

# Solar Energy Conversion Using Platinum Group Metal Co-ordination Complexes

## A REVIEW OF CURRENT RESEARCH

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*Co-ordination complexes of ruthenium and rhodium have been shown to have potential applications in solar energy conversion. When illuminated with visible light on a laboratory scale these complexes catalyse photolysis reactions or exhibit photogalvanic effects to produce hydrogen or electricity. These processes and the problems involved in their immediate scale-up to practical solar energy conversion devices are discussed in this paper.*

Ever since farmers first began to harvest the products of photosynthesis, man has been indirectly utilising the energy received on earth from the sun. More direct applications of solar radiation in mirrors and reflectors and for the performance of physical work such as the evaporation of brine to yield valuable salts are equally as old. However, because of the lack of suitable technology and the ease of access to alternative energy sources which are independent of climate and weather conditions, the harvesting of solar energy has been sadly neglected almost to the present day. Only over the past decade or two has the growing concern about the rapid depletion of the world's natural non-renewable resources stimulated extensive research into the direct conversion of solar radiation into alternative forms of energy. These conversion processes may be broadly classified (1) as:

- (a) thermal conversion, for example solar furnaces,
- (b) direct electrical generation, including photovoltaic or photogalvanic devices,
- (c) photochemical processes, such as photosynthesis or photolysis of water to form hydrogen and oxygen.

This article considers the potential application of co-ordination complexes of ruthenium and rhodium in the photogeneration of hydrogen gas or electricity. Electrically generated power needs to be stored for use when the sun is not available. At present, the only practical solution is to use conventional storage batteries which have to meet stringent specifications including good cycle lives, low open-circuit losses, good charging efficiencies and low maintenance requirements. An attractive long-term solution, however, would be to store electrical energy as hydrogen obtained from the electrolysis of water. Hydrogen produced in this way, or by the direct photolysis of water, could be a major pollution-free fuel provided problems of storage and handling can be overcome (2).

### Ruthenium Complexes for the Photolysis of Water

The cleavage of water into gaseous hydrogen and oxygen requires approximately 70 kcal/mol (3). Light quanta in the visible region of the electromagnetic spectrum (400 to 700 nm) have low energies, Figure 1, and therefore to achieve water photolysis in this region a

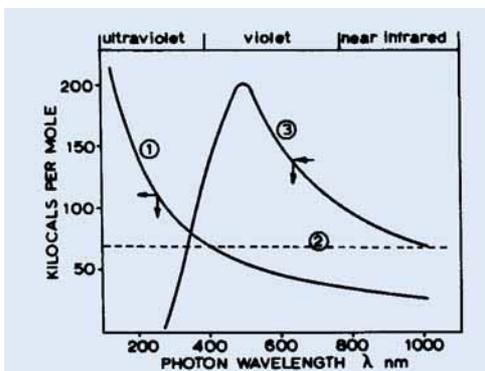


Fig. 1 Energy content of quanta and solar irradiance (after S. N. Paleocrassas, *Solar Energy*, 1974, 16, (1), 45). (1) quanta, (2) water dissociation energy and (3) solar irradiance

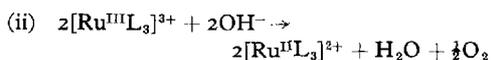
step-wise process involving more than one photon is necessary. Moreover, since water is transparent to visible light a photocatalyst is required to absorb the incident light and transfer its energy to water molecules via redox reactions.

Irradiation of the tris(2,2'-bipyridyl)ruthenium(II) cation,  $[\text{Ru}(\text{bipy})_3]^{2+}$ , with visible light results in the promotion of an electron from a molecular orbital of mainly metal character to one of mainly ligand character (4), Figure 2. This charge transfer excited state can act as both an electron donor or electron acceptor (5), and examination of the reduction

potential for this energy-rich species (6) indicates that it should reduce water, as protons, to hydrogen over a wide pH range. While this is a thermodynamically favourable reaction, in practice no reduction is observed and the continuing luminescence of the complex in aqueous solution suggests that the reduction reaction is too slow to compete with excited state decay. The reduction may also be inhibited by back electron transfer processes which regenerate the starting materials. If the reduction reaction



where  $[\text{*RuL}_3]^{2+}$  is the excited state of the complex, could be achieved, then the previously reported oxidation of hydroxide ion (7)



could occur. This would produce oxygen and regenerate the original ruthenium complex. The overall reaction would thus be the cyclic catalytic photolysis of water.

In 1976 Whitten reported the catalytic photocleavage of water by ruthenium complexes containing bipyridyl ligands bearing long chain organic substituents (8). The complexes initially reported to be active are shown in Figure 3 and luminesce in air when illuminated with visible light. Monolayer assemblies of these complexes on glass

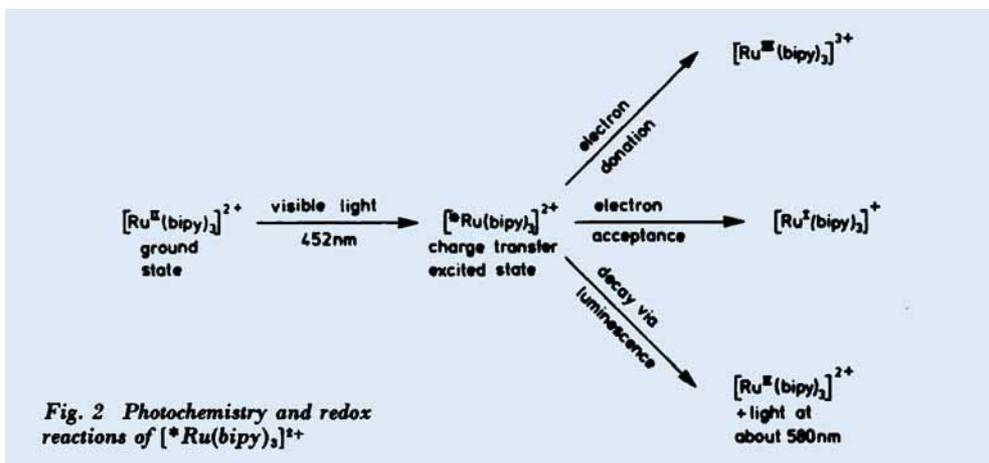
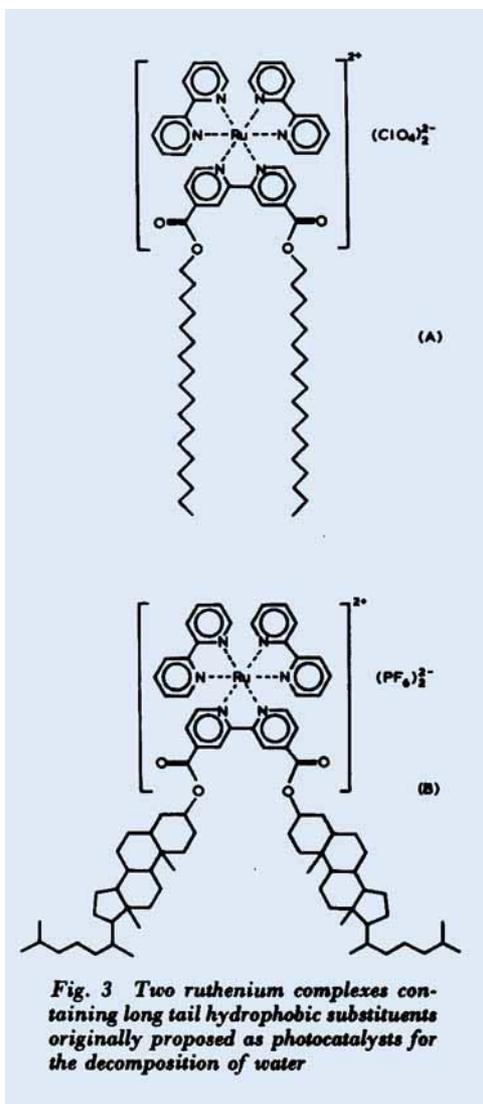


Fig. 2 Photochemistry and redox reactions of  $[\text{*Ru}(\text{bipy})_3]^{2+}$



slides immersed in water and irradiated with a medium pressure mercury lamp or with sunlight no longer luminesced and were reported to produce gaseous hydrogen and oxygen. More than  $10^3$  molecules of gas per molecule of ruthenium complex were produced and  $30 \text{ cm}^2$  of the monolayer produced  $0.5 \text{ cm}^3$  of gas every 24 hours over a two- to three-week period. The observed quantum yield, which is the proportion of excited state species which react to produce hydrogen, was about 10 per cent. This was higher than that

observed in photosynthesis in most plants and indicated a relatively efficient process. More recent experiments carried out by Whitten (9) and by other research groups have failed to reproduce the original observation of water photolysis. These later experiments have employed highly purified complexes whereas the original material successfully used to photocleave water was subsequently shown to contain about 3 per cent of impurities. Two major contaminants have been identified tentatively as the complexes shown in Figure 4. Assemblies of the highly purified complexes were rapidly degraded upon illumination of the assembly in water with up to 90 per cent of the complex being lost from the glass support within 24 hours. The ruthenium was subsequently identified as being present in the water as hydrolysed derivatives of the original complex, for example the dicarboxylic acid complex (C) in Figure 4. Recent work has also shown (9, 10) that the packing of the complex molecules in the assembly is extremely sensitive to impurities, with the highly purified complexes having much higher molecular areas than impure samples. The spectral properties of pure complex (A), Figure 3, in solution are similar to those of  $[\text{Ru}(\text{bipy})_3]^{2+}$  (11) but with both the absorption and luminescence maxima occurring at longer wavelengths, as shown in the Table. However, the spectral characteristics of complex (A) in monolayer assemblies are considerably different from those in solution. Samples of (A) of varying purity all exhibited absorption maxima at higher energy than in solution and at constant wavelength irrespective of sample purity, while strong variations were observed in both the position and intensity of the emission maxima. These spectral differences suggest strong co-operative interactions between molecules in the assemblies and demonstrate the influence of impurities upon the electronic properties of the assemblies.

The free radicals  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  are likely intermediates in the catalytic photocleavage reported by Whitten and for the reaction to

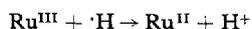
Spectral Absorption and Emission Maxima for Ruthenium Complexes			
Complex	Medium	Absorption, nm	Emission, nm
[Ru(bipy) <sub>3</sub> ]Cl <sub>2</sub>	H <sub>2</sub> O solid	450 (11) 452 (4)	582 (11) ~580 (4)
[Ru(bipy)(bipy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>  (A)	CHCl <sub>3</sub> monolayer assembly	468 (9) 425 (9) 480 (sh) all samples	660 (9) 645-670 (9) depending on purity

The numbers in parenthesis relate to the references, sh=shoulder.

proceed both the recombination of these radicals to form water:



and back electron transfer reactions of the type

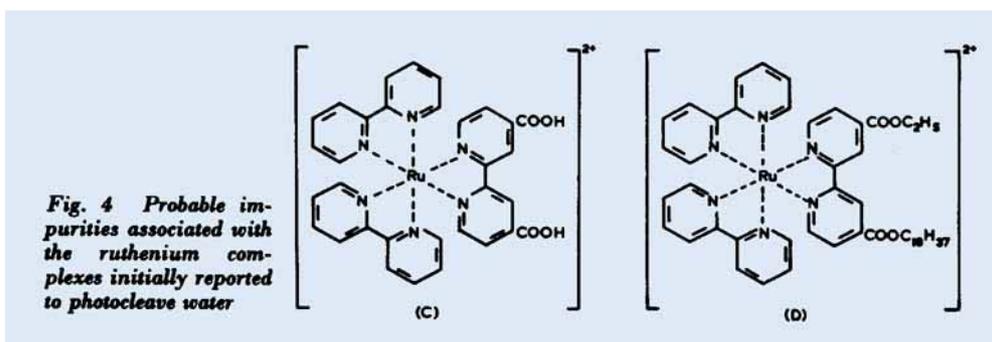


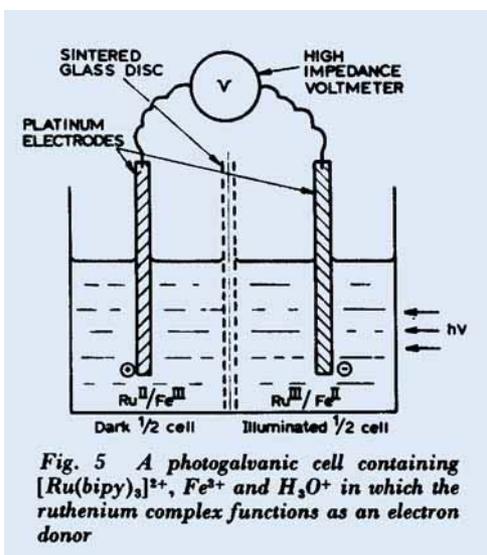
must be inhibited. The experimental work to date suggests that these conditions may have been met only in the monolayer assembly used by Whitten. This in turn implies that the original observation was strongly influenced by the impurities present in the complex or by a particular monolayer structure which has not been reproduced in subsequent experiments. It is likely that both factors are important, and possible that a particular impurity determines the formation of a particular assembly structure. For example, impurities containing hydrogen bonding moieties such as the carboxylic acid groups in complex (C), Figure 4, could modify the structure of the monolayer assembly and lead

to stronger co-operative interactions between molecules. Such an effect could explain the disparity in the molecular areas in monolayers of purified and impure complexes.

Unfortunately, many of the important questions relating to the mechanism of the photolysis reaction, such as the function of the long tail substituents and the influence of molecular packing on the stability and co-operative interactions within the monolayer assemblies must remain the subject of speculation until the original photolysis reaction has been successfully reproduced.

The original observation is an important one because it demonstrates that under the right conditions the photolysis of water can be achieved with ruthenium complexes. On the other hand, it seems unlikely that monolayer systems will ever form the basis of a practical process of solar energy conversion because of the large surface areas which would need to be covered with films having reproducible





properties. A more promising area involves research on dissolved ruthenium complexes (12) in an attempt to find a homogeneous photolysis reaction which would be more amenable to scaling-up into a practical energy conversion process.

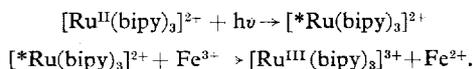
### Photogalvanic Cells Containing Ruthenium Complex Electrolytes

Illumination of dilute aqueous solutions of many redox couples leads to a change in the potential of the couple (13). Photogalvanic cells based upon this principle have been known for several decades, for example iron-thionine photocells (14), but have not been seriously considered as a practical means of converting light into electricity because of their low efficiencies. However, the efficiencies of such cells may now be considerably improved by the recent developments in thin layer devices and semiconductor electrodes. Simultaneously, new cells without the inherent disadvantages of some of the older systems are now emerging.

As previously stated the excited state of  $[\text{Ru}(\text{bipy})_3]^{2+}$  can function as both an electron donor or electron acceptor, and photogalvanic cells in which the complex functions in either

of these modes have been described recently.

In an example of the complex acting as an electron donor two half-cells both containing  $[\text{Ru}(\text{bipy})_3]^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_3\text{O}^+$  are connected through an external circuit with one half-cell illuminated while the other is kept dark (6), Figure 5. In the illuminated half-cell photo-induced electron transfer generates  $[\text{Ru}(\text{bipy})_3]^{3+}$  and  $\text{Fe}^{2+}$ :



The changed composition of the illuminated half-cell results in a change in its potential relative to the dark half-cell and electrons flow through the external circuit in the direction determined by the dominant couple, from the dark to the illuminated half-cell. The reversibility of the cell is ensured by mass transfer of  $\text{Fe}^{2+}$  to the dark half-cell where it reacts with anodically produced  $[\text{Ru}^{\text{III}}(\text{bipy})_3]^{3+}$  to regenerate  $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{2+}$  and  $\text{Fe}^{3+}$ .

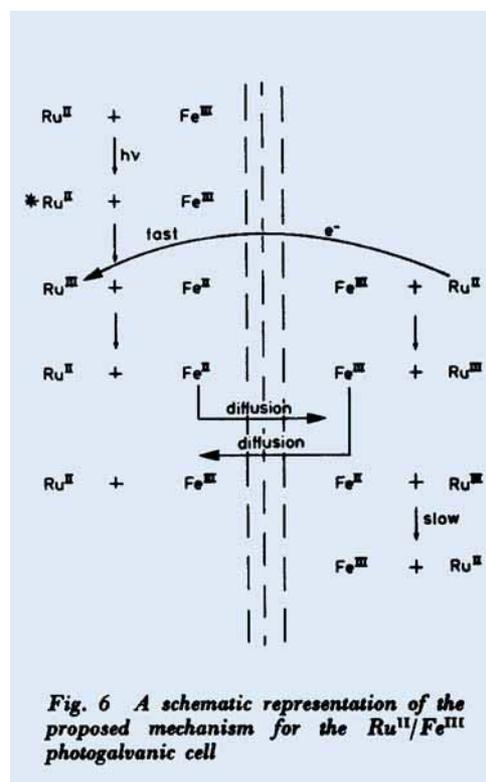
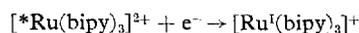


Figure 6 shows the reactions proposed in this cell. The observed open-circuit photo-potential depends upon the incident light intensity and on the acid used in the cell but under typical conditions potentials of 100 to 180 mV have been observed. The long term stability of the system is relatively good since only approximately 20 per cent of the ruthenium complex is degraded after 6 days on a cycle of exposure of the cell to a 500W tungsten lamp for 10 seconds in every minute. Only a very small catalytic amount of ruthenium complex is required and the small long term loss could easily be rectified by addition of further ruthenium complex without the cost of the complex becoming a prohibitive factor.

In the absence of an efficient quencher, such as  $\text{Fe}^{3+}$ , the excited state ruthenium complex can function as an electron acceptor towards a gold electrode (15). The reactions occurring in this cell are:



at the illuminated cathode



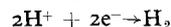
at the dark anode.

This cell is sensitive to dissolved molecular oxygen and is best operated under an inert atmosphere. Current yields are very low, only 2 to 16  $\mu\text{A}$ , because decay of the excited complex to its ground state is about  $10^5$  times more probable than electron transfer at the gold electrode.

A photocell based on  $[\text{Ru}(\text{bipy})_3]^{2+}$  which has been proposed (7) but not yet reported contains a metal electrode and an n-type semiconductor electrode immersed in a solution of the complex buffered at pH 9 and connected via an external circuit. It was proposed that illumination at the semiconductor electrode would produce  $[\text{Ru}(\text{bipy})_3]^{2+}$  which, under favourable conditions, would inject an electron into the conduction band of this electrode leaving  $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{3+}$  which could then oxidise hydroxide ions to oxygen as previously described.

The electron at the semiconductor elec-

trode would flow through the external circuit to reduce water or hydrogen ions at the metal electrode to dihydrogen:



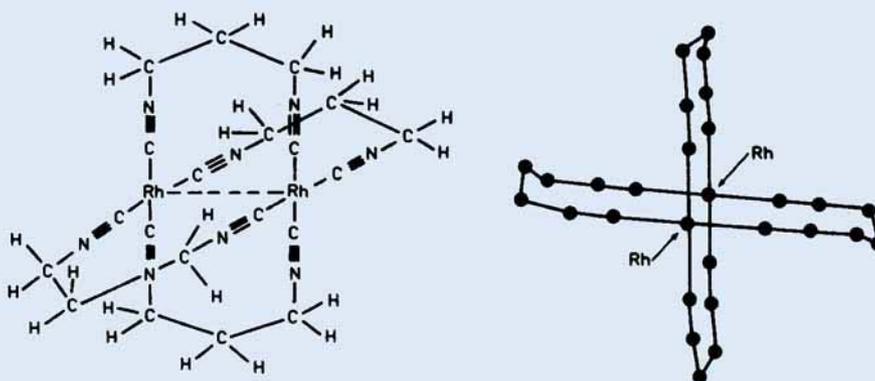
The original ruthenium complex would be regenerated in reaction (ii), page 119. Many factors may be critical to the realisation of such a cell. Choice of electrode material may be one important factor since not only would it be desirable to use a cathode whose over-potential for the production of hydrogen is small, but the semiconductor electrode must be chosen so that the excited electron has sufficient energy to reach its conduction band.

Although a cell containing a semiconducting tin oxide electrode and based on  $[\text{Ru}(\text{bipy})_3]^{2+}$  has been reported (16), the cell mechanism here is probably similar to that proposed for the  $\text{Ru}^{\text{II}}/\text{Fe}^{3+}$  cell previously described with methyl viologen taking the place of  $\text{Fe}^{3+}$  as the homogeneous quencher. Open circuit currents of 160  $\mu\text{A}$  may be observed in this cell which functions to reduce atmospheric oxygen to hydrogen peroxide, but the observed quantum yield is again low at about 0.5 per cent.

Electron transfer from an excited species such as  $[\text{Ru}(\text{bipy})_3]^{2+}$  to an electrode will be sensitive to many effects including the ionic and molecular environment of the complex, its excited state lifetime and its proximity to the electrode surface. An active area of current research is the study of the chemical linking of such reactive species to electrodes to facilitate electrochemical reactions (17). Preliminary evidence suggests that ruthenium bipyridyl complexes attached to an electrode surface could provide a completely reversible electroactive system and studies of this sort could give a valuable impetus to the search for more efficient photoelectrochemical energy conversion systems.

Photocells based on  $[\text{Ru}(\text{bipy})_3]^{2+}$  have several advantages (6) over some of the better known photogalvanic systems such as iron-thionine photocells. These are:

- (a)  $[\text{Ru}(\text{bipy})_3]^{2+}$  is very stable with respect to reaction with oxygen in the presence of



**Fig. 7** A dimeric rhodium complex containing four bridging 1,3-diisocyanopropane ligands which has recently been reported to photogenerate hydrogen from acid solutions

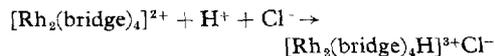
- an efficient quencher, as for example  $\text{Fe}^{3+}$
- (b) The maximum absorption of the complex  $[\text{Ru}(\text{bipy})_3]^{2+}$  is close to the maximum intensity peak in the solar spectrum, as shown in Figure 1.
- (c) No reactive intermediates giving rise to undesirable side effects, which is a major drawback with the iron-thionine system, are involved in the kinetics.

Photochemical cells based on  $[\text{Ru}(\text{bipy})_3]^{2+}$  have emerged only very recently and no doubt the inefficient design of the present cells could be drastically improved. At the same time preliminary experiments with different ruthenium complexes indicate that the quantum yield may also be improved. It is unrealistic to expect such cells to generate large amounts of power but it is not inconceivable that cells of this sort connected in series could have applications in the electrolysis of water to hydrogen.

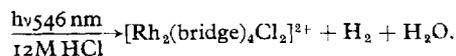
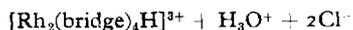
### Bridged Rhodium Complexes for Hydrogen Production

An unusual dimeric complex of rhodium containing four bridging 1,3-diisocyanopropane ligands and having a windmill-like structure, Figure 7, has been reported recently (18) to possess novel properties which may

have relevance in solar energy conversion schemes. In this complex, orbital interaction between the two metal atoms results in intense electronic absorption in the visible spectrum. When the blue solution of the complex in 12M hydrochloric acid is irradiated with light at 546 nm the yellow complex  $[\text{Rh}_2(\text{bridge})_4\text{Cl}_2]^{2+}$  and gaseous hydrogen are produced in a non-cyclic reaction. The mechanism has not yet been fully established but the available evidence points to an initial protonation of the dimer:

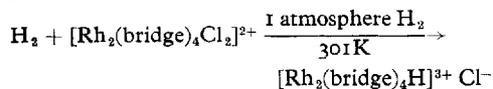


where the complex formed is a proton adduct rather than a hydrido complex. This is followed by a second electron transfer reaction which is light induced:



In concentrated hydrochloric acid the quantum yield for this reaction is very low, only about 0.5 per cent, but this is increased considerably to about 4.4 per cent in concentrated hydrobromic acid, and this observation may provide a clue to methods of further increasing the quantum yield. The excited

state species has been formulated as  $[\text{Cl}^- \dots \text{Rh}^{3/2} \dots \text{Rh}^{3/2} \dots \cdot \text{H}]^{2+*}$  and it has been suggested that the  $\sigma$ -binding interactions along this internuclear axis are stronger than in the ground state and therefore favour the production of hydrogen over back-transfer to the Rh(I) complex. In practice the back reaction:



is indeed slow and takes several days to go to completion.

This type of homogeneous reaction is a very attractive proposition for future energy conversion processes provided it can be made cyclic with regeneration of the original Rh(I) complex. Attempts to achieve this end by methods such as coupling the rhodium system to a semiconductor cell for the simultaneous production of oxygen and regeneration of the active Rh(I) complex by reduction are currently under investigation (12). Such work is still at a very early stage and some formidable problems will need to be solved before such a combination could be considered as a practical method for the production of hydrogen. Not the least of these problems will be to increase

the very low quantum yields presently found in both the rhodium complex and semiconductor cell reactions.

## Conclusions

Research into solar energy conversion processes nowadays includes not only work in established areas such as thermochemical, photovoltaic and bio-photolytic methods but also in novel areas such as energy conversion via photoassisted valence isomerisation reactions (19, 20). The area involving coordination compounds of the platinum group metals forms only a small but apparently rapidly growing part of the overall picture. Many of the different methods using platinum group metal complexes which have been described are promising, but all are presently at an embryonic stage and require considerable research and development before they could become practical systems for solar energy conversion. Nature has been using the sun as a direct energy source for photosynthesis since life first evolved on earth. Present research on solar energy conversion attempts to emulate nature, and is therefore one of the most challenging projects for the modern scientist.

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