

ACTION OF ALKYL HALIDES ON HOMO- AND HETERO-PORPHYRIN DIMERS INVOLVING A RHODIUM-INDIUM BOND, PRODUCING PORPHYRIN COMPLEXES CONTAINING METAL-CARBON AND METAL-HALIDE BONDS

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Abstract—The reactivity of the novel family of metalloporphyrin dimers containing a Rh—In bond towards alkyl halides is presented. The chemical reactivity of the homoleptic (same porphyrin ligand) and heteroleptic (different porphyrin ligand) porphyrin complexes with Rh—In metal-metal bond has been examined by photo- and thermal-processes in the presence of alkyl halides under anaerobic conditions in the dark. The photolytic and thermal reactions have been studied to define the polarity of the Rh—In single bond, as well as to identify the products. The presence of complexes containing Rh—C bonds in the reaction mixture detected by UV-vis spectroscopy postulates the formulation $\text{Rh(I)}^- : \rightarrow \text{In(III)}^+$ for the polarity of the metal-metal bond. In order to characterize the products we compare our spectroscopic results with those of the literature and those of authentic Rh—C containing complexes.

As has been mentioned by Collman and co-workers,¹ studies of multiple bonding between transition metals within discrete complexes offer fundamental insight into the nature of bonding between metal atoms. This understanding facilitates the prediction of physical properties and the reactivities of metal complexes containing metal-metal multiple bonds. We will focus on the chemistry of Rh—In single bond (one transition and one main group metal), and we will describe a total of four homoleptic and heteroleptic dimers. The properties of this metal-metal bond can be studied by changing variables one at a time. In this work, the variable under investigation is the electron density of the porphyrin ring.

In 1982, Wayland and co-workers² reported the reaction of (octaethylporphyrinato)rhodium(II) dimer $[(\text{OEP})\text{Rh}]_2$, with H_2O and CO to afford the formyl(octaethylporphyrinato)rhodium(III),

(OEP)RhCHO. An analogous system has been described by Miller and co-workers³ where the dimer $[(\text{OEP})\text{Rh}]_2$ reacted with CO in the presence of ethanol in CH_2Cl_2 to give (octaethylporphyrinato)rhodium(III) chloride, (ethoxycarbonyl) (octaethylporphyrinato)rhodium(III), and formyl(octaethylporphyrinato)rhodium(III). Photolysis of the latter in CH_2Cl_2 at 300 nm afforded (octaethylporphyrinato)rhodium(III) chloride. (Octaethylporphyrin)rhodium(II) dimer, also reacts with toluene and related methyl-substituted aromatics at the methyl C—H bonds to form organometallic benzyl derivatives.⁴ One more addition reaction of $[(\text{OEP})\text{Rh}]_2$ with propene, forming (OEP)Rh- $\text{CH}_2\text{CH}(\text{CH}_3)$ -Rh(OEP) has been reported.⁵

The above very brief overview to the chemical reactivity of the Rh—Rh bond permits us to consider the importance of the reactivity study on complexes containing Rh—M bonds by various chemical reagents. Before closing the above overview it seems useful to refer to complexes of

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ruthenium which present similar chemical reactivity, close to rhodium and containing metal-metal bond.⁶

EXPERIMENTAL

Chemicals

All chemicals were reagent grade and were used without further purification except as noted below. Alumina type basic I (activated at 150°C), and all solvents were distilled and dried over molecular sieves under anaerobic conditions. All reaction procedures were carried out also under nitrogen or argon.

Methods and instruments

All manipulation of oxygen- and water-sensitive materials were performed by Schlenk tube techniques under purified N₂ or argon. UV-vis spectra were recorded on a Lambda-6 Perkin-Elmer spectrophotometer or on an ORIEL diode-array visible spectrophotometer, using 5 × 10⁻³ mol dm⁻³ solutions of toluene. Samples for IR measurements were prepared as 1% dispersions in CsI pellets or Nujol mulls and recorded on an FT-IR 1760 series Perkin-Elmer spectrophotometer.

Instrumentation used for the thermal and photo reactivity of the M—M bonded dimers with R—X

Around 0.5 mg of dimer was diluted in 50 cm³ of toluene and 50 μl of CH₃I were added. The mixture was stirred and heated under reflux. An aliquot was withdrawn through a cannula and directed by a peristaltic pump to a specially designed cell where it was analyzed by the Lambda-6 Perkin-Elmer or the ORIEL diode array spectrophotometer. The sample under pressure of the pump was recirculated into the reaction mixture.

For the photo reactivity studies, an aliquot of the above solution was introduced to the spectrometer cell. The sample via a fibre optic cable from a tungsten lamp (500 W), was irradiate, at the Soret band or by white light, and the decay time of the reaction mixture was monitored by a UV-vis diode array spectrophotometer.

Synthesis and purification of complexes containing Rh—C, In—C and Rh—In bonds

(Por)Rh—In(Por') (where Por or Por' = OEP or TPP). The four homoleptic and heteroleptic dimers containing Rh—In bond were prepared as has been described in the literature.⁷

(Por)Rh—C₁₄H₂₉ (Por = OEP or TPP). (Por)Rh—Cl (50 mg) and 3 cm³ of the C₁₄H₂₉MgBr (0.4 mmol) solution were added to 20 cm³ of dry toluene. The mixture was stirred and heated slightly for 30 min. The resulting solution was extracted with 20 cm³ of water and dried over MgSO₄. After evaporation of the solvent, the residue was chromatographed on basic Al₂O₃ (pH 9.5) using toluene as eluent. Condensation of the orange elute yielded red-brown compounds which possess the UV data in toluene listed in Table 1. The reactions were almost quantitative. Upon irradiation with white light, both alkyl-rhodium porphyrins cleaved to give the corresponding chlorometalloporphyrinic moieties. Formation of chlorometalloporphyrin derivatives were possible due to traces of chloride units which were present in toluenic solutions, as has been observed in similar cases. [Found C, 72.0; H, 8.8; N, 6.7. Calc for (OEP)Rh—C₁₄H₂₉: C₅₀H₇₃N₄Rh. C, 72.1; H, 8.8; N, 6.7; Rh 12.3%. Found C, 76.4; H, 6.2; N, 6.1. Calc for (TPP)Rh—C₁₄H₂₉: C₅₈H₅₇N₄Rh. C, 76.3; H, 6.3; N, 6.1; Rh, 11.3%.]

(Por)In—C₁₄H₂₉ (Por = OEP or TPP). (Por)In—Cl [(OEP)In—Cl: 0.22 mmol/(TPP)In—Cl: 0.197 mmol] (150 mg) and 8 cm³ of the C₁₄H₂₉MgBr solution (1.05 mmol) were dissolved in 50 cm³ of dry toluene. The resulting mixture was vigorously stirred and heated slightly for 30 min, then extracted with 50 cm³ of water and dried over anhydrous MgSO₄. Chromatography on basic alumina with toluene yielded a green compound (TPP)In—C₁₄H₂₉ and a red one (OEP)In—C₁₄H₂₉. The UV data in toluene are listed in Table 1. The reactions were quantitative. The two compounds were light sensitive and the In—C bond cleaved after 30 min exposure on white light at 450 W. [Found C, 71.2; H, 8.6; N, 6.5; In, 13.5. Calc for (OEP)In—C₁₄H₂₉: C₅₀H₇₃N₄In. C, 71.1; H, 8.7; N, 6.6; In, 13.6%. Found C, 75.7; H, 6.1; N, 6; In, 12.3. Calc for (TPP)In—C₁₄H₂₉: C₅₈H₅₇N₄In. C, 75.32; H, 6.21; N, 6.06; In, 12.41%.]

RESULTS AND DISCUSSION

We have reported the synthesis and characterization of a series of homoleptic and heteroleptic porphyrin dimers containing a rhodium-indium bond but different porphyrin ligands.⁷ Their photodecomposition rates give a very good estimate of the metal-metal bond strength.

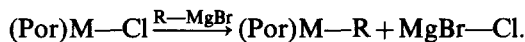
In this work we present the study of regioselective addition of alkyl halides on the above mentioned dimers, which provide us with important information concerning the bond polarity. The reaction products detected by UV-vis spectroscopic data,

Table 1. UV-vis data for complexes (Por)Rh—C₁₄H₂₉ and (Por)In—C₁₄H₂₉ in toluene (λ /nm, ϵ /dm³ mol⁻¹ cm⁻¹ in parentheses)

Compound	B-	Bands	Q-	Bands
(OEP)Rh—C ₁₄ H ₂₉		396 (6.3)	511 (0.7)	543 (2.4)
(TPP)Rh—C ₁₄ H ₂₉		413 (26.4)	520 (3.0)	
(OEP)In—C ₁₄ H ₂₉	366 (28.7)	435 (63.3)	558 (9.1)	592 (4.2)
(TPP)In—C ₁₄ H ₂₉	358 (18.1)	445 (170.6)	581 (4.6)	626 (5.6)

correspond to complexes involving metal-carbon and metal-halide bonds. The fact that only Rh—C and In—X products have been observed confirms the proposed polarity of the Rh—In bond. From the two experimental approaches used, photo and thermal reactions in presence of RX, only the latter leads to the (Por)Rh—R and (Por)In—X complexes. As we present later this difference of chemical behavior could be caused by the different alkyl halide used in the present study and/or by a different mechanism of the reaction process. For this reason, (Por)RhC₁₄H₂₉ and (Por)InC₁₄H₂₉ which have not been investigated before, have been characterized by UV-vis, ¹H-NMR, IR and elemental analysis.

Several alkyl derivatives of rhodium- and indium-porphyrins, [(Por)M—(R) or (Ar) where M = Rh and In] are known, e.g. (Por)In—R [with R = CH₃, CH₂CH₃, CH(CH₃)₂, (CH₂)₃CH₃, C(CH₃)₃]⁸ and (Por)Rh—R (with R = CH₃, CH₂CH₃, *n*-C₃H₇, *n*-C₄H₉, *n*-C₅H₁₁, *n*-C₆H₁₃, *n*-C₉H₁₉).⁹ The four compounds needed for our investigations were prepared by a Grignard reagent method:



[where (Por) = (OEP) or (TPP), M = Rh or In and R = CH₃ or C₁₄H₂₉].

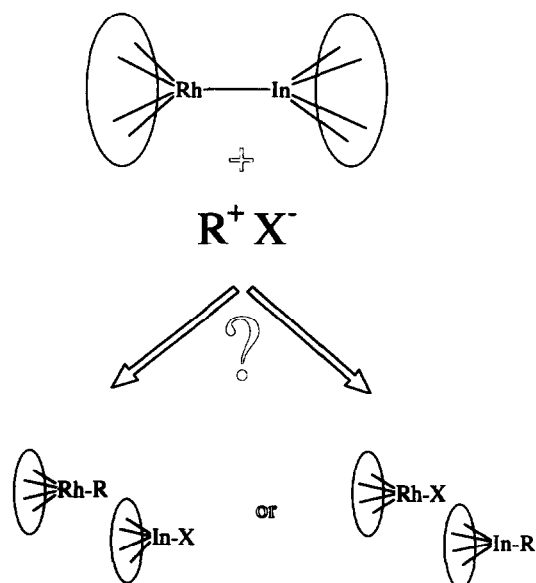
This is an efficient and high-yield synthesis (~85–95%) of (Por)M—R. The products were characterized by elemental analysis, UV-vis, FT-IR, and ¹H-NMR spectroscopies, but their further study is outside the scope of this work.

Reactivity of (Por)Rh—In(Por) and (Por)Rh—In(Por)' towards alkyl halides

Thermal reactivity. A prominent feature in the thermolysis of (Por)Rh—In(Por) and

(Por)Rh—In(Por') compounds is the production of equal amounts of (Por)Rh⁽⁰⁾ and (Por)In⁽⁰⁾ entities (Scheme 1). According to Wayland,¹⁰ the formulation Rh(I)⁻: → In(III)⁺ was supported by the reactivity of (OEP)Rh—In(OEP) with alkyl iodides. This described dimer reacted quantitatively with methyl iodide either thermally (125°C) or photolytically ($\lambda > 530$ nm, 25°C).

Test of the reactivity of the four complexes towards alkyl halides can confirm the suggested formulation Rh(I)⁻: → In(III)⁺ of the metal-metal bond, and extend the literature data to other heterometallic dimers with Rh—In bond but different combinations of coordinated macrocycles. All reactions concerning the thermal reactivity of the four heterodimers occur in the dark. This precaution is necessary for two reasons. The first rea-



Scheme 1. Possible reaction scheme of addition of RX on the dimers.

son is that the initial compounds (Por)Rh—In(Por) and (Por)Rh—In(Por)' in solution, are both very sensitive to the light. Secondly, the complexes formed, (Por)M—R, experience the same sensitivity to the light. At this point we must specify that the metal-carbon complexes have been tested and, as it has been suggested, are very easily decomposed by light. The sensitivity of the latter depends on the number of carbon atoms of the chain: with the sensitivity increasing with the length of the chain. We discuss further this behavior at the end of this section.

In the following discussion we compare the evolution of the UV-vis spectrum before and after the thermal addition of the alkyl iodides and whenever necessary we compare also with the pure photochemical degradation of the heterodimers again monitored *via* their electronic spectra. The reactivity of the different dimers has been studied by allowing them to react with an excess of two different alkyl halides, CH₃I and C₁₄H₂₉Br in boiling toluene. The reaction progress has been followed by UV-vis spectroscopy. The detailed description is as follows.

Figure 1a. Shows the final UV spectrum of the addition reaction of (OEP)Rh—In(OEP). Compared with the initial spectrum (same figure), it shows a new absorption in the Soret region at 393 nm and two new Q-bands at 513 and 544 nm (note the strong absorption at 544 nm). By referring also to the literature^{9b} we confirm that these new peaks are characteristic of (OEP)Rh—CH₃. For (OEP)In—I it is not so simple to detect its presence in the reaction mixture because its UV spectrum is not easily distinguished from that of (OEP)In—Cl. The Soret band of the indium compound occurs at 408 nm, and it is 2 nm blue-shifted compared with the chloroindium-porphyrin absorption. This is probably due to the simultaneous presence of other absorption bands.

Figure 1b. Shows the final UV-vis spectrum of the reaction mixture between (OEP)Rh—In(TPP) and CH₃I. By comparison with the initial spectrum and the photodecomposition of (OEP)Rh—In(TPP) alone in toluene (see Fig. 2b), the difference is not too evident. However, we notice that in Fig. 2b, the Soret band of (TPP)Rh—Cl, which occurs at 405 nm, is well separated and easily distinguishable from the corresponding peak of (OEP)In—Cl. For the present reaction, the resulting UV-vis spectrum exhibits a Soret band at 427 nm (which corresponds to (OEP)In—I) and a shoulder to this peak at 408 nm. Other differences exist in the region of the Q-bands. The most intense of the peaks in Fig. 2b is at 556 nm, with 5 nm difference from the main Q-band of (TPP)In—Cl (561 nm). We

obtained a mixture with the desired addition products and the corresponding chlorometalloporphyrins. This data has been confirmed by the chromatographic analysis of the reaction mixture.

Figure 1c. Depicts the final UV-vis spectrum of the thermal reaction between (TPP)Rh—In(OEP) and methyl iodide. The Soret band appears at 412 nm with a shoulder at 431 nm. The absorptions in the Q-band region are observed at 522 (well-detected by the second derivative), 540 and 579 nm. In the spectrum of the photochemical degradation (Fig. 2c) there was no band at 522 nm. An absorption of (TPP)Rh—CH₃ can be assigned to this band by reference to the literature [412 and 524 nm in THF].^{9b} It is interesting to note that the UV spectrum of the final addition mixture exhibits a broad Soret band. We conclude that thermally we have observed the addition of CH₃I as has been expected. Chromatographic analyses also confirm the existence of the above complexes.

Figure 1d. Shows the UV-vis spectrum of the resulting solution of the reaction between the last dimer, (TPP)Rh—In(TPP), and CH₃I. If we compare it to the previous photodecomposition studies (see Fig. 2d), we observe clear differences in both the Soret and Q-band regions. First, in this case there is a shoulder, at 412 nm, of the most intense Soret peak at 429 nm. The shoulder appears exactly where the broad Soret band of the addition solution of (TPP)Rh—In(OEP) is observed. We assume that it corresponds to the presence of (TPP)Rh—CH₃.

One of the Q-bands of the (methyl)rhodium porphyrin is also present at 524 nm. In this region, the peaks at 561 and 603 nm must belong to (TPP)In—I. We notice that there is a shoulder at 533 nm, probably due to the absorption of (TPP)Rh—Cl, meaning that the addition of CH₃I was only partial.

In summary, in three cases out of four, the addition of CH₃I on the dimer occurred clearly and can be monitored by UV-vis spectroscopy. The addition was not complete but this was probably due to the instability of the alkyl-metalloporphyrins formed. Experiments with (OEP)Rh—In(TPP) gave ambiguous results. There were some new peaks but we could not conclude that we had obtained the desired addition. This is probably due to the band overlap of all the complexes in the above mixture. In this case only the chromatographic analyses permit to us to identify the formed complexes. However, this study allows us to confirm Wayland's suggestion that the metal-metal bond can be formulated as Rh(I)⁻: → In(III)⁺.

After comparison of the above data, we succeeded in extracting some interesting information

about the addition rates. From the addition reaction the presence of the compounds formed does not permit us to have clear information about the decay process by the evolution of bands corresponding to initial or to formed compounds. We can only deduce a few observations by the final decay time of each one. The fastest reaction involved (OEP)Rh—In(OEP) (decay time 110

min), and the slowest was for dimer (TPP)Rh—In(TPP) (330 min), for the other two reactions intermediate durations have been observed [140 and 282 min for (TPP)Rh—In(OEP) and (OEP)Rh—In(TPP), respectively]. From the photodecomposition study we can conclude that the metal-metal bond strength addition would follow the order:

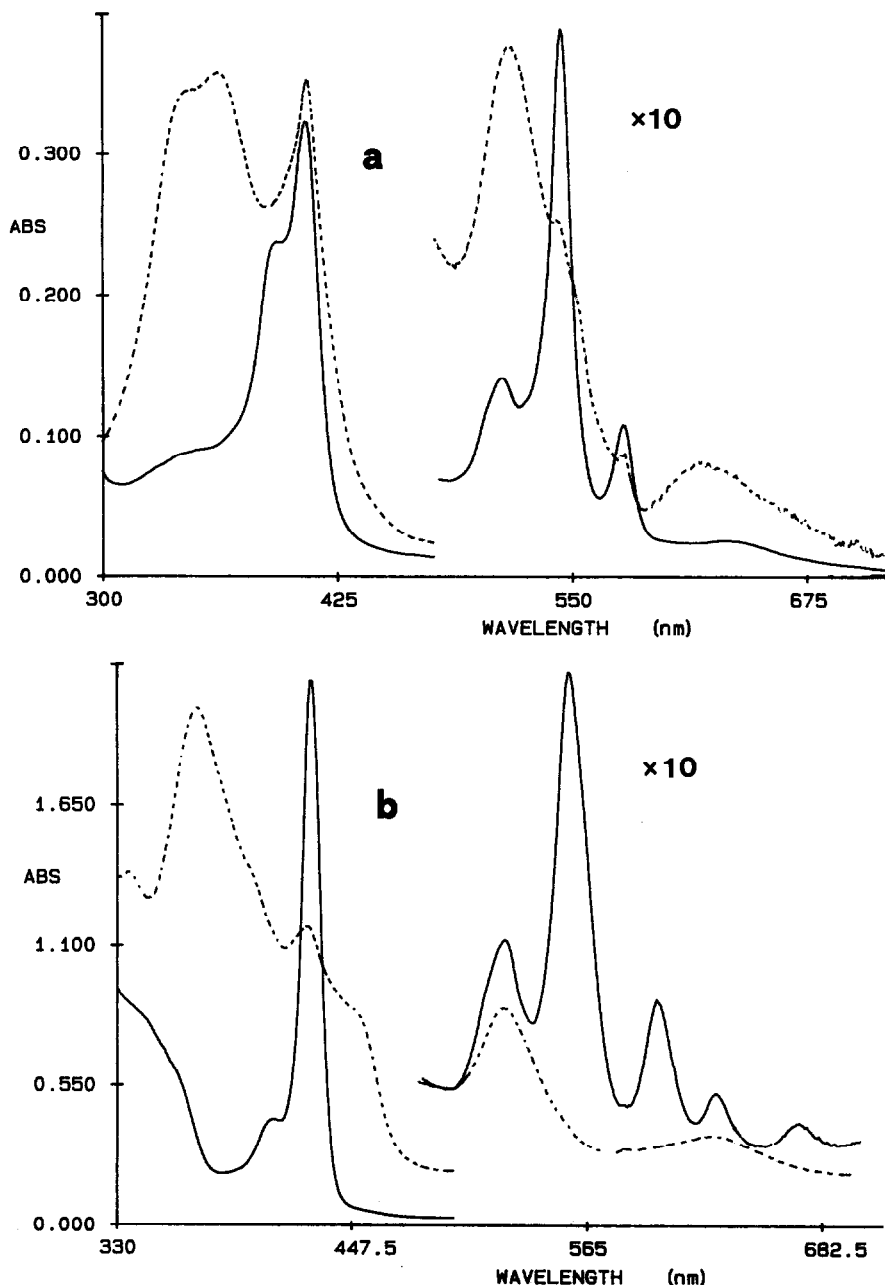


Fig. 1. UV-vis of the reaction mixture (solid line) between CH_3I and the dimers, and their initial spectrum (dashed line). (a) (OEP)Rh—In(OEP); (b) (OEP)Rh—In(TPP); (c) (TPP)Rh—In(OEP); (d) (TPP)Rh—In(TPP).

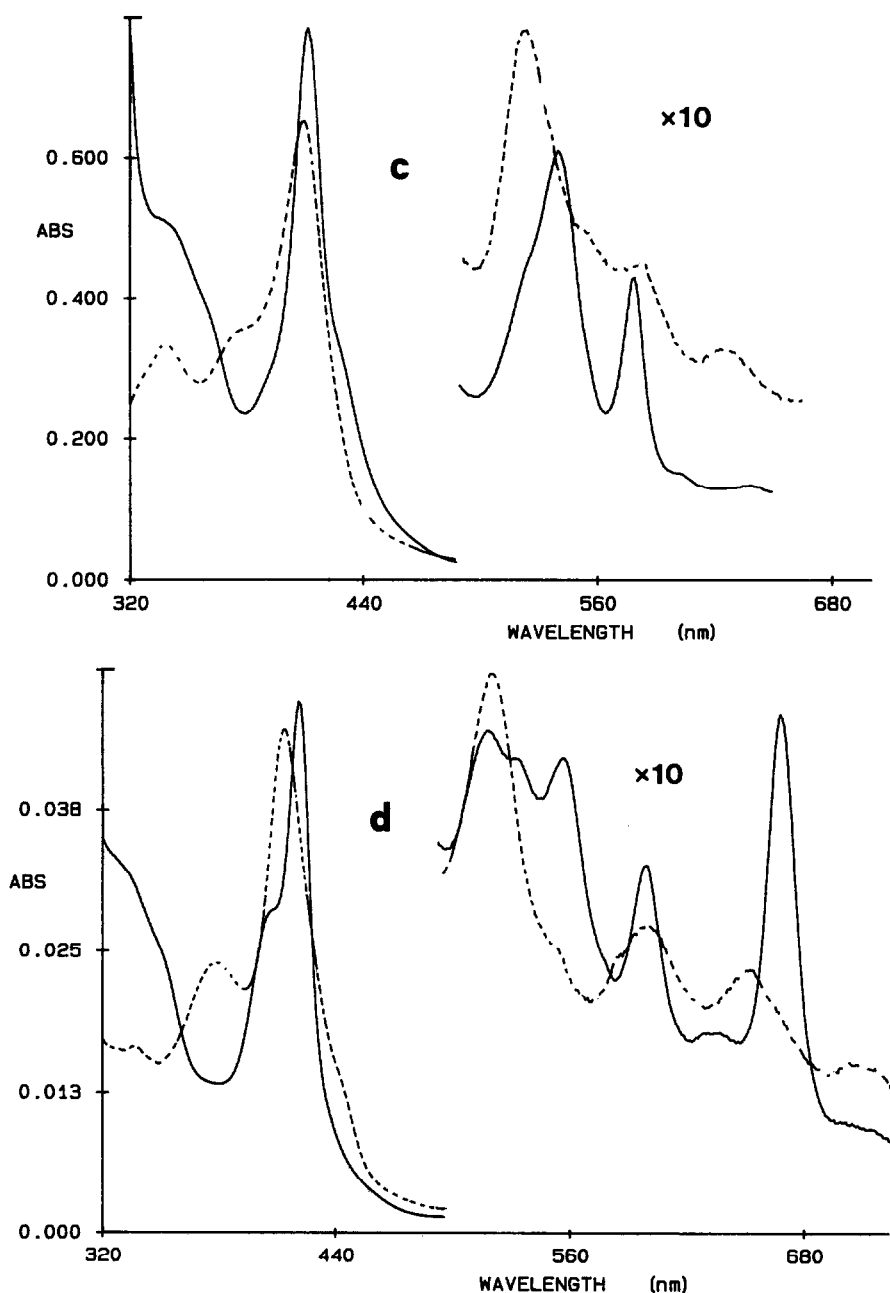


Fig. 1—continued

(OEP)Rh—In(OEP) < (OEP)Rh—In(TPP)
 < (TPP)Rh—In(OEP) < (TPP)Rh
 —In(TPP).

In comparison, Fig. 3 presents the decay of a characteristic band from each one of the four complexes in the study. This band was chosen because there is no overlapping with other bands corresponding to the compounds formed. So the bands at 362, 408, 370 and 417 nm have been chosen

for the (OEP)Rh—In(OEP), (TPP)Rh—In(OEP), (OEP)Rh—In(TPP) and (TPP)Rh—In(TPP), respectively. This diagram presents the absorption of the above mentioned bands during the decomposition for all cases. We observe that for the first seconds (0–5 sec) of the photodecomposition the complexes follow the order:

(TPP)Rh—In(OEP) > (TPP)Rh—In(TPP) >
 (OEP)Rh—In(TPP) > (OEP)Rh—In(OEP)

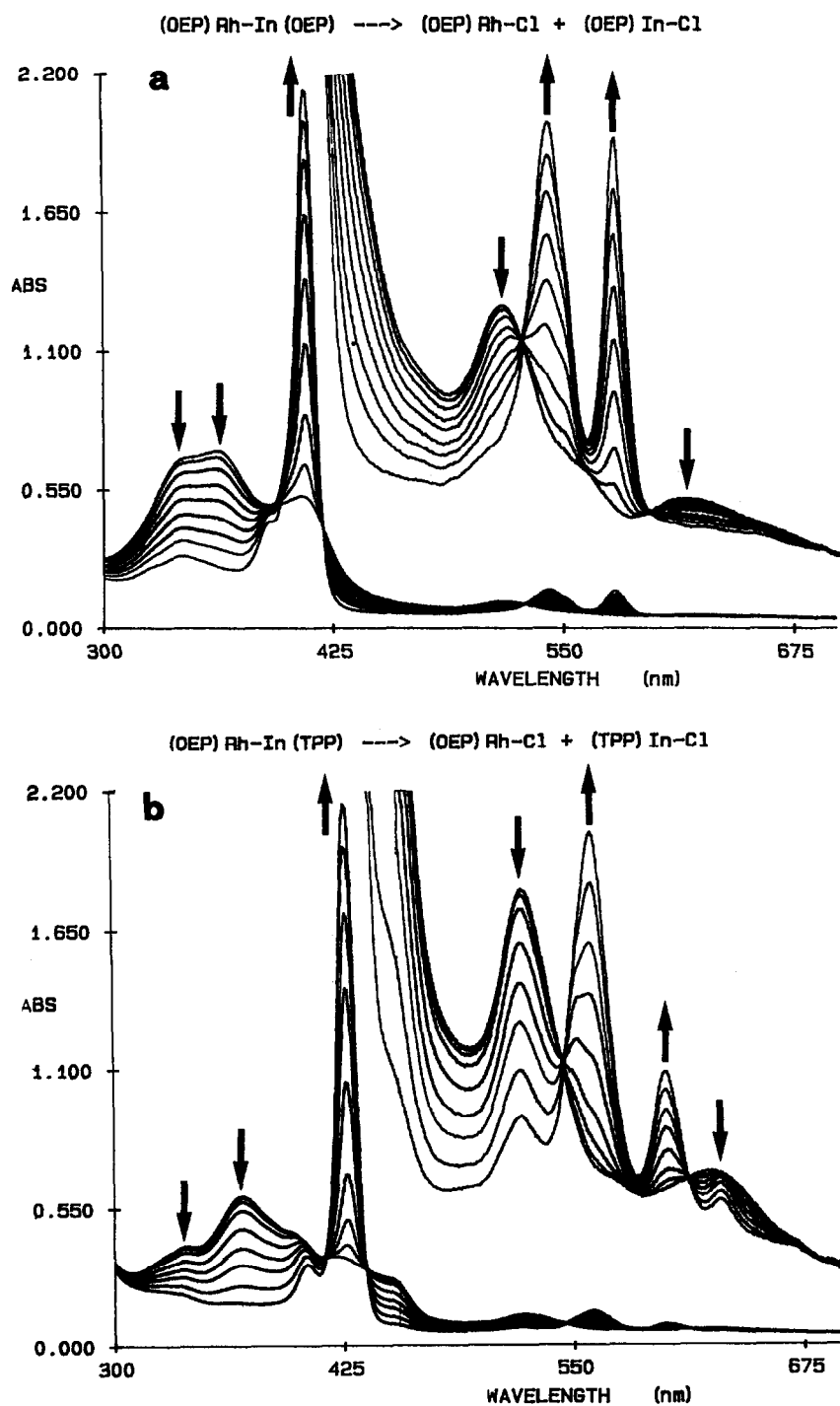


Fig. 2. UV-vis data for control of the four dimers during the photodecomposition in toluene. (a) (OEP)Rh-In(OEP); (b) (OEP)Rh-In(TPP); (c) (TPP)Rh-In(OEP); (d) (TPP)Rh-In(TPP).

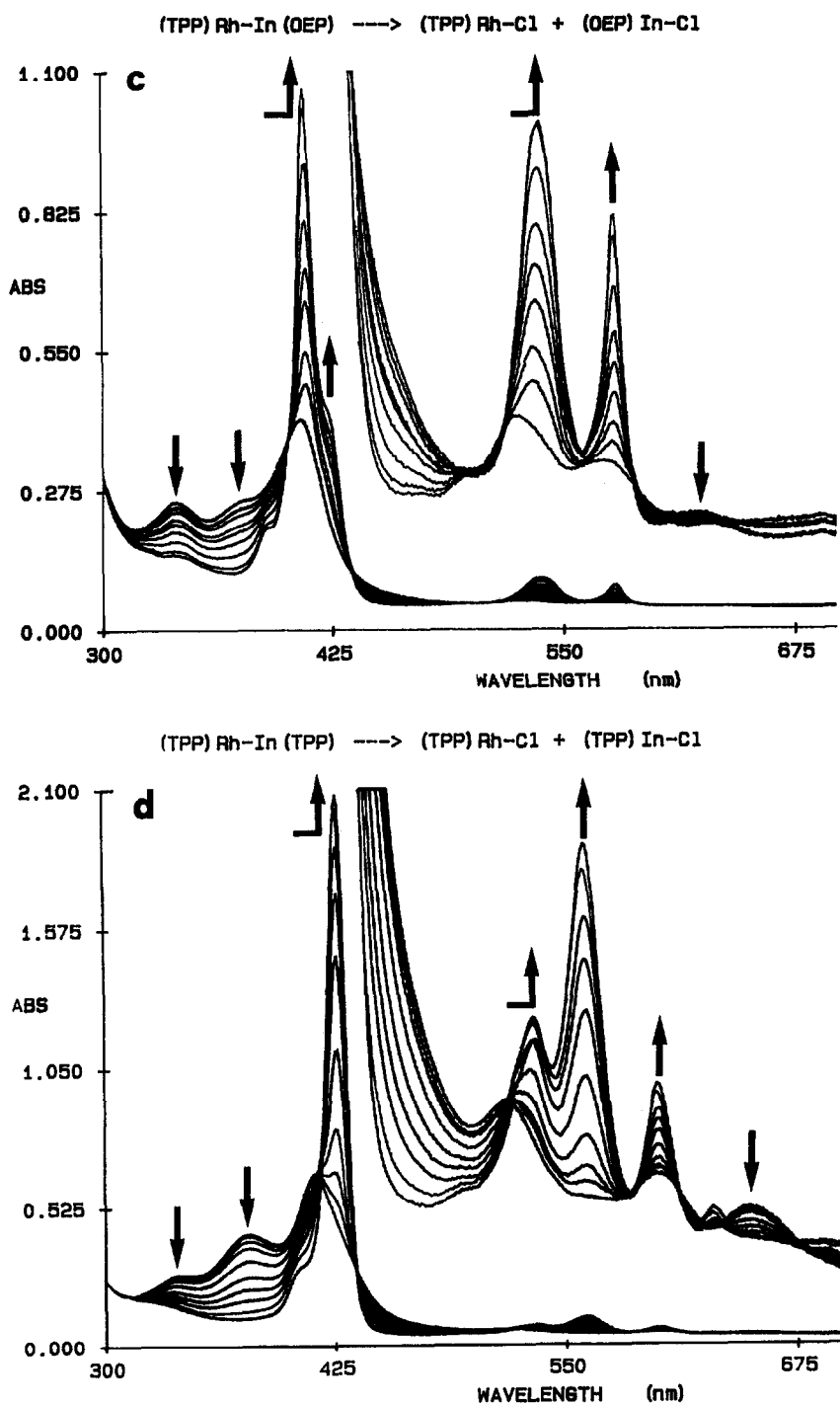


Fig. 2—continued

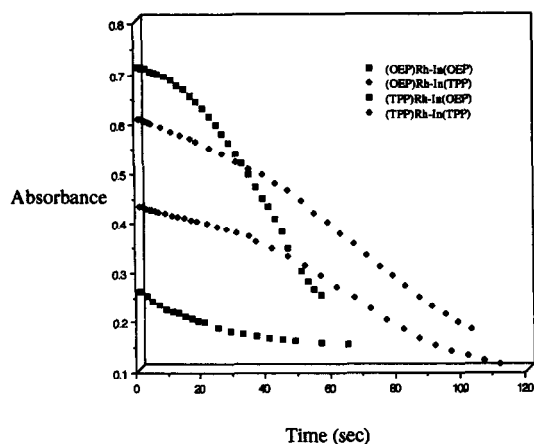
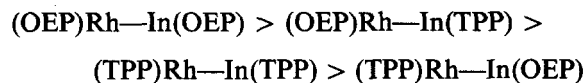


Fig. 3. Decay times for the four dimers. The maxima used for (a) (OEP)Rh—In(OEP); (b) (OEP)Rh—In(TPP); (c) (TPP)Rh—In(OEP); and (d) (TPP)Rh—In(TPP) are at 362, 370, 408 and 417, respectively.

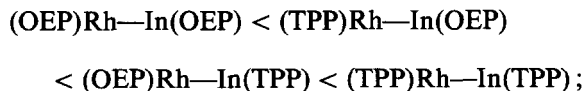
After the 30 sec until the complete transformation of the initial dimer the decay of these complexes follow the order:



which is a complete inversion of the first one.

The above inversion of the decay process is difficult to explain and even risqué. An hypothesis is the different electron ability of the macrocycles involved. It is well known that OEP is a stronger σ donor than the TPP ring. For this reason the dissociation of (TPP)Rh—In(TPP) is faster than the (OEP)Rh—In(OEP) compound at the beginning. Following the reaction the latter comes faster to the dissociation process perhaps by a synergetic effect from the formed intermediates (e.g. presence of free radical species).

Finally the decay time for the four complexes follows the order (as we can also deduce from Fig. 4):



which is the same as that for the photodegradation reaction. From this comparative study we can deduce that the final decay time of the initial heterodimers from the thermal addition of the CH_3I or from their photodecomposition follows the same order. Under few reservations this is probably due to the same dissociation process.

We have also tried the thermal reactivity of the four heterometallic dimers with $\text{C}_{14}\text{H}_{29}\text{Br}$ but the result as we can confirm by the UV-vis spec-

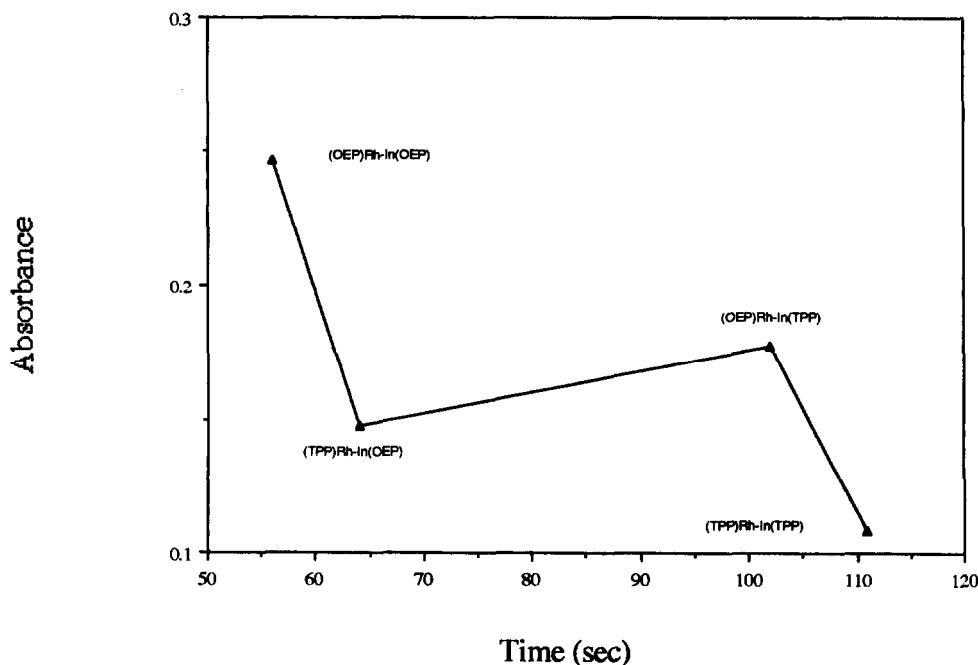
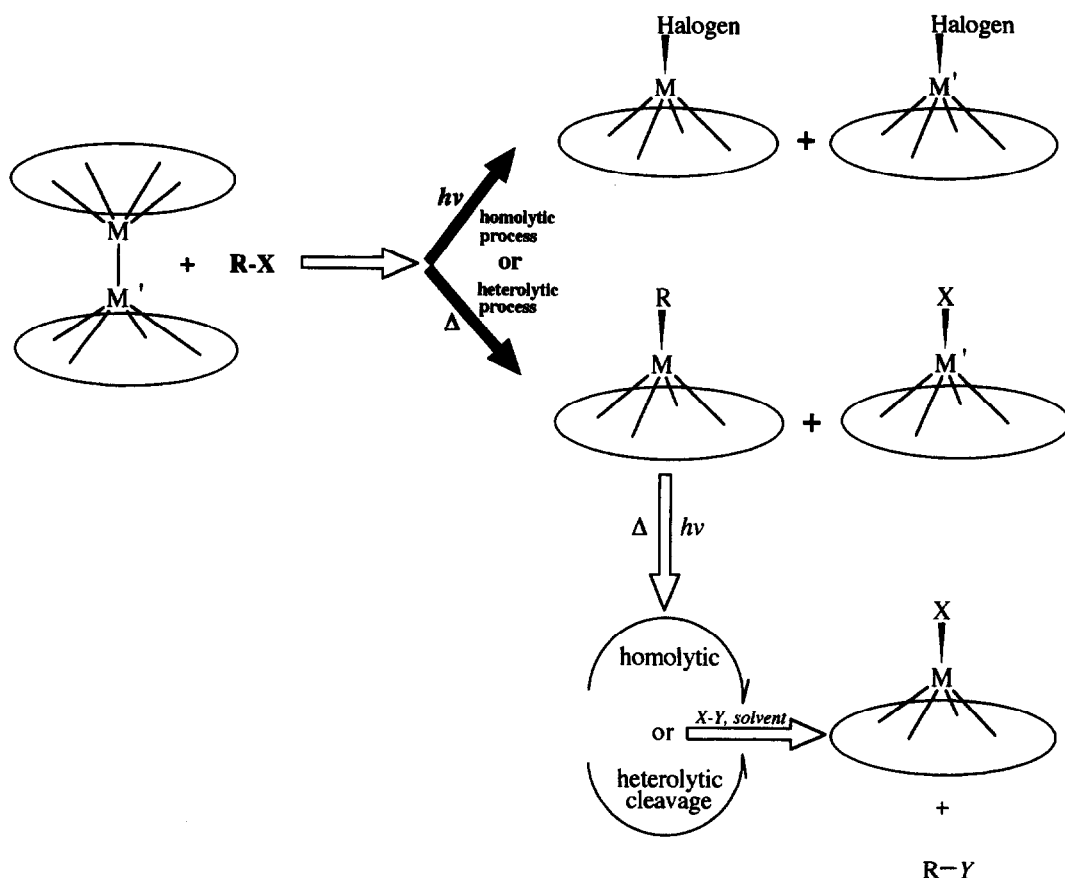


Fig. 4. Final decay times for the four dimers.



Scheme 2. Proposed mechanistic scheme for the chemical activity of the dimers, where $\text{M} = \text{Rh}$ and $\text{M}' = \text{In}$.

troscopy was the simple cleavage of the Rh—In bond without addition of alkyl bromide. This addition was possibly effective, but the products of addition, in particular the alkyl-metallo porphyrins, cleaved immediately after their formation (Scheme 2). This result was in agreement with the experiments carried out on the pure form of the alkyl-metalloporphyrins and their instability to the temperature control in solution.⁷

Photolytic reactivity

We experienced the same behavior for the photolytic reaction between CH_3I or $\text{C}_{14}\text{H}_{29}\text{Br}$ and our new metal-metal bonded complexes. However, upon irradiation (with the same instrumental conditions as for the photodecomposition studies) the final result was the same as after a simple cleavage of the metal-metal bond without any addition of R-X to the dimers. We suppose that the addition occurred but the Rh—C bond formed cleaved photolytically exactly as the Rh—C bonds of the

tetradecacarbon rhodium porphyrin compounds did. Another explanation could be the homolytic cleavage of the metal-metal bond and the very fast reaction with the already existing chloride ions, or any other anionic species in the reaction mixture.

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