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# Matrix and solution photochemistry of $[C_5(CH_3)_5Rh(CO)_2]$

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## Abstract

The photochemical behaviour of $[C_5(CH_3)_5Rh(CO)_2]$ has been examined in a polystyrene matrix and in a hexane solution. Photodissociation of CO yields the coordinatively unsaturated $[C_5(CH_3)_5RhCO]$ fragment as the primary photoproduct. Photodissociation of the $C_5(CH_3)_5$–Rh bond is observed in solution upon long wavelength irradiation of the $[C_5(CH_3)_5Rh(CO)_2]$ giving $^{\cdot}Rh(CO)_2$ and $C_5(CH_3)_5^{\cdot}$ radicals as primary photoproducts. The identity of the radicals has been demonstrated by spin trapping ESR spectroscopy experiments. After prolonged photolysis in a polystyrene matrix, the C–H activation product $[C_5(CH_3)_5Rh(CO)(H)(\text{polystyrene})]$ is formed *via* $[C_5(CH_3)_5RhCO]$. The role of the $[C_5(CH_3)_5RhCO]$ intermediate in solution reactions is discussed.

## 1. Introduction

It is generally agreed that the photochemistry of complexes of the type $CpML_2$ ($Cp = C_5H_5$; $M = Ir$, Rh; $L = CO$, $CH_2{=}CH_2$) involves generation of the coordinatively unsaturated intermediates CpML [1]. Such species have proved to be too reactive for direct observation in solution, but can be observed in matrices at low temperatures [2].

There is increasing recognition of the essential role of coordinatively unsaturated species in the C–H photoactivation exerted by organometallics [3]. Since CpML species are generated by photolytic expulsion of 2-electron ligands, they are electronically unsaturated species. The variation in coordination number and the rapid interchange between 16-electron and 18-electron configurations can lead to C–H activation of organic substrates by oxidative-addition reaction.

One goal of the present work was the generation of reactive intermediates of importance in catalytic synthesis in a translationally restricted environment of a polymeric film. The use is described of FTIR, UV-Vis and ESR spectroscopic criteria in comparing the behaviour of photoproducts of $[Cp^*Rh(CO)_2]$ ($Cp^* = C_5(CH_3)_5$) in polymer film with those obtained in solution.

## 2. Results

### 2.1. Spectral properties of $[Cp^*Rh(CO)_2]$ incorporate into the polymer

The UV-visible spectrum of $[Cp^*Rh(CO)_2]$ incorporated in the polystyrene film before and after photolysis is shown in Fig. 1. The visible absorption bands that appear in the spectrum of the film are consistent with those observed for $[Cp^*Rh(CO)_2]$ in solution (Table 1).

TABLE 1. $[Cp^*Rh(CO)_2]$ at 298 K ($\lambda_{max}$ nm)

| Medium | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ |
|---|---|---|---|---|
| Hexane | 250 | 280sh | 318 | 420sh |
| Methylcyclohexane | | 280 | 315 | 418sh |
| Polystyrene film | | 280sh | 318 | 420sh |

### 2.2. Photochemistry of $[Cp^*Rh(CO)_2]$ in a polystyrene matrix (PS)

Films of polystyrene containing $[Cp^*Rh(CO)_2]$ are stable for at least 1 week in the dark. When irradiated with polychromatic light (300 nm $\leq \lambda \leq$ 400 nm) a decrease in absorption at 318 nm, associated with the Rh–CO transition, is observed. However, no photoreactions were observed during 20 h of irradiation of the films at $\lambda \geq$ 380 nm.

Monitoring of the photoreactions by IR spectroscopy revealed that the two terminal CO bands (2018 and 1952 $cm^{-1}$) smoothly decreased in intensity

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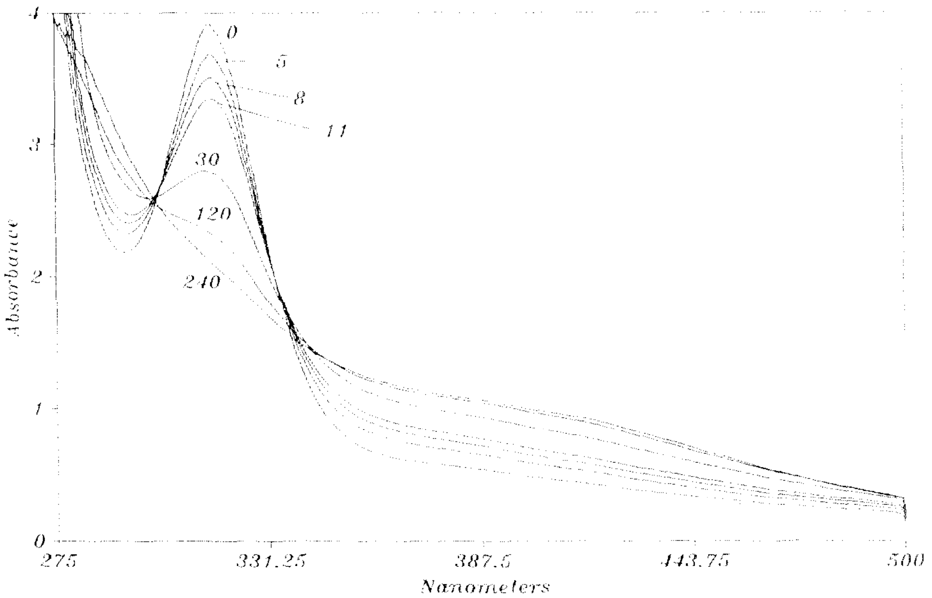


Fig. 1. UV-visible spectra changes of [Cp*Rh(CO)$_2$] during photolysis in polystyrene film (times in minutes).

during photolysis (Fig. 2). Free CO (2132 cm$^{-1}$) was produced upon consumption of [Cp*Rh(CO)$_2$], as well as a species with a CO absorption in the terminal region at 2048 cm$^{-1}$. These results and the quite striking similarity between the IR spectrum and that previously observed for monocarbonyl complexes in an argon matrix [4] allow identification of the metal-containing photolysis product as the naked 16-electron species [Cp*RhCO]. We thus conclude that upon irradiation of [Cp*Rh(CO)$_2$] in a polystyrene matrix, the primary photo-process is the loss of carbon monoxide (eqn. (1)).

$$[\mathrm{Cp^{*}Rh(CO)_2}] \xrightarrow[300 \leq \lambda \leq 400\ \mathrm{nm}]{h\nu} [\mathrm{Cp^{*}Rh(CO)}] + \mathrm{CO} \quad (1)$$

However, extended photolysis afforded a second new band at 2085 cm$^{-1}$ (Fig. 3). Comparative photolysis experiments were also carried out in low temperature organic glasses. Irradiation ($\lambda$ = 313 nm) of

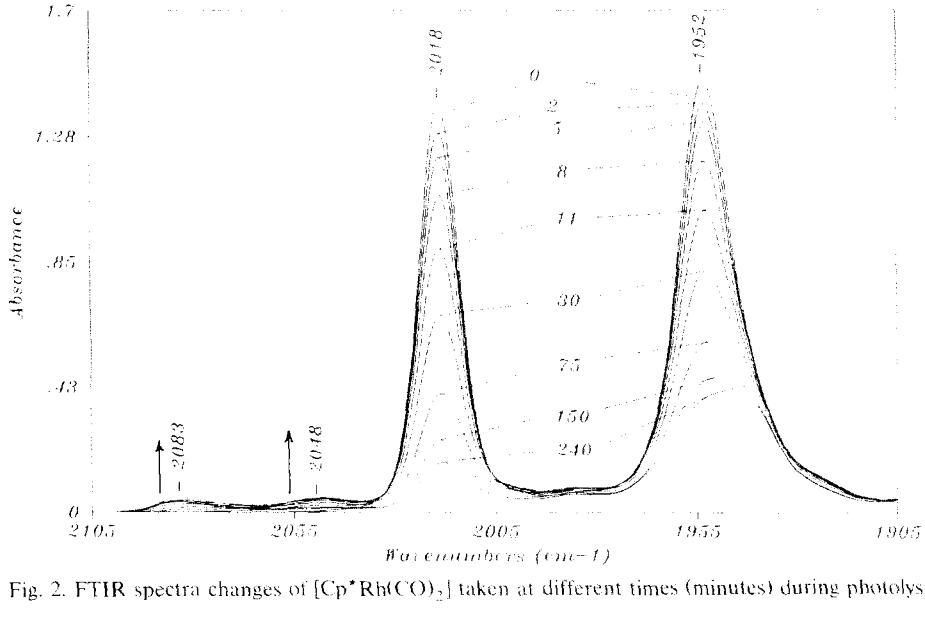
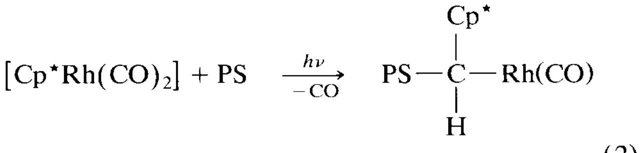


Fig. 2. FTIR spectra changes of [Cp*Rh(CO)$_2$] taken at different times (minutes) during photolysis in polystyrene film.

$[Cp^*Rh(CO)_2]$ at 93 K in a rigid methylcyclohexane matrix resulted in the consumption of 60% of the precursor and the appearance of a single terminal $\nu$(CO) mode at 2035 $cm^{-1}$ and a band at 2070 $cm^{-1}$ of intensity comparable with that observed in the polystyrene matrix. The band of 2070 $cm^{-1}$ can be assigned to $\nu$(Rh–H) of the alkane oxidative-addition product $[Cp^*Rh(CO)(H)(C_7H_{13})]$. This conclusion is confirmed by the results obtained in the irradiation of $[CpRh(CO)_2]$ in a rigid methylcyclohexane matrix [5]. These experimental observations lead to the assignment of the metal-containing product of photolysis in polystyrene as the $[Cp^*Rh(CO)(H)(R)]$ hydride complex. Apart from $[Cp^*Rh(CO)_2]$, polystyrene is the only species present that contains C–H bonds and, so it is reasonable to believe that the product formed is $[Cp^*Rh(CO)(H)(polystyrene)]$. Thus, the insertion shown in eqn. (2) is the first observed photochemical reaction in a polystyrene matrix of $[Cp^*Rh(CO)_2]$:



$$[Cp^*Rh(CO)_2] + PS \xrightarrow[-CO]{h\nu} PS—\underset{H}{\overset{Cp^*}{C}}—Rh(CO) \qquad (2)$$

### 2.3. Photochemistry of $[Cp^*Rh(CO)_2]$ in solution

At room temperature, the irradiation ($300 \le \lambda \le 380$ nm) of $[Cp^*Rh(CO)_2]$ in hexane solution gives $[Cp^*_2Rh_2(CO)_3]$. This result parallels that observed [5] for irradiation of $[CpRh(CO)_2]$. The photochemical reaction can be envisaged as giving the observed product *via* a transient species $[Cp^*Rh(CO)]$. In an extension of these studies, a hexane solution of $[Cp^*Rh(CO)_2]$ was photolyzed in the presence of TCNE, and the photoproduct was $[Cp^*Rh(CO)(TCNE)]$, rather than $[Cp^*_2Rh_2(CO)_3]$. The mechanism best in accord with this result is that represented by eqns. (3), (4) and (5):

$$[Cp^*Rh(CO)_2] \xrightarrow{h\nu} [Cp^*Rh(CO)] + CO \qquad (3)$$

$$[Cp^*Rh(CO)_2] + [Cp^*Rh(CO)] \longrightarrow [Cp^*_2Rh_2(CO)_3] \qquad (4)$$

$$[Cp^*Rh(CO)_2] + TCNE \xrightarrow[-CO]{h\nu} [Cp^*Rh(CO)(TCNE)] \qquad (5)$$

The 16-electron $[Cp^*Rh(CO)]$ intermediate formed must have been trapped by the TCNE, whereas in the absence of TCNE the intermediate reacts bimolecularly with the starting material at nearly a diffusion-controlled rate to give $[Cp^*_2Rh_2(CO)_3]$ (eqn. (4)). Thus, the combination of matrix-isolation experiments with FTIR detection and solution photochemical experiments, in the presence of TCNE provides unequivocal evidence that the 16-electron species $[Cp^*Rh(CO)]$ is the primary photoproduct.

In order to provide more information about the photochemistry of $[Cp^*Rh(CO)_2]$ in homogeneous solutions, additional irradiations at a variety of wavelengths ($\lambda$ = 380, 416, 500 nm) were performed. The photoreaction took a quite different course, $[Cp^*_2Rh_2$-

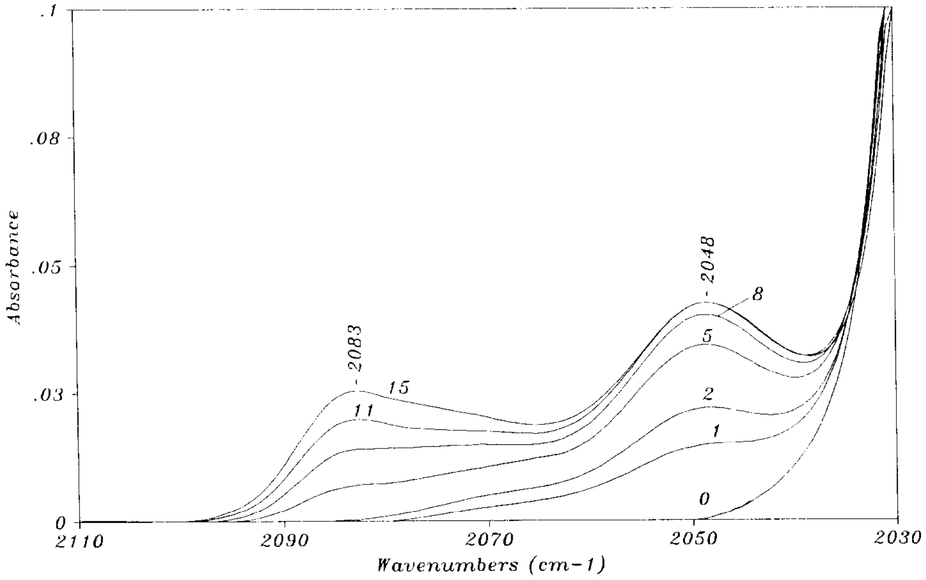


Fig. 3. FTIR spectra taken after photolysis of $[Cp^*Rh(CO)_2]$ in polystyrene film showing the formation of the hydride complex $[Cp^*Rh(CO)(H)(polystyrene)]$.

$(CO)_3]$ being formed in greatly reduced yield ($\approx 2\%$), and a yellow solid being the major product. Although formed in a good yield, it was difficult to handle because of its high oxygen-sensitivity. However, irradiation ($\lambda = 380$ nm) of $[Cp^{\star}Rh(CO)_2]$ in the presence of $Sn(CH_3)_3Cl$ gave the complex $[Rh(CO)_3(Sn(CH_3)_3)_3]$ as the major product. The formation of this product suggests that homolytic cleavage of the $Rh-C_5Me_5$ bond is the primary photoprocess leading to the formation of $^{\cdot}Rh(CO)_2$ and $C_5(CH_3)_5^{\cdot}$ radicals. In keeping with this view, irradiation of $[Cp^{\star}Rh(CO)_2]$ in the presence of nitrosodurene as radical trap led to formation of spin adducts of radicals. Figure 4(A) shows that the nitrosodurene gives two spin adducts: one giving a triplet of triplets and the other a triplet of rather broad lines. The centre of the latter is shifted towards higher $g$ values ($g = 2.012 \pm 0.001$ in $CH_2Cl_2$), whereas the triplet of triplets has a $g$ value ($g = 2.0061 \pm 0.05$) typical of spin adducts of carbon-centred free radicals. In the case of the broad triplet, the considerable shift in $g$ suggests a Rh-centred radical.

This assignment was supported by a computer simulation of the ESR spectrum (Fig. 4(B)). Satisfactory computer simulations were obtained only by taking into account an additional hyperfine splitting by one $^{103}Rh$ nucleus ($I = \frac{1}{2}$, 100% natural abundance). Since the carbon-centred and the Rh-centred radicals are formed simultaneously in a 1:1 ratio, the species $^{\cdot}Rh(CO)_2$ appears to be most likely to give rise to the trapped metal-centred radical.

The hyperfine splitting into three triplets of 1:2:1 intensity is due to the interaction between the unpaired electron and the two equivalent nuclei having a nuclear spin $I = \frac{1}{2}$. Thus this spin adduct is judged to be formed from the radical $C_5(CH_3)_4CH_2^{\cdot}$, generated by fast rearrangement of the primary $C_5(CH_3)_5^{\cdot}$ radicals. This type of rearrangement is in keeping with a considerable body of kinetic evidence [6].

All the observations concerning photolysis at $\lambda > 380$ nm are consistent with homolytic cleavage as the principal result of excited-state decay (eqn. (6)).

$$[Cp^{\star}Rh(CO)_2] \xrightarrow{h\nu} [Cp^{\star} + {}^{\cdot}Rh(CO)_2] \qquad (6)$$

$$Cp^{\star} = C_5(CH_3)_5^{\cdot}$$

Moreover, the photochemical formation of $[Rh(CO)_3(Sn(CH_3)_3)_3]$ as the major product when photolysis is performed in the presence of $Sn(CH_3)_3H$ is consistent with homolytic cleavage of the $Rh-Cp^{\star}$ bond.

Assignment of the electronic transitions leading to labilization of the CO ligand and homolytic cleavage of the $Cp^{\star}-Rh$ bond of $[Cp^{\star}Rh(CO)_2]$ is not straightforward. The present results suggest that the LF lowest excited states (associated with irradiation with $\lambda > 380$ nm) have a substantial $Rh-Cp^{\star}$ antibonding character.

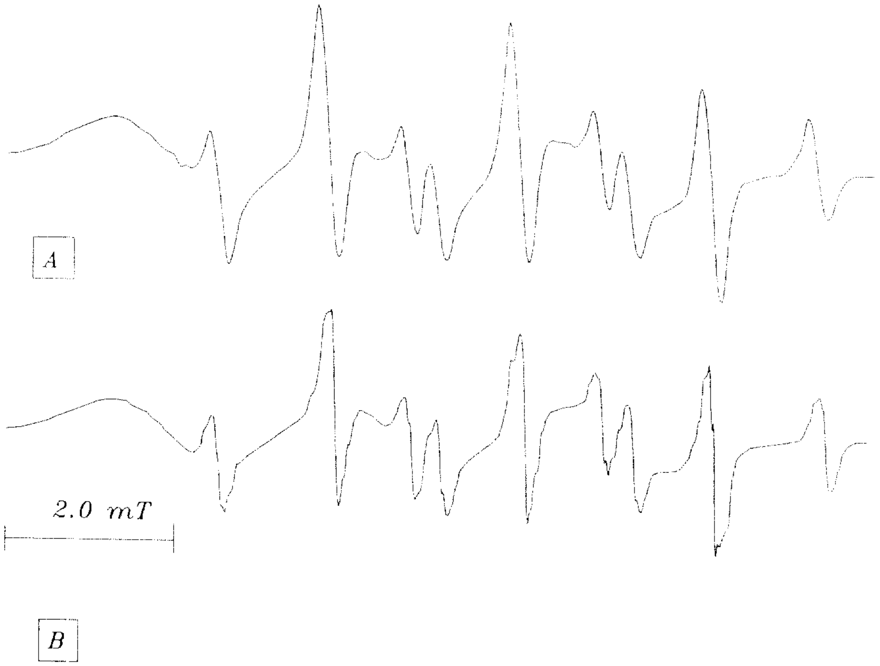


Fig. 4. (A) ESR spectrum of the spin adduct of the Rh centred radicals (broad lines) and $^{\cdot}CH_2Cp$ (triplet of triplet), respectively, generated by photolysis ($\lambda = 380$ nm) of $[Cp^{\star}Rh(CO)_2]$ (0.01 M) in the presence of nitrosodurene (0.005 M) in dichloromethane. (B) Computer simulation based on the parameters reported in ref. 9.

The observed loss of CO ($300 \leq \lambda \leq 380$ nm) could be interpreted in terms of reaction from one of the highest occupied molecular orbital related to the Rh–CO bond, and this would be in agreement with the M → *CO–CT transition observed for the complex in the 250–350 nm region.

## 3. Conclusions

The matrix photochemistry of [$Cp^*Rh(CO)_2$] is rather different from its solution photochemistry. Irradiation of [$Cp^*Rh(CO)_2$] in a polystyrene matrix gives a [$Cp^*Rh(CO)$] fragment, which photo-activates the polystyrene C–H bond to yield the insertion product [$Cp^*Rh(CO)(H)$(polystyrene)].

For irradiation at $\lambda = 350$ nm, the behaviour of [$Cp^*Rh(CO)_2$] in solution is similar to that in a matrix. In solution, however, the primary photoproduct [$Cp^*$-Rh(CO)] is transient, and immediately reacts with the remaining starting material to form [$Cp^*_2Rh_2(CO)_3$]. In the polymeric matrix, the film environment influences the fate of the intermediate [$Cp^*Rh(CO)$]. The translational motion of the photogenerated 16-electron fragment is restricted because it is probably bound to the polystyrene in a $\sigma$ (or agostic) complex [$Cp^*RhCO \cdots R{-}H$], as observed for mononuclear iron or rhenium fragments with ethene [10].

Completely different photochemical solution-matrix behaviour is observed for irradiation at $\lambda \geq 380$ nm. In solution, the principal photochemical event is the homolytic cleavage of the $Cp^*$–Rh bond. In a polystyrene matrix, no significant photoreaction is observed. Recombination is far faster in these films because the radicals cannot separate, and recombination is a very rapid process.

## 4. Experimental section

### *4.1. General information*

All manipulations were conducted under nitrogen or argon on a Schlenk vacuum line or in an evacuated drybox.

Infrared spectra were recorded on a Bruker Model IFS 88 Fourier Transform (FT) spectrometer. UV-visible spectra were recorded with a Perkin-Elmer Lambda 6 spectrometer. Elemental analysis were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Ferrara. Unless otherwise indicated, all solvents and reagents were purchased from commercial suppliers and used without further purification. A commercial sample (Aldrich) of polystyrene pellets (average molecular weight 280,000, G.T. 100°C) was used. The complex [$C_5(CH_3)_5Rh(CO)_2$] was prepared by the published method [2].

For the photolysis experiments, either a 150-W medium pressure Hanau Hg lamp or a Hanau 250-W high pressure Hg lamp equipped with suitable interference filters was used. The polystyrene film was obtained by evaporation of a solution containing 2.5% (w/w) of [$C_5(CH_3)_5Rh(CO)_2$] in dichloromethane.

### *4.2. Photolysis of [$C_5(CH_3)_2Rh(CO)_2$] in hexane: synthesis of [$(C_5(CH_3)_5)_2Rh_2(CO)_3$]*

A hexane (10 ml) solution of [$C_5(CH_3)_5Rh(CO)_2$] (0.15, 0.51 mmol) was irradiated at $\lambda = 313$ nm for 30 h in a quartz vessel. Removal of solvent and recrystallization from dichloromethane gave dark red crystals of [$(C_5(CH_3)_5)_2Rh_2(CO)_3$]. Anal. Found: C, 49.12; H, 5.42; $M = 560$. $C_{23}H_{30}O_3Rh_2$ calc.: C, 49.30; H, 5.39%; $M = 560.299$. IR: $\nu$(CO) 1984s, 1940m in KBr pellets.

### *4.3. Photoreaction of [$C_5(CH_3)_5Rh(CO)_2$] with TCNE*

Irradiation ($\lambda = 313$ nm) in an evacuated sealed quartz tube of a hexane solution (10 ml) of [$C_5(CH_3)_5$-$Rh(CO)_2$] (0.15 g) and TCNE (0.06 g) (molar ratio 1 : 1) for 30 h produced a dark-orange colour and separation of a dark-brown solid. After collection of the solid by filtration and recrystallization from dichloromethane, dark brown crystalline [$C_5(CH_3)_5Rh(CO)$(TCNE)] was obtained, as identified from its IR spectrum [$\nu$(CO) at 1985 $cm^{-1}$, $\nu$(CN) at 2130 $cm^{-1}$] and elemental analysis. Removal of solvent from the filtrate yielded a small amount of [$(C_5(CH_3)_5)_2Rh_2(CO)_3$] (approx. 2%) based on starting [$C_5(CH_3)_5Rh(CO)_2$].

### *4.4. Photoreaction of [$C_5(CH_3)_5Rh(CO)_2$] with Sn ($CH_3)_3$Cl: synthesis of [$Rh(CO)_3(Sn(CH_3)_3)_3$]*

Irradiation ($\lambda > 380$ nm, 50 h) of [$C_5(CH_3)_5Rh$-$(CO)_2$] (2.25 mmol) and $Sn(CH_3)_3Cl$ (6.75 mmol) in deaerated hexane (10 ml) produced a dark-red solution. The solution was concentrated and chromatographed on alumina. Elution with hexane yielded two bands, one yellow and the other red. The first yielded a yellow liquid, which solidified when kept under vacuum overnight. After recrystallization from dichloromethane/hexane, yellow solid [$Rh(CO)_3(Sn$-$(CH_3)_3)_3$] was obtained (approx. 80%). Anal. Found: C, 21.3; H, 3.98. $C_{12}H_{27}O_3RhSn_3$ calc.: C, 21.2; H, 4.0%. IR: $\nu$(CO) at 2065, 2034, 2000 $cm^{-1}$. The second (red) band, eluted with 30% dichloromethane/hexane, gave dark red crystals of [$(C_5(CH_3)_5)_2Rh_2(CO)_3$] (approx. 2%) identified from its IR spectrum.

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