

Picosecond Photolysis of a Metal Dihydride: Rapid Reductive Elimination of Dihydrogen from Ru(dmpe)₂H₂ (dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂)

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Irradiation of Ru(dmpe)₂H₂ (dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂) in cyclohexane solution with a picosecond pulsed laser at 300 nm leads to immediate formation of Ru(dmpe)₂ and H₂. The experiments show that metal–hydrogen bond cleavage, H–H bond formation, and rearrangement of the metal–phosphine skeleton occur within the instrument rise time of ca. 16 ps. A partial decay of the transient with a rate constant of 2.5 × 10⁹ s⁻¹ is also observed. The transient spectral data obtained for the short- and long-lived transients are similar.

Introduction

The development of ultrafast laser systems has prompted new questions about the first steps in photochemical and photophysical processes. The primary events observed following picosecond laser irradiation of coordination compounds include the formation of charge-transfer excited states, CO dissociation from transition-metal carbonyls and haem proteins, and the breaking of metal–metal bonds.^{2–12} A further photoprocess frequently observed in steady-state experiments is the reductive elimination of H₂ from transition-metal dihydride complexes.¹³ Here we report the first study of such a reaction on the picosecond time scale. The reaction in question, the elimination of H₂ from Ru(dmpe)₂H₂ [dmpe = (CH₃)₂PCH₂CH₂P(CH₃)₂], has already been studied by time-resolved spectroscopy on longer time scales and by matrix isolation in our laboratory and by steady-state methods elsewhere.^{14,15}

Steady-state photolysis experiments with deuterium labeling indicate that elimination of dihydrogen is concerted.¹⁵ Nanosecond laser flash photolysis (308 nm, ca. 5-ns pulse width) on Ru(dmpe)₂H₂ in dry degassed arene or alkane solution resulted in a transient formed within 30 ns, the response time of the setup.¹⁶ The transient exhibited an intense three-band visible absorption spectrum (λ_{max} at 467, 555, and 745 nm in cyclohexane; see Figure 1) and decayed via second-order kinetics.¹⁴ The second-order rate constant for reaction of the transient with H₂ is 6 × 10⁹ dm³ mol⁻¹ s⁻¹, close to the diffusion limit for cyclohexane, thus indicating that there is negligible barrier to recombination with H₂. On the basis of the above findings and the observation of the same species in low-temperature matrices, the transient was assigned as Ru(dmpe)₂ in its electronic ground state. The spectral evidence is most consistent with a D_{2h} square-planar system.

The nanosecond experiments showed that Ru(dmpe)₂ is a suitable system for studying hydrogen loss using picosecond UV/vis absorption spectroscopy. The Ru(dmpe)₂ fragment has a distinctive and relatively intense absorption spectrum. It is formed in a high quantum yield (0.85 ± 0.05) as measured by transient actinometry.¹⁷ Moreover, when Ru(dmpe)₂H₂ is irradiated under an atmosphere of dihydrogen, the reaction is completely reversible. It is calculated that under 1 atm of hydrogen (the conditions used in the picosecond experiments) the transient lifetime (k⁻¹) is 39 ns. The formation of Ru(dmpe)₂ (Scheme 1) involves the cleavage of two metal–hydrogen bonds, the formation of one H–H bond, and the rearrangement of the four metal–phosphorus bonds into the square-planar geometry. We now report picosecond experiments designed to determine the time scale of the reductive elimination process and to identify any reaction intermediates or excited states.

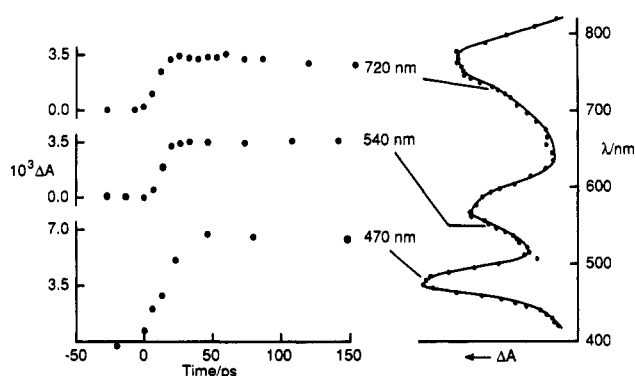
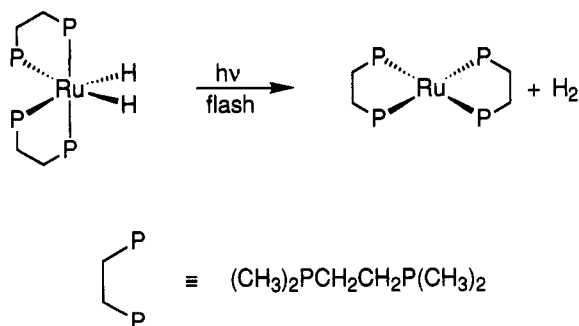


Figure 1. Transient signals following laser flash photolysis of Ru(dmpe)₂H₂ in cyclohexane solution under 1 atm of hydrogen at 300 K monitored at 470, 540, and 720 nm over a 150-ps time scale (left). The signals rise within 16 ps, the response time of the setup. The detection wavelengths for the picosecond traces (left) are mapped onto the transient UV/vis spectrum of Ru(dmpe)₂ obtained 400 ns after laser flash photolysis (308 nm) of Ru(dmpe)₂H₂ in cyclohexane solution under 1 atm of argon at 300 K (right).

SCHEME 1: Photoreductive Elimination of Dihydrogen from Ru(dmpe)₂H₂



Experimental Section

The experiments which were carried out at the Laser Support Facility in the Rutherford Appleton Laboratories involved a standard “pump–probe” setup described elsewhere.¹⁸ The 300-nm, 5-Hz pump pulse was generated by frequency doubling the output from a Nd:YAG pumped dye laser. It was attenuated to 2 μJ by passing through a 0.2-mm iris, giving an energy density of 6.4 mJ cm⁻². The pulse length was ca. 8 ps measured using a rapid scanning autocorrelator assuming a sech² pulse profile. The sample was probed one wavelength at a time with light from a white light continuum which was selected by the appropriate interference filter with a bandwidth of 10 nm. The change in

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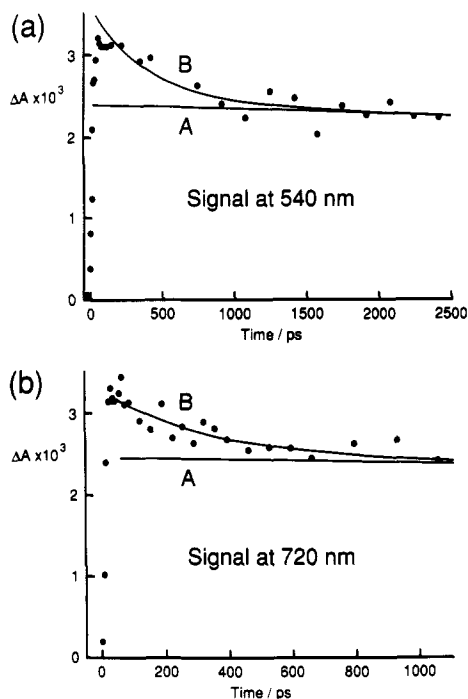


Figure 2. Comparison of the calculated and experimental decays at 540 nm (a) and 720 nm (b). The points represent the experimental data while the calculated exponential decay due to the reaction of $\text{Ru}(\text{dmpe})_2$ with H_2 (rate constant $2.56 \times 10^7 \text{ s}^{-1}$) is shown as line A. Line B is the trace due to the superposition of the decay corresponding to the reaction with H_2 and a faster component with a rate constant of $2.5 \times 10^9 \text{ s}^{-1}$ for the signal at 540 nm (a) and a rate constant of $3 \times 10^9 \text{ s}^{-1}$ for the signal at 720 nm (b).

transmission was measured at a series of time delays set from an optical delay line. Two photodiodes were used to record both the sample and reference signal concurrently. The reference sample was irradiated by the probe beam only. Identical sample and reference solutions of $\text{Ru}(\text{dmpe})_2\text{H}_2$ in dry degassed cyclohexane were prepared in 1-mm quartz cuvettes under an atmosphere of H_2 . The solutions had an absorbance of approximately 1 at the pump wavelength, 300 nm.

Results and Discussion

The 300-nm photolysis resulted in a response-time-limited rise (16 ps) in absorbance at 470, 540, and 720 nm; the signal at 470 nm had approximately twice the intensity of the latter two (Figure 1). No rise in absorbance over the initial 20 ps was observed at 500 and 610 nm, consistent with the presence of two troughs between three peak maxima. Furthermore, the signal at 540 nm showed a ca. 16% decay in 4 ns. Since the response varied linearly with pump energy density over the range $1.3\text{--}27 \text{ mJ cm}^{-2}$, the events must result from single photon absorption. These preliminary observations are consistent with the absorption spectrum and kinetics of $\text{Ru}(\text{dmpe})_2$ discussed earlier.

Although the decay kinetics of the transient over 4 ns closely resemble those anticipated for the recombination of $\text{Ru}(\text{dmpe})_2$ with H_2 , there was also evidence of a much faster process occurring at short time delays. Figure 2a shows the data points for the rise and decay at 540 nm over the first 2.6 ns. Overlaid on these points are two solid lines; line A represents the exponential decay due to the reaction with H_2 ($[\text{H}_2] = 3.8 \times 10^{-3} \text{ mol dm}^{-3}$ in cyclohexane under 1 atm of H_2), and line B represents the sum of this decay and a second faster component with a rate constant of $2.5 \times 10^9 \text{ s}^{-1}$.¹⁹ The trace recorded at 720 nm (Figure 2b) also exhibited evidence for a faster decay with a rate constant of $3 \times 10^9 \text{ s}^{-1}$. The fast rate constants are identical within experimental error.

At this stage there is no unambiguous assignment of the short-lived transient. However, the data obtained does enable us to

make some informed deductions. (1) We have been able to exclude the possibility that the fast decay arises from rotation of the photofragment, since the relative polarization of pump and probe beams has no effect on the kinetics.²⁰ (2) State correlation diagrams indicate that expulsion of H_2 from $d^6 \text{ML}_4\text{H}_2$ complexes should generate ML_4 in an electronic excited state, either singlet or triplet.²¹ However, the spectral data of the fast transient and the long-lived species are very similar. It is unlikely that such a similarity would be observed if the fast decay was caused by conversion between electronic states. Therefore, we would assign both the short- and long-lived transient to $\text{Ru}(\text{dmpe})_2$ in its electronic ground state. (3) Consideration of photon energies and bond strengths indicates that the photoproducts must be formed with substantial internal energy. The 300-nm pump pulses correspond to an energy of 397 kJ mol^{-1} . Belt et al. have recently measured the bond dissociation energy of the Ru–H bond in $\text{Ru}(\text{dmpe})_2\text{H}_2$ by photoacoustic calorimetry as 259 kJ mol^{-1} .¹⁷ Taking the H–H bond energy as 436 kJ mol^{-1} , the excess energy in the nascent photofragments can be calculated as 315 kJ mol^{-1} .²² The rate of geminate recombination may be limited by the rate of vibrational relaxation (i.e., dissipation of excess energy). The above findings indicate that the data are most compatible with the rapid decay arising from vibrational relaxation and any associated geminate recombination, even though we would have expected these processes to be faster.

Conclusions

The principal conclusion is that loss of H_2 from $\text{Ru}(\text{dmpe})_2\text{H}_2$ and distortion of $\text{Ru}(\text{dmpe})_2$ into its equilibrium geometry is a very fast process occurring within 16 ps of laser excitation. The resulting signal exhibits a fast decay, ca. 400 ps, superimposed on the normal recombination with H_2 . Further investigations into these processes are required. Such studies depend on obtaining high-quality time-resolved spectra: an appropriate apparatus is under construction.

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References and Notes

- (1) (a) University of York. (b) Rutherford Appleton Laboratories.
- (2) Doorn, S. K.; Dyer, R. B.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 6398.
- (3) Simon, J. D.; Peters, K. S. *Chem. Phys. Lett.* **1983**, *98*, 53. Xie, X.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 1130.
- (4) Wang, L.; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 8695.
- (5) Sprague, J. R.; Arrivo, S. M.; Spears, K. G. *J. Phys. Chem.* **1991**, *95*, 10528.
- (6) Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 8963.
- (7) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876.
- (8) Yu, S.-C.; Xu, X.; Lingle, R.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668.
- (9) Shank, C. V.; Ippen, E. P.; Bersohn, R. *Science* **1976**, *193*, 50.
- (10) Terner, J.; Strong, J. D.; Spiro, T. G.; Nagumo, M.; Nical, M.; El-Sayed, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1313.
- (11) Martin, J. L.; Migus, A.; Poyart, C.; Lecarpentier, Y.; Astier, R.; Antonetti, A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 173.
- (12) Zang, J. Z.; Harris, C. B. *J. Chem. Phys.* **1991**, *95*, 4024.
- (13) Anfinrud, P. A.; Han, C.-H.; Lian, T.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 574.
- (14) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.
- (15) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425.
- (16) Traverso, O.; Bergamini, P.; Sostero, S. *J. Organomet. Chem.* **1986**, *299*, C11.
- (17) $\text{Ru}(\text{dmpe})_2\text{H}_2$ has an absorption maximum at 210 nm, $\epsilon = 4900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, and a shoulder at 260 nm in pentane solution.
- (18) Belt, S. T.; Scaiano, J. C.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1993**, *115*, 1921.
- (19) Wilkinson, F.; Worall, D.; McGarvey, D.; Goodwin, A.; Langley, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2385.
- (20) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.
- (21) Baran, J.; Langley, A. J.; Jones, W. J. *Chem. Phys.* **1984**, *87*, 305.
- (22) Veillard, A. *Photoprocesses in Transition Metal Complexes, Bio-systems and Other Molecules. Experiment and Theory*; Kochanski, E., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.
- (23) Herzberg, G. *J. Mol. Spectrosc.* **1970**, *73*, 1.