, Se, Te, which is consistent with the presence of bridging hydrido groups. Proton resonances for compounds that are thought to have bridging hydrido-atoms fall within τ 18.6 (ref. 8) and 34.0 (refs. 5, 8) ppm.

IR Spectra

The IR spectra in the carbonyl region are similar for all the compounds $H_2Ru_3(CO)_9X$, and indicate a low molecular symmetry. No vibrations due to bridging carbonyls are observed.

Magnetic measurements

Magnetic susceptivitiy measures indicate that the compound $H_2Ru_3(CO)_9S$ is paramagnetic and has two unpaired electrons. This result is confirmed by evidence from the NMR spectrum in solution.

DISCUSSION

The compounds $H_2Ru_3(CO)_9X$ appear to be the initial products of the reactions described, the final products being "polymers". This is consistent with the previous reports on the reactions of $Ru_3(CO)_{12}$ with chalcogen compounds. The complexes $H_2Ru_3(CO)_9X$, $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ are obtained under similar conditions and show similar NMR resonances and comparable mass spectra, which is evidence for some structural similarities. The formation of hydrido–chalcogen–carbonyls even under CO pressure in absence of solvent is probably due to the presence of moisture in the gas or in the reactors.

In contrast to the results with iron and cobalt compounds, the complexes $Ru_3(CO)_9X_2$ are not formed in these reactions, probably owing to the different atomic size, and the greater energy of the M–M bond in the ruthenium carbonyls. The reactions of $Ru_3(CO)_{12}$ with cyclohexene sulphide and CS_2 also differ markedly from those involving $Fe_3(CO)_{12}$ and $Co_2(CO)_8$.

On the basis of the mass. IR, and NMR spectra, and of the magnetic data, we suggest as structures for the compounds $H_2Ru_3(CO)_9X$ the alternatives shown in Fig. 1, in which two ruthenium atoms are equivalent while the other has a different environment. These structures account for the existence of an Ru_3X^+ ion in the mass spectra, and also for the position of the NMR resonances. They also account for the existence of two unpaired electrons.

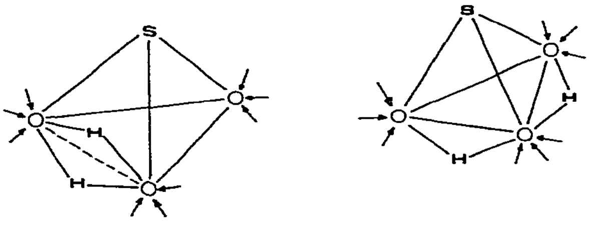

Fig. 1.

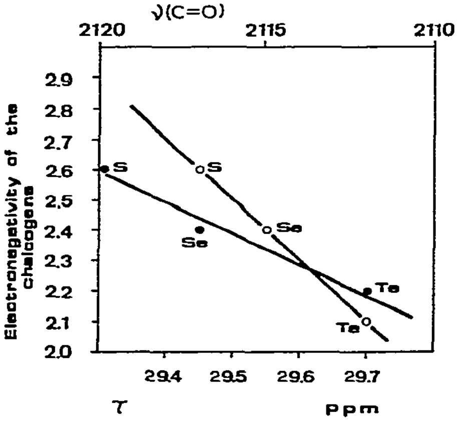

Fig. 2.

The chalcogen atom has an obvious influence on the M–M, M–C and M–H bonds in the complexes (see Fig. 2); the NMR chemical shift or CO stretching frequencies are linearly related to the chalcogen electro-negativities. In the mass spectra, furthermore, the abundance of trimetallic fragments, and of the ions Ru_3X^+ and $Fe_3X_2^+$ is dependent on the chalcogen. Complexes containing the most electronegative ligand (e.g. sulphur) show the strongest clusters in accordance with the results of early kinetic studies on the compounds $Fe_3(CO)_9X_2$[10].

It is noteworthy that this is one of the few cases in coordination chemistry in which it is possible to show an unequivocal correlation between the small but significant variations in the NMR chemical shift and an established characteristic of the substituent.

Further investigations on the structures of these compounds, which, along with $Co_3(CO)_9S$, represent examples of paramagnetic trinuclear carbonyl complexes, are in progress.

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