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

REACTIONS OF $Ru_3(CO)_{12}$ WITH ASYMMETRICALLY SUBSTITUTED ACETYLENES. A NEW TYPE OF INTERACTION BETWEEN ACETYLENES AND A METAL-ATOM CLUSTER

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(Received January 4th, 1972)

SUMMARY

The compounds $Ru_3(CO)_9X$ (where $X = C_2$(t-Bu)H and C_2(Ph)H) have been obtained from the reactions of $Ru_3(CO)_{12}$ with t-BuC≡CH and PhC≡CH. Their IR, NMR and mass spectra are reported and discussed.

A hydrido signal in the NMR spectrum and other evidence point to a new type of structure, different from that proposed by Blount and his coworkers for $Fe_3(CO)_9$-C_2Ph_2.

INTRODUCTION

In their studies on the reactions of iron carbonyls with acetylenes, Hubel and his coworkers[1] obtained trinuclear compounds of the type $Fe_3(CO)_9X$ [$X = C_2Ph_2$, $C_2(CH_3)Ph$, $C_2(Ph)H$, etc.], in the structures of which the acetylene was considered to be a formal donor of six electrons. Owing to the position of the acetylene with respect to the metal-atom cluster (as indicated by X-ray crystallography), Blount and his coworkers[2] suggested the presence of a special type of empty, three-centre bonding MO, which was described as "formally analogous to the recently determined, symmetrical, bent, delocalized metal–hydrogen–metal systems in ... $HFe_3(CO)_{11}^-$"[2a].

We later studied the reactions of $Ru_3(CO)_{12}$ with symmetrically substituted acetylenes, and obtained the compound $Ru_3(CO)_9(C_2Ph_2)$[3], which was thought to be structurally similar to $Fe_3(CO)_9(C_2Ph_2)$. We have now studied the reactions of some asymmetrically substituted acetylenes with $Ru_3(CO)_{12}$, and obtained, among the other products, the monosubstituted trinuclear compounds $Ru_3(CO)_9X$ [where $X = C_2$(t-Bu)H and C_2(Ph)H], which show some interesting features.

EXPERIMENTAL

Conventional glass vessels were employed, equipped with magnetic stirrers and reflux condensers. The reactions were carried out under dry nitrogen and followed by TLC as previously reported[3].

Preparation of $Ru_3(CO)_9[C_2(t\text{-}Bu)H]$

An excess (2 mole/mole of carbonyl) of 3,3-dimethyl-1-butyne was treated with $Ru_3(CO)_{12}$ in petroleum ether (40–70°) or n-heptane under reflux. In the first solvent gradual reaction of the carbonyl occurred, and 100% yields of $Ru_3(CO)_9[C_2(t\text{-}Bu)H]$ were obtained*. In n-heptane, the reaction was less easily controlled, and within 20 min the green $Ru_3(CO)_8[C_2(t\text{-}Bu)H]_2$, having bridging CO groups and other products, were formed thus lowering the yield of the monosubstituted compound.

The mixture was filtered, and evaporated under vacuum, and the solid washed with diethyl ether until the solution was only pale yellow. The residue was pure $Ru_3(CO)_9[C_2(t\text{-}Bu)H]$. This compound is air-stable for months, very slightly soluble in aliphatic alcohols and ethers and in aliphatic and aromatic hydrocarbons, and quite soluble without decomposition in acetone and isobutyl methyl ketone (9 and 14 mmole/l respectively) and cold trifluoroacetic acid.

Preparation of $Ru_3(CO)_9[C_2(Ph)H]$

The compound was obtained by treating $Ru_3(CO)_{12}$ with phenylacetylene, in petroleum ether or n-heptane. Under all the reaction conditions, several products were formed simultaneously, and the highest yield of the monosubstituted product was about 30%.

The same product is also produced, in 40% yield, from the reaction of $Ru_3(CO)_{12}$ with phenylpropiolic acid in benzene, together with two unidentified products. The aromatic solvent was employed because of the insolubility of the acid in aliphatic solvents.

Analysis of the products

The compounds were analyzed with the aid of an F & M 186 Model C,H,N Analyzer and a Perkin–Elmer 303 Model Atomic Absorption Spectrophotometer; the IR spectra in CCl_4 were recorded with a Beckmann IR-12 (KBr optics), and the

TABLE 1

PHYSICAL PROPERTIES AND SPECTRA OF THE COMPOUNDS $Ru_3(CO)_9X$

	$X =$	
	$C_2(t\text{-}Bu)$	$C_2(Ph)H$
Physical state	Pale-yellow crystals	Orange-yellow crystals
M.p. (°C)	156–157° (dec.)	101–102°
Mol.wt. found (calcd.)	640 (637.5)	664 (659.1)
IR spectrum	2097 m, 2070 vs, 2054 vs 2022 vs, 1992 m	2099 m, 2074 vs, 2056 vs 2026 vs, 1994 m(sh)
NMR spectrum (τ)	8.6 s (9 H) 31.8 s (1 H)	2.75 m (5 H) 31.4 s (1 H)

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* Preliminary kinetic studies of the reaction show that the rate law is of the type:

$$k_{obs} = k_1 \cdot [\text{carbonyl}] + k_2 \cdot [\text{carbonyl}] \cdot [\text{ligand}]$$

in accord with the results obtained by Candlin and Shortland[4] for the reactions of $Ru_3(CO)_{12}$ with Group V ligands. The further substitution of $Ru_3(CO)_9[C_2(t\text{-}Bu)H]$ gave many products, some of which arise from the breakdown of the cluster.

NMR spectra in CCl_4 with a JEOL JNM-C-60 HL instrument. Mass spectra were recorded with an Hitachi–Perkin–Elmer RMU-6H instrument; dibromotetrafluorobenzene was used as internal standard.

The physical properties and the IR and NMR spectra of the compounds prepared are listed in Table 1.

RESULTS

Mass spectra

The mass spectra of $Ru_3(CO)_9X$ [$X=C_2(t\text{-}Bu)H$ and $C_2(Ph)H$] show very strong similarities; the ions $Ru_3(CO)_nX^+$ ($n=9$–0) were observed in high abundance together with the corresponding doubly charged ions, the most abundant being Ru_3X^+ and Ru_3X^{2+}, while Ru_3^+ and Ru_3^{2+} were present in smaller quantities. No ions corresponding to loss of one hydrogen atom or of (H+CO) were observed.

Fragmentation of the organic moiety occurred also, but the complex isotopic pattern and the closeness of the ions caused superimpositions and made counting difficult. There is loss of CH_3, CH_2, H_2 and H groups [when $X=C_2(t\text{-}Bu)H$] and C_2H_n ($n=2$–4), C_4H_n ($n=2$–4), H_2 and H groups [when $X=C_2(Ph)H$]. The percentage abundances of the trimetallic fragments were 98 and 95 respectively: no binuclear fragments were detected.

By contrast, $Ru_3(CO)_9(C_2Ph_2)$ decomposes in the mass spectrometer to give $Ru_2(CO)_6(C_2Ph_2)_2$ and other, unidentified, products.

NMR spectra

The ^1H NMR spectra of $Ru_3(CO)_9X$ show a sharp singlet in the hydride region. The intensity ratio indicates that the high-field signal is due to the acetylenic proton, suggesting an interaction between it and the metal atoms. Such an hydrido signal is not present in the case of $Ru_3(CO)_9(C_2Ph_2)$.

IR spectra

The IR spectra of the $Ru_3(CO)_9X$ species do not show appreciable differences from that of $Ru_3(CO)_9(C_2Ph_2)$[3] indicating that there is similar symmetry in all three compounds. In all cases, no absorptions due to bridging CO-groups were present.

DISCUSSION

The high percentage abundances of the trimetallic fragments, in the mass spectra of the $Ru_3(CO)_9X$ species are good evidence for the stabilisation of the cluster by the acetylene; they are even greater than those observed in the unsubstituted $Ru_3(CO)_{12}$[5] and in the substituted compounds $H_2Ru_3(CO)_9Y$ (where Y=S, Se, Te)[6].

Another stabilizing factor when $X=C_2(t\text{-}Bu)H$ may be the bulk of the tert-butyl group[7]. This group has, moreover, a strong $+I$ inductive effect, and thus renders the acetylene more basic; the rate law observed for the reaction agrees well with these facts. The course of the reaction involving phenylpropiolic acid, from which $Ru_3(CO)_9[C_2(Ph)H]$ and not $Ru_3(CO)_9[C_2(Ph)COOH]$ was obtained, and the NMR results indicate that one hydrogen atom in the acetylene may be of particular structural significance. On the other hand, the IR spectra show a strong similarity to that of $Ru_3(CO)_9(C_2Ph_2)$.

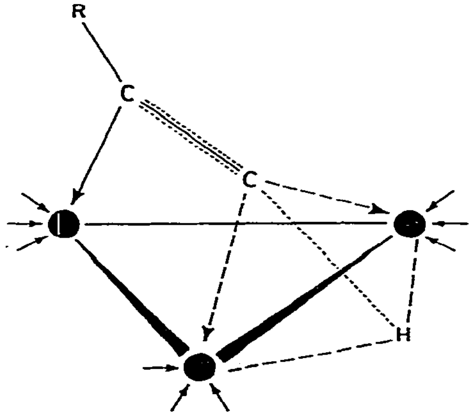

Fig. 1.

On the basis of the above facts we suggest for the $Ru_3(CO)_9X$ complexes the structure shown in Fig. 1, having the same symmetry found by Blount[2] for $Fe_3(CO)_9(C_2Ph_2)$, but in which the proposed three-center MO is really occupied by a hydrogen atom, whereas steric factors and repulsions rule out the presence of a tert-butyl or phenyl group in this position. The proposed structure shows an analogy to that found in the polymeric $[Cu(C_2Ph)]_n$[8], and does not require an excessive elongation of the C–C acetylenic bond, such as would be required in view of the greater size of the ruthenium cluster if the structure originally proposed by Blount were correct.

Further structural studies on these compounds are in progress.

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