

# ULTRAFAST PHOTODISSOCIATION OF HYDROGEN FROM $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$ : A TIME-RESOLVED INFRARED STUDY

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Microsecond and picosecond time-resolved infrared studies of  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  have demonstrated that reductive elimination of  $\text{H}_2$  is complete within 5 ps of UV photolysis.

*Keywords:* Time-resolved infrared spectroscopy; ultrafast; photodissociation; reductive elimination; organometallic photochemistry; hydrogen

## INTRODUCTION

The reductive elimination of  $\text{H}_2$  or other small molecules from organometallics is a general route to coordinatively unsaturated intermediates which are highly reactive and capable of undergoing a range of oxidative reactions [1]. This class of reaction has been less well studied than that of CO elimination, and the aim of this study was to use time-resolved infrared (TRIR) spectroscopy to study the reductive elimination of  $\text{H}_2$  from  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  [2].

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## RESULTS AND DISCUSSION

The UV-visible spectrum of  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  comprises a strong band in the UV, with a shoulder at ca. 320 nm, and the IR spectrum comprises a single, medium intensity band in the  $\nu(\text{CO})$  region at  $1940\text{ cm}^{-1}$ .

Microsecond TRIR studies were performed on  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  in benzene- $\text{d}_6$ . The sample was photolysed in the UV at 355 or 308 nm, and single-shot transient kinetics were obtained using the IR output of a diode laser and an MCT detector. The sample was contained in a closed flow system, under 1 atm of  $\text{H}_2$  to ensure reversibility. The TRIR spectrum obtained 10  $\mu\text{s}$  after photolysis was found to comprise one band at  $1940\text{ cm}^{-1}$  arising from bleaching of the precursor absorption, and two bands at 1845 and  $1973\text{ cm}^{-1}$  arising from photoproducts. The TRIR signal at  $1940\text{ cm}^{-1}$  was found to rise with the instrument response function and to recover partially (20%) with a pseudo first-order rate constant of  $1.2 \times 10^5\text{ s}^{-1}$ . The new band at  $1845\text{ cm}^{-1}$  also rose instantly and decayed with a rate constant of  $2.0 \times 10^5\text{ s}^{-1}$ .

The new band at  $1845\text{ cm}^{-1}$  is downshifted by  $95\text{ cm}^{-1}$  from that of the precursor. This decrease in  $\nu(\text{CO})$  is characteristic of an increase in back-bonding, arising from an increase in electron density at the metal centre, and therefore is indicative of a change in oxidation state of the metal. Hence, the  $1845\text{ cm}^{-1}$  band is assigned to the Ru(0) species,  $\text{Ru}(\text{PPh}_3)_3(\text{CO})$ , produced on loss of  $\text{H}_2$  from the Ru(II) precursor,  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$ .

Picosecond TRIR studies were performed on a similar sample of  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  in benzene- $\text{d}_6$ , under 1 atm of  $\text{H}_2$ . The sample was photolysed at 304 nm (5 ps pulses), and transient kinetics were obtained using the IR output of CO or diode lasers and upconversion detection [3]. The TRIR spectrum obtained 25 ps after photolysis was found to comprise one band at  $1940\text{ cm}^{-1}$  arising from bleaching of the precursor absorption, and one band at  $1841\text{ cm}^{-1}$  arising from the  $\text{Ru}(\text{PPh}_3)_3(\text{CO})$  fragment. No features were observed at  $2050\text{--}1950\text{ cm}^{-1}$ . The TRIR signals obtained at 1941 and  $1843\text{ cm}^{-1}$  were found to rise with the instrument response function and then to remain constant at  $\leq 2\text{ ns}$ , showing that reductive elimination of  $\text{H}_2$  from  $\text{Ru}(\text{PPh}_3)_3(\text{CO})(\text{H})_2$  is complete in  $< 5\text{ ps}$ . The photochemical scheme is summarized in Figure 1.

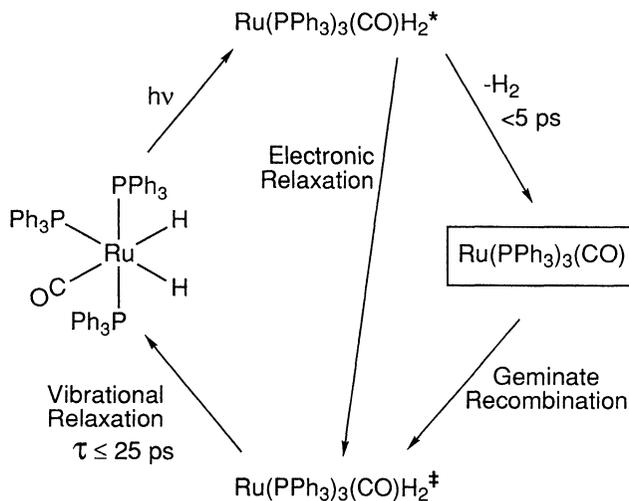


FIGURE 1 Photochemical scheme for  $\text{Ru(PPh}_3)_3(\text{CO})(\text{H})_2$ .

## CONCLUSION

This is the first example of the TRIR study of this general reaction class on the ultrafast timescale, and it establishes unequivocally that a metal dihydride complex undergoes  $\text{H}_2$  photodissociation in  $< 10^{-11}$  s.

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### References

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