

relative sequence of catalytic efficiency.

The earlier literature²¹ reports a case of aluminum trichloride catalyzed formation of COCl_2 at 30–35 °C with chloroform as solvent. We have checked the experiment and found that only in the presence of light is phosgene formed under the specified conditions. The scope of the observed catalytic reaction is now under current investigation. Manchot and Lehmann¹⁷ report that RhCl_3 releases Cl_2 at 90 °C in the presence of CO. However, no COCl_2 was observed. $\text{Rh}_2(\text{C}-\text{O})_4\text{Cl}_2$ oxidatively adds dichlorine at room temperature with CCl_4 as solvent with no formation of phosgene.²² Thus,

rhodium does not appear to be an appropriate catalyst for the room-temperature combination of carbon monoxide with dichlorine to phosgene.

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Registry No. Carbon monoxide, 630-08-0; dichlorine, 7782-50-5; $\text{Au}(\text{CO})\text{Cl}$, 50960-82-2; AuCl_3 , 13453-07-1; $[\text{Pd}(\text{CO})\text{Cl}_2]^-$, 44252-60-0; $\text{NH}_2\text{Et}_2[\text{Pt}(\text{CO})\text{Cl}_3]$, 82456-40-4; $\text{Pd}_2(\text{CO})_2\text{Cl}_4$, 43062-39-1.

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Photochemically Induced Reductive Elimination of Hydrogen from a Binuclear Platinum Hydride¹

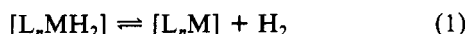
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Photolysis of $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6]$ (Ia), $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, using 362 ± 8 nm light occurs with quantum yields of 0.81 (MeCN solution) and 0.57 (pyridine solution) to give $[\text{Pt}_2\text{H}(\text{L})(\mu\text{-dppm})_2][\text{PF}_6]$ (Iic, L = MeCN; Iid, L = pyridine) and H_2 in quantitative yield. The primary isotopic effect on the quantum yields (from similar studies of $[\text{Pt}_2\text{D}_3(\mu\text{-dppm})_2][\text{PF}_6]$ (Ib)) is given by $\phi_{\text{H}}/\phi_{\text{D}} = 1.8$ and 1.6 in MeCN and pyridine solutions, respectively, and the reductive elimination is shown to be intramolecular (a mixture of Ia and Ib gives very largely H_2 and D_2 with little HD). The reaction can be sensitized with triphenylene but not by Michler's ketone, indicating that reaction is initiated from the singlet excited state.

Introduction

The thermally or photochemically induced reductive elimination of H_2 from mononuclear polyhydrido derivatives of transition metals has been studied in depth.^{2–5} The primary reaction, which may be reversible, is often described by the general equation (1) and involves a concerted intramolecular reductive elimination.^{2–7}



In some cases, for example, with $[\text{IrH}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, both thermal and photochemical activation is possible, but in other cases, for example, with $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$, only photochemical activation is effective.⁷ The product $[\text{L}_n\text{M}]$ is necessarily coordinatively unsaturated and is often highly reactive; it may undergo self-reaction, typically by ortho metalation (e.g., when $[\text{L}_n\text{M}] = [\text{IrCl}(\text{PPh}_3)_3]^+$), or react with solvent (e.g., when

$[\text{L}_n\text{M}] = [(\eta^5\text{-C}_5\text{H}_5)_2\text{W}]^8$). The species $[\text{L}_n\text{M}]$ is expected to be an active catalyst in many cases although this area has not been developed. It may be possible to trap the primary product $[\text{L}_n\text{M}]$ with added ligand L^1 , but in the typical case where $[\text{L}_n\text{MH}_2]$ is an 18-electron complex, L^1 is not involved in the rate-determining reductive-elimination step.^{2–4}

In contrast, although there are several examples of thermally induced reductive elimination of H_2 from binuclear and polynuclear transition-metal hydrides, very little is known about the mechanism of such reactions.⁹ Although almost all mononuclear polyhydrido derivatives of transition metals undergo photochemically induced reductive elimination of H_2 ,^{4,5,10} few examples of polynuclear transition-metal hydrides undergoing such a reaction have been reported.¹¹ For example $[\text{Re}_4\text{H}_4(\text{CO})_{12}]$ is emissive in hydrocarbon solutions but is not photochemically decomposed.¹²

We recently reported a very clean binuclear reductive elimination of H_2 from the cation¹³ $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$

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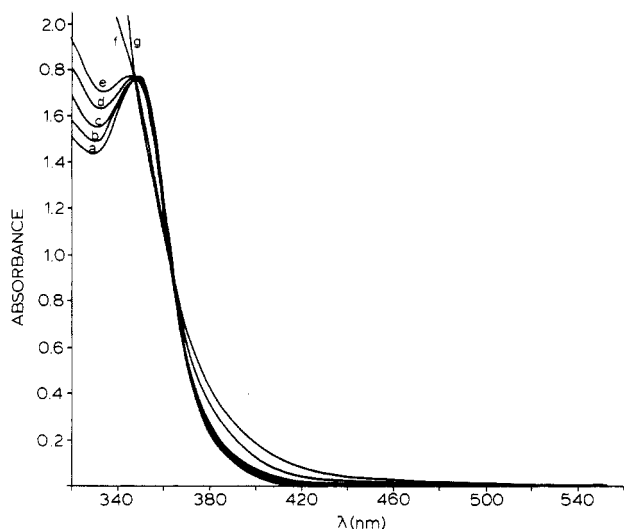


Figure 1. Electronic spectral changes accompanying the 362 ± 8 nm photolysis of Ia in pyridine, with the following number of counts of irradiation: (a) 0; (b) 1; (c) 2; (d) 4; (e) 6; (f, g) extended irradiation.

diator. The solutions were rigorously degassed prior to irradiation. A typical set of spectra obtained during irradiation of Ia in pyridine solution is shown in Figure 1. The extent of reaction was determined by monitoring the optical density at 333 nm, and when correction was made for absorption of light by the product, good linear plots of quanta absorbed by I vs. extent of conversion were obtained. The resulting quantum yields (Experimental Section) are remarkably high. The isotopic effect on the quantum yields, ϕ_H/ϕ_D , was 1.6 for photolysis in pyridine solution and 1.8 in acetonitrile.

Prolonged photolysis of IId in acetonitrile solution led to further changes in the absorption spectrum. However, this reaction was so slow that it did not interfere with the above quantum yield determinations. No serious attempt was made to study this secondary reaction. Admission of air to solutions of IId prepared as above led to further spectral changes, with a decrease in absorbance at 450 nm and an increase at 400 nm. However, there were no isosbestic points and we have not succeeded in characterizing the products of this subsequent reaction.

The performance of specific quenching experiments to distinguish between singlet and triplet pathways was not possible because of the high extinction coefficients of the complex throughout the ultraviolet region. It was, however, possible to sensitize the reaction in MeCN and monitor its course by means of the terminal Pt-H stretching absorption in the IR spectrum. Concentrations were chosen such that $\sim 90\%$ of the incident light was absorbed by the sensitizer, triphenylene ($E_s = 83.4$ kcal/mol; $E_T = 66.5$ kcal/mol).^{21,22} The spectral distribution of the low-pressure Hg lamp used was such that small amounts of light were emitted in the 313- and 366-nm regions. Although the filter solution used removed most of this light, the amount of reaction induced by this light was determined experimentally. This was achieved by determining the rate of reaction when a Pyrex filter was interposed between the sample and the light source. This rate was then subtracted from the rates at which the sensitized and directly induced reactions occurred. A further correction was made for the 10% light absorbed directly by Ia. The final ratio of rate sensitized/rate direct was, from these rather crude measurements, limited by the degree of conversion possible

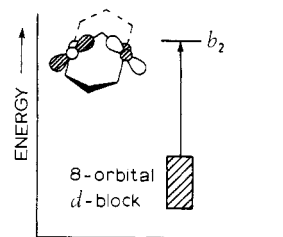


Figure 2. Qualitative MO energy level diagram for Ia, adapted from ref 26.

and by the inaccuracy of the IR measurements. The value found was 0.57 ± 0.12 at a concentration of Ia of 6.1×10^{-3} mol L⁻¹.

The sensitization experiment alone does not distinguish singlet from triplet energy transfer, but since attempted sensitization by the efficient triplet sensitizer Michler's ketone was negative and since the triplet energies of triphenylene and Michler's ketone ($E_T = 62$ kcal/mol)²¹ are close, we conclude that singlet energy transfer is operative. Assuming the lifetime τ of the triphenylene singlet in acetonitrile is essentially the same as in cyclohexane ($\tau = 37$ ns),²³ we can approximate the rate of energy transfer by eq 3, whence k_q , the rate constant

$$\text{rate sensitized/rate direct} = k_q[\text{Ia}]/(k_q[\text{Ia}] + \tau^{-1}) \quad (3)$$

for energy transfer, is $(6 \pm 2) \times 10^9$ M⁻¹ s⁻¹. This is somewhat below that of diffusion control (2.7×10^{10} M⁻¹ s⁻¹ from the modified Debye equation). With allowance for diffusion separation before energy transfer²⁴ this would be expected to be about 10^{10} M⁻¹ s⁻¹. However, energy transfer to bulky complexes has often been found to be somewhat inefficient even when exothermic²⁵ and the approximate value we report is not unreasonable. We are therefore led to believe that the reaction takes place from a singlet, not a triplet, state.

Discussion

According to the calculations of Hoffman and Hoffmann,²⁶ the LUMO in the cation Ia is an orbital of b_2 symmetry, which is nonbonding between the platinum atoms and the μ -H ligand but is antibonding between the two platinum atoms, while the HOMO is one of a block of eight closely spaced d-block orbitals (Figure 2). The irradiation using 362- or 366-nm light is expected to lead to the transition $d \rightarrow b_2$ ($\lambda_{\text{max}} = 349$ nm in MeCN). The sensitization experiment indicates that the photochemistry results directly from the primary singlet excited state, and the labeling experiment shows that the reductive elimination of H₂ is an intramolecular reaction. Unfortunately the cation Ia is fluxional so that it is not possible to label the bridging or terminal hydride ligands separately and hence to determine unequivocally which two hydride ligands are lost on photolysis.

The simplest interpretation of the above data is that the primary excitation of Ia leads to a significant increase in the Pt-Pt separation as a result of occupation of the b_2 molecular orbital.²⁶ This would force the bridging hydride to move with one of the Pt atoms, since a symmetrical μ -hydride with a very long Pt-Pt distance would be unfavorable. One way in which this deformation could occur would be to give a complex of structure III, analogous with that of $[\text{Pt}_2\text{Me}_3(\mu\text{-dppm})_2]^+$ (IV).²⁷ Reductive elimination of H₂ at a single platinum

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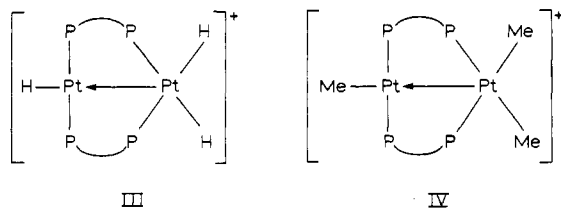
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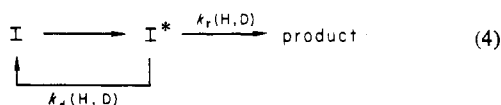
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center could then occur as in mononuclear complexes. It is generally accepted that the alternative reductive elimination of H₂ by coupling of separate Pt-H groups is orbitally forbidden in the ground state, although this rule may not apply in the excited state.²⁸

It has been argued previously that the role of tertiary phosphine ligands in inducing thermal reductive elimination of H₂ from Ia is to give an intermediate [Pt₂H₃(PR₃)(μ-dppm)₂]⁺, in which there is no bridging hydride ligand and from which reductive elimination can occur easily.¹⁸ Direct reductive elimination from Ia, in which the terminal and bridging hydride ligands are mutually trans, is difficult to envisage. The photochemical excitation may then act in a similar way by breaking the Pt₂(μ-H) linkage. In the photolysis, there is no evidence for direct participation of pyridine or acetonitrile prior to the reductive-elimination step (except possibly to provide a new decay channel). The observations that the quantum yield for photolysis of Ia in acetonitrile (0.81) is greater than in pyridine (0.57), whereas pyridine is a much better ligand for platinum, and that photolysis of Ia occurs readily in nondonor solvents or in the solid state argue against such solvent participation. Rather, it seems that the donor solvent simply traps the primary product, [Pt₂H(μ-dppm)₂]⁺, formed on reductive elimination of H₂. That the donor solvents do not interact strongly with Ia in the ground state is shown from the UV, IR, and NMR spectra of solutions of Ia, which are very similar to those in nondonor solvents.

The observation of a considerably lower isotopic effect on the quantum yields for photolysis of Ia vs. Ib, when compared with the corresponding isotopic effects for the thermal reactions induced by triphenylphosphine or dppm, for which $k_H/k_D \approx 3.5$,¹⁸ is of interest since no such comparison appears to have been made previously, even for reactions of mononuclear complexes. The result is, however, difficult to interpret. In the simplest case defined by



it is easily shown that

$$\phi_H/\phi_D = [k_r(\text{H})/k_r(\text{D})][(k_r(\text{D}) + k_d(\text{D})) / (k_r(\text{H}) + k_d(\text{H}))]$$

= isotope effect $\times \tau(\text{H})/\tau(\text{D})$

Unfortunately, the complexes I did not show observable fluorescence (or phosphorescence) so that we have been unable to determine the isotopic effect on the lifetime of the singlet excited state, $\tau(\text{H})/\tau(\text{D})$. Qualitatively, $\tau(\text{H})/\tau(\text{D})$ is expected to be less than unity, but there are insufficient precedents to allow an estimate of how great such an effect might be.¹² Thus the observed magnitudes of ϕ_H/ϕ_D of 1.6 (L = pyridine) and 1.8 (L = acetonitrile) are considered minimum values for the isotope effects on the rate constants for reductive elimination from the excited states, $k_r(\text{H})/k_r(\text{D})$, and it is not clear whether the isotope effects for these rate constants are significantly different from the value of k_H/k_D found for the thermal reactions.²⁹ However, the result certainly indicates

that partial Pt-H bond cleavage is involved in the transition state for reductive elimination.

The present work and those immediately preceding^{18,19} show for the first time that intramolecular reductive elimination of hydrogen can occur very efficiently from a binuclear transition-metal hydride by photochemical activation, that the reaction probably occurs from the first singlet excited state, and that there is a significant primary isotope effect on the rate constant for the reductive-elimination step. It is not possible to determine unequivocally the intimate mechanism of the photochemical reaction, and we recognize that the mechanism proposed, although consistent with the data, with theory, and with the general chemistry of the complex cation Ia, is only one of a number of such possible mechanisms.

Experimental Section

IR spectra were recorded with a Beckman 4250 spectrophotometer, UV-visible spectra with a Cary 118 spectrophotometer, and NMR spectra with a Varian XL100 spectrometer. Chemical shifts are quoted with respect to Me₄Si (¹H) or trimethyl phosphate (³¹P). Analysis for H₂ by gas chromatography was carried out using a Varian Model 1420 gas chromatograph with a Molecular Sieve 5A column (6 ft $\times$ 1/8 in.) and isotope analysis using a Varian MAT 311A mass spectrometer.

[Pt₂D₂(μ-D)(μ-dppm)₂][PF₆]. This was prepared by a modification of the method used for [Pt₂H₂(μ-H)(μ-dppm)₂][PF₆].¹³ Solid Na[BD₄] (0.5 g) was added slowly (2 h) in small portions (0.01 g) to a stirred suspension of [PtCl₂(dppm)] (1.0 g) in MeOD (20 mL) in a flask flushed with N₂, and the resulting mixture was stirred for 1 h. The mixture was filtered, the solid was extracted with CH₂Cl₂ (10 mL), and the filtered solution was added to a solution of NH₄[PF₆] (0.36 g) in CH₃OD (20 mL). The volume was reduced to 15 mL with use of a rotary evaporator, and the white crystals of [Pt₂D₂(μ-D)(μ-dppm)₂][PF₆] that formed were filtered, washed with pentane, and dried under vacuum. IR (Nujol): $\nu(\text{PtD})$ 1537 cm⁻¹; $\nu(\text{PtH})$ absent; cf. for Ia, $\nu(\text{PtH})$ 2100 cm⁻¹.

UV-visible spectrum of Ia: λ_{max} 348 nm, ϵ 4.90 $\times$ 10³ L mol⁻¹ cm⁻¹ (pyridine solution); λ_{max} 349 nm, ϵ 4.09 $\times$ 10³ L mol⁻¹ cm⁻¹ (MeCN solution). NMR data for Ia in CD₃CN: $\delta(\text{PtH})$ -6.9, ¹J(PtH) = 1152 Hz, ²J(PtH) = 112 Hz; $\delta(\text{Pt}_2(\mu\text{-H}))$ -5.85, ¹J(PtH) = 546 Hz; $\delta(^{31}\text{P})$ 17.9, ¹J(PtP) = 2755 Hz, ²J(PtP) = 6 Hz, ²J(PP) = 64 Hz, ³J(PP) = 17 Hz. NMR data for Ia in C₅D₅N (0 °C): $\delta(\text{PtH})$ -6.7, ¹J(PtH) = 1146 Hz; $\delta(\text{Pt}_2(\mu\text{-H}))$ -5.9, ¹J(PtH) = 545 Hz; $\delta(^{31}\text{P})$ 17.3, ¹J(PtP) = 2760 Hz, ²J(PtP) = 20 Hz, ²J(PP) = 59 Hz, ³J(PP) = 19 Hz.

[Pt₂H(py)(μ-dppm)₂][PF₆]. A solution of Ia (0.2 g) in pyridine (2 mL) contained in a Pyrex tube (10 mL) was deoxygenated by bubbling pure N₂ for 45 min. The sample was photolyzed, with a 150-W xenon lamp placed 25 cm from the sample, for 40 min at 0 °C. Water and Corning O-52 filters were used to remove IR and wavelengths shorter than 360 nm, respectively. The yellow solution obtained was added to petroleum ether (bp 30–60 °C, 5 mL), when the product precipitated as a yellow oily solid. The solvents were decanted off, and the product was dried under vacuum, giving a yellow solid. IR (Nujol or pyridine solution): $\nu(\text{PtH})$ 2000 cm⁻¹. NMR (C₅D₅N): $\delta(\text{PtH})$ -7.66, ¹J(PtH) = 938 Hz, ²J(PtH) = 66 Hz, ²J(PH) = 16 Hz, ³J(PH) = 5 Hz; $\delta(\text{CH}_2\text{P}_2)$ 5.4 (m); $\delta(^{31}\text{P})$ 17.2, ¹J(PtP) = 3480 Hz, and 7.7, ¹J(PtP) = 2890 Hz, ²J(P^AP^B) = 59 Hz, ⁴J(P^AP^B) = 31 Hz. Anal. Calcd for C₅₅H₅₀F₆NP₃Pt₂: C, 47.7; H, 3.6; N, 1.0. Found: C, 47.8; H, 3.6; N, 1.3.

[Pt₂H(MeCN)(μ-dppm)₂][PF₆]. A solution of Ia (0.11 g) in MeCN (15 mL) contained in a Pyrex flask (25-mL capacity) was deoxygenated by three freeze-pump-thaw cycles. The irradiation was effected using a focused beam from a 150-W xenon lamp 25 cm from the sample, filtered as in the previous experiment. When reaction was complete (~20-min irradiation), the solution was cooled to 0 °C and the solvent was removed under high vacuum, leaving the product as an orange solid in analytically pure form. IR: Nujol, $\nu(\text{PtH})$ 2030 cm⁻¹; MeCN solution, $\nu(\text{PtH})$ 2020 cm⁻¹. NMR (CD₃CN): $\delta(\text{PtH})$ -9.0, ¹J(PtH) = 963 Hz, ²J(PtH) = 76 Hz, ²J(PH) = 15 Hz, ³J(PH)

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(29) For example, we note that if eq 4 applies and if $k_d(\text{H}) \approx k_d(\text{D})$, then the ratios $k_r(\text{H})/k_r(\text{D}) \approx 5$ (CH₃CN) and 2.5 (py) can be calculated. If, as expected,¹² $k_d(\text{H}) \geq k_d(\text{D})$, these should be minimum values for $k_r(\text{H})/k_r(\text{D})$, but if eq 4 does not apply, this interpretation is invalid.

= 5 Hz; $\delta(\text{CH}_2\text{P}_2)$ 4.5, $^2J(\text{Pt}^{\text{A}}\text{H}) = 71$ Hz, $^2J(\text{Pt}^{\text{B}}\text{H}) = 52$ Hz, $J(\text{PH}) = 9$ Hz; $\delta(^{31}\text{P})$ 15.6, $^1J(\text{PtP}) = 3522$ Hz, and 6.4, $^1J(\text{PtP}) = 2840$ Hz. Anal. Calcd for $\text{C}_{52}\text{H}_{48}\text{F}_6\text{NP}_3\text{Pt}_2$: C, 46.4; H, 3.6; N, 1.0. Found: C, 46.3; H, 3.6; N, 1.1.

Studies of Hydrogen Evolution. A solution of Ia (0.065 g, 4.9×10^{-5} mol) in MeCN (25 mL) was deoxygenated by bubbling N_2 for 45 min. The reaction vessel was a flat-sided Pyrex flask, fitted with a side arm with a 1-mm quartz cuvette attached to allow monitoring of the course of the reaction by UV-visible spectroscopy. The solution was irradiated with use of a 400-W mercury lamp placed 15 cm from the sample, and H_2O and Corning O-52 filters were used. The photolysis was monitored by UV-visible spectroscopy. The reaction was stopped before completion and, from the optical density change at 333 nm, it was calculated that 3.7×10^{-5} mol of Ia had reacted. A sample of the gas phase (1.0 mL) was taken through a septum with a gas syringe and the H_2 determined by GC (after a preliminary calibration was made). The total H_2 formed was $(3.7 \pm 0.3) \times 10^{-5}$ mol.

For isotope analyses, a sample (0.05 g of Ia, Ib, or a mixture) was placed in a small reaction vessel (~ 10 mL) fitted with a stopcock, and the solvent CH_3CN (2 mL) was condensed into the vessel at 77 K under vacuum. The solution was warmed to room temperature and photolyzed as above. The vessel was then attached to the gas inlet system of the mass spectrometer, the solution was cooled to 77 K, and the gas phase was admitted to the mass spectrometer.

Quantum Yield Determinations. Irradiations were carried out with a Jasco CRM-FA Spectroirradiator equipped with a counter. The light used had wavelength centered at 362 nm (bandwidth 7 nm), and the light flux and counter were calibrated by using ferrioxalate actinometry.³⁰

In a typical experiment, a solution of Ia in MeCN (5 mL, 4.16×10^{-4} M) was degassed by three freeze-pump-thaw cycles, pumping each time to a residual pressure of 5×10^{-5} torr at 77 K. The solution was then flame sealed in a 1-cm quartz cuvette. The reaction was monitored by the change in optical density of the solution at 333 nm, since the greatest changes were observed at this wavelength. As a result, the experiments were not carried out in the usual way since less than 90% of the incident light at 362 nm was absorbed (Figure

1). After each irradiation the concentrations of both Ia and IIc were calculated from the absorbance at 333 nm. The average concentrations over the irradiation period and hence the percent light absorbed by each species were then calculated. Linear plots of [Ia] vs. quanta absorbed by Ia were obtained (correlation coefficients > 0.99), and the quantum yields were calculated from the slopes of these lines.

The quantum yields determined were 0.81 (Ia in MeCN), 0.45 (Ib in MeCN), 0.57 (Ia in pyridine), and 0.35 (Ib in pyridine).

Singlet Sensitization. In a typical experiment, a solution of Ia in MeCN (5 mL, 6.16×10^{-3} M) was added to triphenylene (0.0153 g). The IR spectrum of the resulting solution was recorded (NaCl plates, 1-mm pathlength) from 2200 to 2000 cm^{-1} . The sample contained in the IR cell was then irradiated with light from a Model UVS-11 Mineralight Lamp ($\lambda = 254$ nm) placed 5 cm from the sample. A 1-cm quartz cuvette containing aqueous KI (9.8×10^{-5} M)- I_2 (3.1×10^{-5} M) was used as a filter. After 5 min of irradiation, the IR spectrum (2200–2000 cm^{-1}) was recorded, and the above process was repeated three times. The extent of reaction was monitored from the changes in absorbance at 2098 cm^{-1} , corresponding to the maximum absorbance due to $\nu(\text{PtH})$ of Ia. The experiment was also carried out on the initial solution without triphenylene.

This procedure was repeated with a Pyrex plate interposed between the light source and the filter solution in order to remove the 254-nm line. Repeated determinations gave an estimate of the error to be attributed to light from the source with $\lambda > 300$ nm. Again, the solutions of Ia in MeCN both with and without triphenylene were studied.

Triplet Sensitization. Michler's ketone (0.040 g) was added to a solution of Ia in MeCN (5 mL, 1.61×10^{-3} M). The solution was then irradiated and the reaction monitored as for the singlet-sensitized reaction. No change in absorbance at 2098 cm^{-1} was detected on prolonged irradiation of the solution containing the ketone.

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Registry No. Ia, 63911-00-2; Ib, 82494-79-9; IIc, 79680-18-5; IID, 82482-55-1; MeCN, 75-05-8; H_2 , 1333-74-0; D_2 , 7782-39-0; HD, 13983-20-5; pyridine, 110-86-1; triphenylene, 217-59-4; Michler's ketone, 90-94-8.

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