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

REACTIONS OF TRIRUTHENIUM DODECACARBONYL WITH DIPHENYLACETYLENE IN ALKALINE SOLUTION

O. GAMBINO, E. SAPPA and G. CETINI
Institute of Chemistry of the University, Turin (Italy)

(Received March 27th, 1972; in revised form May 22nd, 1972)

SUMMARY

From the reaction between $Ru_3(CO)_{12}$ and C_2Ph_2 in aqueous methanolic alkali, the novel substituted hydrido-carbonyl, $H_2Ru_3(CO)_9C_2Ph_2$ has been obtained. This product shows structural features similar to those of the previously reported $H_2Ru_3(CO)_9E$ (E = S, Se, Te) and $H_2Ru_3(CO)_9(C_8H_8)$ compounds.

The properties of the compound are reported, and its role as intermediate in the formation of $Ru_3(CO)_8(C_2Ph_2)_2$ is discussed.

INTRODUCTION

Johnson *et al.*[1] obtained the compounds $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ from the reaction of $Ru_3(CO)_{12}$ with KOH in aqueous methanol followed by acidification with dilute sulphuric acid. Acidification of solutions of $HRu_3(CO)_{10}SEt$ followed by water-dilution[2] gave the compound $H_2Ru_3(CO)_9S$. We synthesized this complex, and others of the series $H_2Ru_3(CO)_9E$ (E = S, Se, Te) by using the same reaction conditions as employed by Johnson but in the presence of EO_3^{2-} ions, and warming of the solution before acidification[3].

From the reaction between $Ru_3(CO)_{12}$ and bicyclo[3.2.1]octa-2,6-diene, in benzene, Domingos *et al.*[4] obtained the compound $H_2Ru_3(CO)_9(C_8H_8)$, in which the hydridic atoms are abstracted from the diene; the structure of this compound is similar to that proposed for the series $H_2Ru_3(CO)_9E$.

We have extended the investigation to the reactions of basic aqueous methanolic solutions of $Ru_3(CO)_{12}$ with C_2Ph_2, the reactions of which with triruthenium dodecacarbonyl in hydrocarbon solvents we have previously reported[5]. In hydrocarbon solvents several acetylene-substituted trinuclear carbonyls were isolated, among them $Ru_3(CO)_9C_2Ph_2$, which gives no ^1H NMR absorption in the hydridic region, whereas the analogous compounds $Ru_3(CO)_9HC_2R$ (R = Ph, t-Bu) show the presence of one hydridic atom[6].

From the reaction in the alkaline medium we have obtained, along with other well known products, a novel product, which analyzes as $H_2Ru_3(CO)_9C_2Ph_2$. Its properties and reactions are described.

EXPERIMENTAL

Conventional glass vessels, equipped with magnetic stirrers, and a nitrogen atmosphere were employed. In a typical experiment, 100 mg of carbonyl were treated with 50 ml of methanol and 20 ml of a 1 *M* aqueous solution of KOH, until $Ru_3(CO)_{12}$ had completely dissolved. A methanolic solution of the acetylene was then added, and the reaction allowed to proceed for 6 h without warming. Acidification was carried out with aqueous 2 *N* H_2SO_4 in stoichiometric quantity, and the resulting mixture was filtered. The solid and liquid phases were separately extracted with CCl_4, and the two CCl_4 fractions were purified by TLC. Using a 10/1 molar excess of C_2Ph_2, a mixture of $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$, $H_2Ru_3(CO)_9C_2Ph_2$ and $Ru_3(CO)_8(C_2Ph_2)_2$, the "violet isomer",[5] was obtained (yields about 20%, 5%, 20% and 15%, respectively) together with smaller quantities of $Ru_3(CO)_9C_2Ph_2$. Results were reproducible.

The products were analyzed by means of an F&M C, H, N Analyzer, and a Perkin–Elmer 303 Model Atomic Absorption Spectrophotometer. IR Spectra were recorded on a Beckman IR-12 (KBr optics), and ^1H NMR spectra on a JEOL JNM-C-60 HL instrument. Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6H instrument.

RESULTS

$H_2Ru_3(CO)_9C_2Ph_2$ is a yellow solid, which forms long needles, m.p. 110–112° without decomposition; it is very soluble in ethyl ether, n-heptane, CCl_4 and CS_2, but slight decomposition was observed when crystals were obtained by evaporating (under air or nitrogen) solutions in CCl_4 or n-heptane.

In boiling 40–70° petroleum ether (3 h), with a 10/1 molar excess of C_2Ph_2, the compound gives 50% yields of the "violet isomer" $Ru_3(CO)_8(C_2Ph_2)_2$, while 40% is recovered unchanged; no other soluble products are formed.

Mass spectrum

In the mass spectrum of the compound (recorded with perfluorotributylamine or $Re_2(CO)_{10}$ as internal standards), the parent ion (*m/e* 738) and those corresponding to the loss of two CO groups are observed, then a double simultaneous loss of H and CO, and finally loss of the remaining CO groups. The ions $Ru_3C_2Ph_2^+$ and the corresponding doubly-charged fragment are the most abundant. Fragmentation of the acetylenic moiety also occurs, with loss of C_2H_2 and C_2; the ions Ru_3C^+, $Ru_2C_2Ph_2^+$ and $RuC_2Ph_2^+$ are observed, but Ru_3^+ is not detectable.

This fragmentation pattern is in good accord with that observed for the series $H_2Ru_3(CO)_9E$, especially in the release of H and CO. The fragmentation of the organic moiety, however, presents, features similar to those observed with the compounds $Ru_3(CO)_9HC_2R$; the high abundance of trimetallic fragments (96.4%) points to a strongly-stabilized substituted cluster, as already observed in the two series $H_2Ru_3(CO)_9E$ and $Ru_3(CO)_9HC_2R$, and its value is close to those observed with $Ru_3(CO)_9HC_2R$.

NMR spectrum

The ^1H NMR spectrum was recorded in CS_2 solution; a sharp absorption at τ 3.05 (10 H) assigned to the phenyl groups, and an unresolved doublet (2 H) at τ 28.9, assigned to two presumably non-equivalent hydrogen atoms, were observed. The hydridic absorption falls very close to the unresolved doublets observed in the $H_2Ru_3(CO)_9E$, and $H_2Ru_3(CO)_9(C_8H_8)$, which contain bridge-bonded protons between the metal atoms.

IR spectrum

The IR spectrum was recorded in n-heptane solution, in which better resolution is obtained; a very large number of absorptions, indicative of low symmetry, was observed; peaks were observed at 2107 s, 2081 vs, 2058 vs, 2043 vs (sh), 2037 s (sh), 2021 vs, 2009 s (sh), 1995 s cm^{-1}, and no absorptions in the bridging-CO region. This behaviour is quite comparable with the one of the $H_2Ru_3(CO)_9E$ compounds.

DISCUSSION

On the basis of the reported experimental evidence, it is reasonable to suggest for $H_2Ru_3(CO)_9C_2Ph_2$ a structure similar to those reported for the $H_2Ru_3(CO)_9E$ and $H_2Ru_3(CO)_9(C_8H_8)$ compounds; thus the acetylenic hydrido-carbonyl here described belongs to the interesting series of compounds characterized by the basic structural group $H_2Ru_3(CO)_9$.

The formation of $H_2Ru_3(CO)_9C_2Ph_2$ in good yields in alkaline media, demonstrates the importance of this preparative method for the synthesis of substituted hydrido-carbonyls. The simultaneous formation of tetranuclear unsubstituted hydrido-carbonyls and of substituted carbonyls and hydrido-carbonyls, indicates that there is competition between mononuclear $Ru(CO)_x^{y-}$ groups and acetylenes or chalcogens, for the $Ru_3(CO)_m^{n-}$ ions.

The reaction of $H_2Ru_3(CO)_9C_2Ph_2$ with an excess of C_2Ph_2 in hydrocarbon solvents, suggests that this complex is an important intermediate in the formation

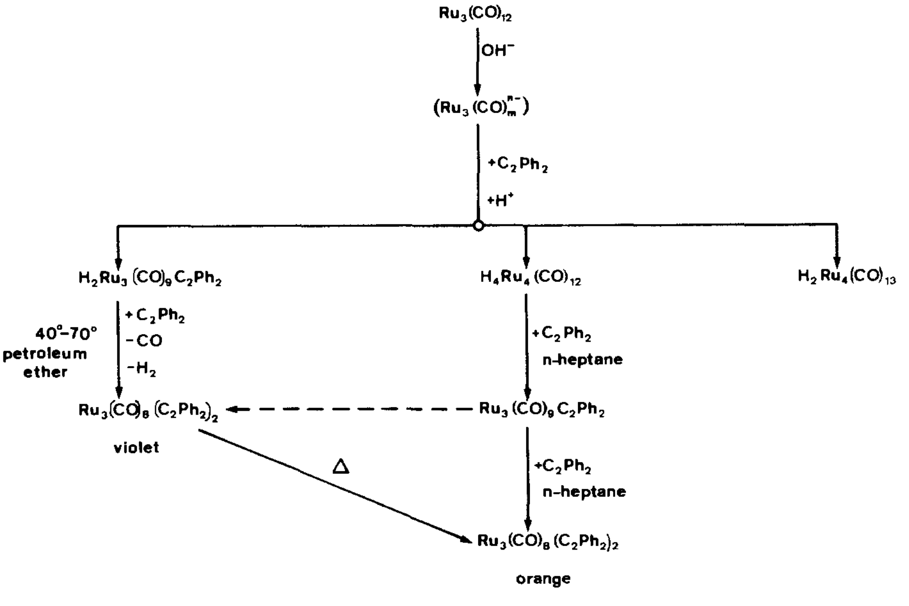

Fig. 1.

of the "violet isomer" $Ru_3(CO)_8(C_2Ph_2)_2$; the proposed reaction pattern is shown in Fig. 1. The reactions indicate, once more, the importance of some hydridic compounds (obtained either in alkaline solution or by abstraction of hydrogen from organic molecules) as intermediates in the synthesis of organometallic compounds.

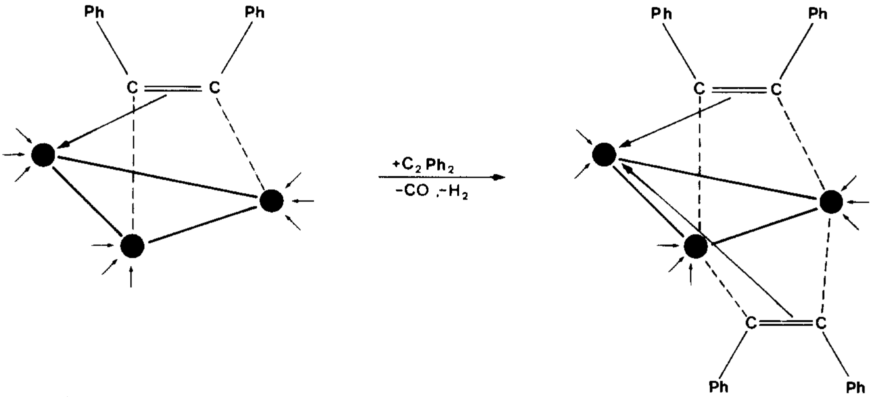

Fig. 2. (Hydrogen atoms omitted.)

It will be seen from Fig. 2 that the reaction between $H_2Ru_3(CO)_9C_2Ph_2$ and C_2Ph_2, to give the "violet isomer" $Ru_3(CO)_8(C_2Ph_2)_2$ whose structure is known, is further evidence of the proposed structure of $H_2Ru_3(CO)_9C_2Ph_2$. Until now, however, the role of the hydridic species in this kind of reaction has scarcely been recognised, for instance $H_4Ru_4(CO)_{12}$ reacts with a 10/1 molar excess of C_2Ph_2 in boiling (40–70°) petroleum ether[7] but neither $H_2Ru_3(CO)_9C_2Ph_2$ nor the "violet isomer" are obtained, $Ru_3(CO)_9C_2Ph_2$ and the "orange isomer" $Ru_3(CO)_8(C_2Ph_2)_2$ being formed in good yields.

The reactions of the ruthenium hydrido-carbonyls with acetylenes, as well as the reactions of $(CH_3)_3C{-}C{\equiv}C{-}H$ with $Ru_3(CO)_{12}$ in alkaline solution, are now being studied in this laboratory.

REFERENCES

1 B. F. G. Johnson, R. D. Johnston, J. Lewis and B. H. Robinson, *J. Chem. Soc. A*, (1968) 2856.
2 A. J. Deeming, R. Ettorre, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, (1971) 1797.
3 E. Sappa, O. Gambino and G. Cetini, *J. Organometal. Chem.*, 35 (1972) 375.
4 A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, 36 (1972) C43.
5 G. Cetini, O. Gambino, E. Sappa and M. Valle, *J. Organometal. Chem.*, 17 (1969) 437.
O. Gambino, G. Cetini, E. Sappa and M. Valle, *J. Organometal. Chem.*, 20 (1969) 195.
6 E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organometal. Chem.*, 39 (1972) 169.
7 O. Gambino, E. Sappa and G. Cetini, unpublished results.