

Photochemistry of Hydrido Ruthenium Clusters

R. AMADELLI, V. CARASSITI, A. MALDOTTI

Centro Fotochimica e Reattività Stati Eccitati Composti Coordinazione, C.N.R., Istituto Chimico, Università, Ferrara, Italy

S. AIME, D. OSELLA

Istituto Chimica Generale ed Inorganica, Facoltà Scienze MFN, Università, Turin, Italy

and M. MILONE

Istituto Chimica Generale ed Inorganica, Facoltà Farmacia, Università, Turin, Italy

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Transition metal clusters have been the object of the attention of several investigators. Various extensive reviews have recently appeared which discuss the chemical and photochemical behavior of these compounds as well as their use as catalysts for a variety of reactions [1–3]. Metal carbonyl clusters of the type $M_3(CO)_12$ ($M = Fe, Ru, Os$) appear to be among the most widely studied, both by chemical and photochemical methods [1].

The dominant photoreaction of $Ru_3(CO)_{12}$ and other trimeric clusters, following irradiation in their low-lying electronic absorption bands, appears to be fragmentation [1]. It is generally assumed that the primary photochemical process is the homolytic cleavage of a metal–metal bond to yield an open framework (diradical species) [4–6].

In this letter we report preliminary results of a photochemical investigation on organo triruthenium carbonyls [7–9], aimed at assessing their resistance to photo-declusterification and their ability to generate coordinatively unsaturated species.

We obtained the two main compounds by reacting $Ru_3(CO)_{12}$ with hexadienes and hexenes [8, 9] through oxidative addition with rupture of a C–H bond, namely, $HRu_3(CO)_9(EtC\cdots CH\cdots CMe)$ (μ_3 -allyl isomer)(I) and $HRu(CO)_9(EtC=C=CHMe)$ (μ_3 -allenyl isomer)(II).

Experimental

The compounds were prepared according to literature methods [7–9]. All solvents were of spectroscopic grade; they were dried over anhydrous $MgSO_4$ and distilled. Solutions were deaerated by means of at least 5 freeze–thaw–pump cycles and then the

appropriate atmosphere (CO, N_2) was admitted into the reaction vessel. Photolysis experiments were carried out using a Hanau medium pressure vapor lamp equipped with filters. Light intensities (3×10^{-8} to 2×10^{-7} ein/min) were determined by ferrioxalate actinometry [10].

Visible–UV spectra were obtained with a Varian Cary 219 spectrometer. Infrared spectra were recorded on a Perkin Elmer 238B spectrometer with a Perkin Elmer 3600 microcomputer using KBr cells.

Results

Visible–UV spectra of (I) and (II) in *n*-hexane are reported in Fig. 1. The spectrum of $Ru_3(CO)_{12}$ is also shown for comparison. Irradiation of (I) was carried out at 404, 334 and 254 nm in *n*-hexane and at 404 and 334 nm in CCl_4 and acetonitrile.

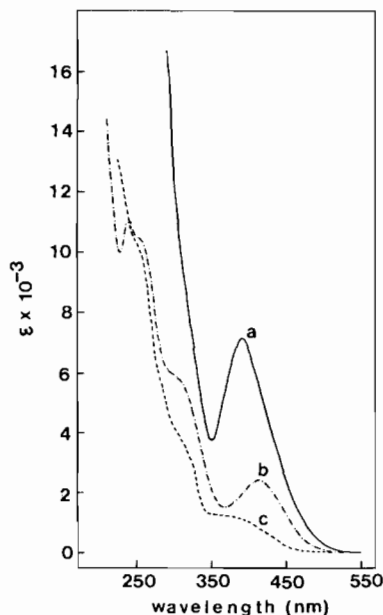


Fig. 1. Visible–UV electronic spectra of: a) $Ru_3(CO)_{12}$; b) $HRu_3(CO)_9(C_6H_9)$ (μ_3 -allyl isomer); c) $HRu_3(CO)_9(C_6H_9)$ (μ_3 -allenyl isomer). Solvent used: *n*-hexane. Temperature: 25 °C.

The visible–UV spectral variations observed after irradiation were similar for the different excitation wavelengths and the different solvents (see e.g. Fig. 2). Two isosbestic points were observed, at 385 and 340 nm. The presence of these isosbestic points indicates that the photoreaction produces only a single product in any appreciable amount. The isosbestic points disappear after an irradiation time of 90 min at 404 nm, 60 min at 334 nm and only a few minutes at 254 nm. Prolonged irradiation (3–5 h at 334 nm)

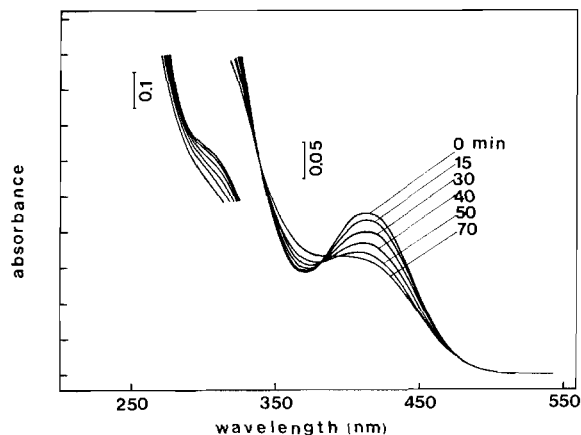


Fig. 2. Visible-UV spectral changes observed upon irradiation of $\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_9)$ (μ_3 -allyl isomer) in CCl_4 . Irradiation wavelength: 334 nm. Temperature: 25 °C.

results in the formation of $\text{Ru}(\text{CO})_3(\text{C}_6\text{H}_{10})$ and $\text{Ru}_3(\text{CO})_{12}$, identified by IR spectroscopy. In CCl_4 , however, $\text{Ru}_3(\text{CO})_{12}$ was not observed. In this case presumably several chloro-substituted compounds are the final products.

The quantum yields for disappearance of (I) were determined by monitoring the decrease in time of the absorption band at 415 nm (Fig. 2), for irradiation wavelengths of 404 and 334 nm. The absorbance decreases linearly with time for irradiation periods shorter than 60 min and then steadily increases as the irradiation time is prolonged. This increase can be ascribed to the formation of $\text{Ru}_3(\text{CO})_{12}$, as reported above, which has a greater ϵ than (I) at $\lambda_{\text{max}} = 415$ nm (Fig. 1).

Apparently, $\text{Ru}_3(\text{CO})_{12}$ is not formed in any appreciable amount in the linear region of the A vs. t plot: it is probably formed from another photolysis product which does not absorb at $\lambda_{\text{max}} = 415$ nm.

The disappearance quantum yields of (I) were $10^{-3} \pm 0.0002$ for the 404 nm irradiation wavelength and $2 \times 10^{-2} \pm 0.002$ for 334 nm, independent of the solvent.

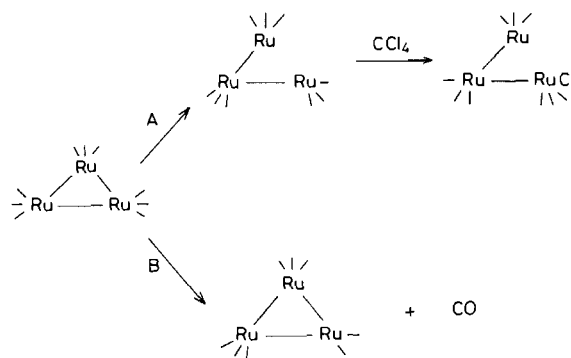
Photolysis experiments were also carried out on solutions of (I) in n-hexane in the presence of PPh_3 in equimolecular amount or ten-fold excess over the cluster. The solution was irradiated directly in an IR cell using glass filters to cut off light of wavelengths lower than 400 nm. The IR spectra obtained after less than 60 min irradiation show the appearance of new bands in the CO stretching region at 2074, 1998 and 1986 cm^{-1} , indicating the formation of $\text{HRu}_3(\text{CO})_8(\text{C}_6\text{H}_9)(\text{PPh}_3)$ [7]. Longer periods of irradiation led to the appearance of several other bands in the region around 1950 cm^{-1} , suggesting the formation of phosphine-substituted compounds of mononuclear ruthenium carbonyls derived from photofragmentation.

Irradiation of (II) at 360 and 313 nm in an IR cell caused the appearance of two new bands in the CO

stretching region at 2012 and 1994 cm^{-1} . This, together with a slight shift of the remaining bands toward higher wavelengths, indicates an isomerization of (II) to (I), as previously observed for its thermal behavior [8].

Discussion

Two possible primary photochemical processes concerning metal carbonyl clusters are generally considered; namely, metal-metal bond breaking and loss of CO. The former process seems to be the most efficient one in dinuclear metal-metal bonded complexes, while the latter is considered more probable in tetranuclear clusters [1]. As far as the present case is concerned, if the primary photochemical act were the cleavage of a Ru-Ru bond to form a diradical species, this would most likely be trapped in the chloro-carbon solvent (path A in Scheme 1) [5]. The



Scheme 1

qualitatively similar photochemical behavior of (I) in the three solvents used and the solvent independent (within experimental error) values of the disappearance quantum yields, seem to suggest that metal-metal bond cleavage, if any, is a very inefficient process. The results reported here are more consistent with loss of CO as the primary photochemical process (path B in Scheme 1). This is also in accord with the fact that the photolysis proceeds in an analogous fashion also at 254 nm (probably a $d(\text{Ru}) \rightarrow \pi^*(\text{CO})$ transition). The mechanism involving loss of CO seems to be corroborated by the behavior observed upon irradiation of (I) under CO atmosphere: qualitative results show that the photo-reaction is retarded considerably. In addition with PPh_3 present no monosubstituted PPh_3 compound is detected, in analogy to what is observed for $\text{Os}_3(\text{CO})_{12}$ [5].

The photochemical behavior of (II) is complicated by transformation into (I) upon irradiation. The latter compound is also involved in photoreactions, as illustrated above, thereby leading to possible competitive and/or parallel reactions.

In conclusion, it seems possible to obtain photochemically from (I) the formation of the coordinatively unsaturated species $\text{HRu}_3(\text{CO})_8(\text{C}_6\text{H}_9)$ with retention of the cluster framework. Interestingly, this species has also been proposed to be operative in the isomerization of olefins catalyzed by (I) [11].

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