DALTON
COMMUNICATION

Ultrafast reductive elimination of hydrogen from a metal carbonyl dihydride complex; a study by time-resolved IR and visible spectroscopy †

Mirco Colombo,[a] Michael W. George,[b] John N. Moore,[a] David I. Pattison,[a] Robin N. Perutz,*[,a] Ian G. Virrels[b] and Tian-Qing Ye[a]

[a] *Department of Chemistry, University of York, York, UK YO1 5DD*
[b] *Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD*

Laser flash photolysis of $[Ru(PPh_3)_3(CO)(H)_2]$ **1** in benzene solution yielded transient $[Ru(PPh_3)_3(CO)]$ which was observed by both microsecond UV/VIS and IR spectroscopy [$\lambda_{max} = 380$ nm, $\nu(CO) = 1845$ cm^{-1}] and reacted with H_2 to reform **1** [$k_2 = (8.4 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}]; photolysis of **1** with an ultrafast laser equipped with IR detection demonstrates that reductive elimination of H_2 and formation of $[Ru(PPh_3)_3(CO)]$ is complete within 6 ps.

Reductive elimination of hydrogen and the reverse reaction, oxidative addition, occupy fundamental positions in transition-metal chemistry. When initiated thermally, such reactions play a crucial role in catalysis. However, it is often the photo-induced reactions which offer a gateway to mechanistic studies, since numerous metal dihydride complexes undergo reductive elimination of hydrogen on ultraviolet irradiation.[1–5] When placed under a hydrogen atmosphere, the photoproduct may react back with hydrogen to regenerate the precursor [equation (1)].[3–5] We have used flash photolysis with UV/VIS detection to

$$[M]H_2 \underset{k_2}{\overset{h\nu}{\rightleftarrows}} [M] + H_2 \qquad (1)$$

observe the primary photoproducts, [M], and to determine the kinetics of the back reaction with hydrogen, notably with $[Ru(drpe)_2]$ (drpe = $R_2PCH_2CH_2PR_2$, dmpe when R = Me, depe when R = Et, *etc.*).[3–5] Such measurements are made with typical ‘nanosecond apparatus’ with an instrumental risetime of *ca.* 50 ns. It is invariably found that formation of the 16-electron transient is complete within the risetime. The early steps of the photochemical reaction, including formation of excited state(s), M−H bond breaking, H−H bond making and rearrangement of the MP_4 skeleton to its new equilibrium geometry must occur within this time.

Ultrafast spectroscopy (time-scale 10^{-13}–10^{-9} s) offers the opportunity of studying the early stages of reaction but is less straightforward and requires very different equipment. In our first investigation of reductive elimination on the picosecond time-scale, we irradiated $[Ru(dmpe)_2H_2]$ with an ultrafast laser and followed the transient UV/VIS absorption over time.[6] We obtained evidence that reductive elimination was already complete *ca.* 16 ps after the laser pulse, but these experiments were confined to a few probe wavelengths and were limited by the lack of conclusive evidence of oxidation states from UV/VIS spectroscopy.

In this communication, we report ultrafast experiments on a related metal carbonyl dihydride complex in which we have followed the reaction from excitation to 2000 ps after the laser pulse by time-resolved infrared (TRIR) spectroscopy using the CO stretching vibration as a reporter.[7] These experiments form the first application of ultrafast IR spectroscopy to study reductive elimination, and provide conclusive evidence that reductive elimination is complete within 6 ps.

Our precursor, $[Ru(PPh_3)_3(CO)(H)_2]$ **1**, has been shown to lose H_2 upon photolysis in steady-state experiments.[8] It is of particular interest because it catalyses insertion of alkenes into C−H bonds at unsaturated carbon (alkene or aromatic) in a β-position relative to a carbonyl group.[9–11] In one of the putative reaction mechanisms, the thermal reaction is initiated by hydrogenation of the alkene to form $[Ru(PPh_3)_3(CO)]$, the same intermediate as would be expected to form upon photolysis.[9]

The white precursor **1** is soluble in benzene and exhibits a shoulder at 325 nm ($\varepsilon \approx 9000$ dm^3 mol^{-1} cm^{-1}) in its UV/VIS absorption spectrum and a $\nu(CO)$ band at 1939 cm^{-1}. On laser flash photolysis‡ (instrumental risetime *ca.* 50 ns), a conspicuous transient is observed with $\lambda_{max} \approx 380$ nm [Fig. 1(*a*)]. The transient decays with pseudo-first-order kinetics ($k_{obs} = 3 \times 10^3$ s^{-1}) under an argon atmosphere. The rate constant increases linearly with concentration of dissolved hydrogen [Fig. 1(*b*)]. The slope of this plot yields the second-order rate constant for reaction of the transient with H_2 in benzene of $(8.4 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}. Transient absorption experiments with **1** dissolved under 1 atm H_2 in tetrahydrofuran (thf) yield a comparable value of k_{obs} (2.1×10^5 s^{-1}) to the experiments with benzene as solvent (2.5×10^5 s^{-1}).‡

Similar experiments were performed with **1** dissolved in C_6D_6 under H_2, but with IR detection.§ A spectrum measured 1 μs after the laser flash revealed loss of precursor at 1940 cm^{-1} and

---

† *Non-SI unit employed*: atm = 101 325 Pa.

‡ [**1**] typically *ca.* 10^{-4} mol dm^{-3} in C_6H_6, 10 mm pathlength, laser at 308 nm, pulse energy at sample *ca.* 5 mJ. Samples were degassed by freeze–pump–thaw methods and H_2–Ar gas mixtures admitted with a total pressure of 1 atm. One measurement was made at higher pressure of H_2, *viz.* 3.2 atm. No significant change in the rate constant under 1 atm H_2 was found when C_6H_6 solvent was replaced by C_6D_6, nor when the concentration of **1** was increased to 5×10^{-4} and 1×10^{-3} mol dm^{-3} (2 and 1 mm pathlengths, respectively). The concentration of dissolved hydrogen was taken as 2.85×10^{-3} mol dm^{-3} atm^{-1}.[12a] The solubility of H_2 in thf has not been documented, but is *ca.* 6×10^{-3} mol dm^{-3} atm^{-1} in Et_2O.[12b] The value derived for the rate constant for reaction of the transient with H_2 in thf is *ca.* 3.6×10^7 dm^3 mol^{-1} s^{-1}.

§ Pump laser at 355 or 308 nm, detection with diode IR laser, sample 2×10^{-3} or 3×10^{-3} mol dm^{-3} dissolved in C_6D_6 (for IR transparency) under 1 atm hydrogen and flowed through an IR cell (CaF_2 windows, 1 mm pathlength) within a closed circulating system (glass with PTFE connections and stainless steel micropump). Notice that the kinetics were sometimes monitored away from the band maxima, in order to use the optimum laser output. The instrument was set up to maximise the signal-to-noise ratio, such that the risetime was *ca.* 500 ns.

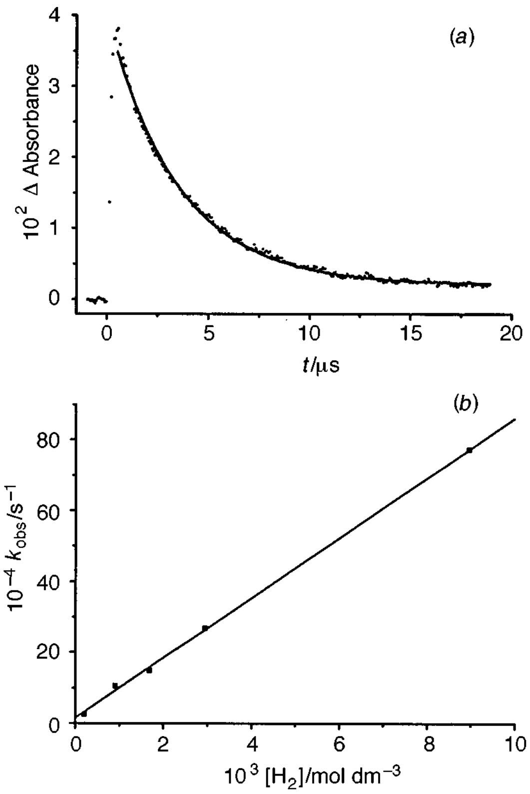


Fig. 1 (*a*) Transient absorption, monitored at 410 nm, following laser flash photolysis (λ_{ex} = 308 nm) of **1** dissolved in benzene under 1 atm H_2; (●) experimental points, (—) exponential fit. (*b*) Plot of the variation of k_{obs} *vs.* concentration of dissolved hydrogen. The slope yields the second-order rate constant for reaction of $[Ru(PPh_3)_3(CO)]$ with hydrogen to reform **1**

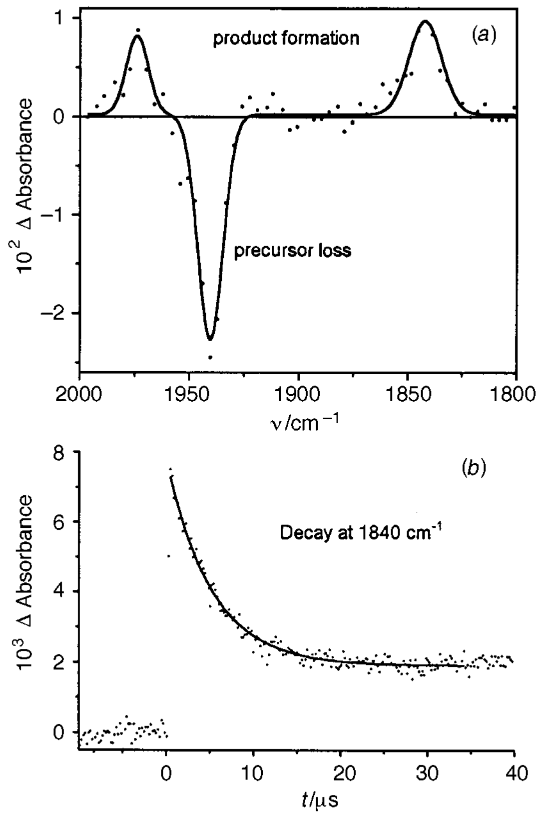
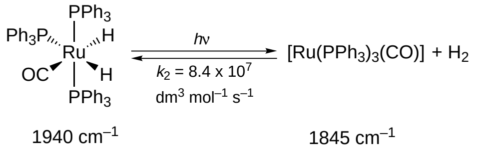


Fig. 2 Microsecond TRIR spectrum recorded 1 μs after laser flash photolysis (λ_{ex} = 355 nm) of **1** dissolved in C_6D_6 under 1 atm H_2. The negative feature is due to bleach of **1**, the positive features are due to photoproducts. (*b*) Microsecond kinetics of the lower wavenumber product band monitored at 1840 cm^{-1} (λ_{ex} = 308 nm)



Scheme 1 Photochemical reactions of complex **1**

formation of product bands with maxima at 1845 and 1974 cm^{-1} [Fig. 2(*a*)]. The kinetics of the first product band were monitored at 1840 cm^{-1}; the band rose within the risetime of the instrument and decayed to about 30% of its initial absorbance with first-order kinetics with a rate constant, k_{obs}, of 2.0×10^5 s^{-1} [Fig. 2(*b*)]. The same value of k_{obs} was obtained at two concentrations of **1** and is consistent with the kinetics from the UV experiments. The second transient band at 1973 cm^{-1} showed a significant risetime of *ca.* 5 μs with rate constants for growth dependent on [**1**] and did not show any subsequent decay over 50 μs.¶ The bleach signal at 1940 cm^{-1} recovered partially (to *ca.* 80% of initial change in absorbance).

The transient species with λ_{max} at 380 nm and ν(CO) at 1845 cm^{-1} is assigned unequivocally as $[Ru(PPh_3)_3(CO)]$ on the basis of its rapid rise, the kinetics of its reaction with H_2, the partial recovery of starting material and the position of the IR band (Scheme 1). The very large shift of *ca.* 100 cm^{-1} in ν(CO) from Ru^{II} in **1** to Ru^0 in $[Ru(PPh_3)_3(CO)]$ is consistent with shifts recently determined for related ruthenium complexes in matrices.[13,14] The lack of kinetic stabilisation by thf provides no support for solvent co-ordination to $[Ru(PPh_3)_3(CO)]$. The co-ordination geometry at ruthenium in $[Ru(PPh_3)_3(CO)]$ cannot be determined from these experiments. In contrast, the relative intensity of the ν(CO) bands provides bond angle information for $[Ru(CO)_2(dmpe)]$.[14] The long-lived species with ν(CO) at 1973 cm^{-1} must be a secondary dinuclear product since it rose relatively slowly with kinetics dependent on [**1**].

The photolysis of **1** has also been monitored by TRIR spectroscopy on the picosecond time-scale.|| An IR spectrum measured 25 ps after the laser pulse revealed two features: a negative peak at 1940 ± 3 cm^{-1} corresponding to the loss of the precursor and a positive peak at 1843 ± 3 cm^{-1} corresponding to formation of $[Ru(PPh_3)_3(CO)]$. No other bands were observed between 1800 and 2050 cm^{-1}. A kinetic trace measured at 1843 cm^{-1} showed a very fast rise and decay within the instrumental response function of *ca.* 6 ps. After this initial period, the signal maintained its amplitude over 2 ns [Fig. 3(*a*)]. The very fast decay corresponds to the solvent response, since a positive signal with these kinetics was observed at all wavenumbers for the solvent alone. The long-lived signal arises from $[Ru(PPh_3)_3(CO)]$; curve fitting shows that this signal appeared within *ca.* 6 ps and remained constant [Fig. 3(*a*)]. A kinetic trace measured at 1941 cm^{-1} showed that the bleaching signal of **1** also rose within 6 ps and remained steady for the succeeding 2 ns [Fig. 3(*b*)]; again, a signal was observed which decayed with the instrument response function.

¶ The observed rate constants for the growth of the 1973 cm^{-1} band were 6.8×10^5 s^{-1} and 9.3×10^5 s^{-1} at [**1**] = 2×10^{-3} and 3×10^{-3} mol dm^{-3}, respectively. The kinetics of the bleach at 1940 cm^{-1} could be fitted satisfactorily to a model comprising a finite rise and a competing decay component corresponding to the rate constants of the two product bands.

|| Ultrafast setup;[7] pump pulses at 304 nm of 4 ps full width at half maximum (6 ps autocorrelation time) duration and 1.05 kHz repetition rate, pulse energy *ca.* 1–2 μJ. IR absorption was measured with a CO laser (1800–1960 cm^{-1} at 4 cm^{-1} intervals) or with a diode laser (1965–2050 cm^{-1}) *via* a detection system employing upconversion. The solutions were handled in the same flow system as for the microsecond experiments, but with a faster flow rate. Complex **1** (*ca.* 10^{-3} mol dm^{-3}) dissolved in C_6D_6 under 1 atm H_2. IR cell of pathlength 1 mm giving an absorbance *ca.* 1 at the pump wavelength and *ca.* 0.3 at 1940 cm^{-1}.

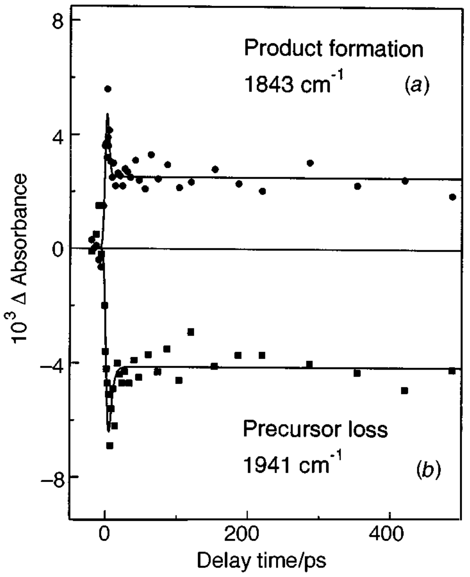


Fig. 3 Ultrafast TRIR kinetics following laser photolysis of **1** dissolved in C_6D_6 under 1 atm H_2 ($\lambda_{ex} = 304$ nm, laser pulse duration = 4 ps) (*a*) at 1843 cm^{-1} showing formation of [Ru(PPh$_3$)$_3$(CO)] (●), (*b*) at 1941 cm^{-1} showing bleaching of **1** (■). The very fast component in both traces lasting *ca.* 6 ps lies within the instrumental response function

Ultrafast experiments on binary metal carbonyls usually show the absorptions of metal carbonyls in *vibrational* excited states of the electronic ground state which decay over tens or hundreds of picoseconds.[15] The vibrational excitation is detected through broadening and shifts in the ν(CO) bands. However, [Ru(PPh$_3$)$_3$(CO)] shows no signs of vibrational relaxation although the photon energy absorbed by **1** greatly exceeds the energy needed to break the bonds, just as when photodissociating CO from metal carbonyls. When expelling CO, the CO bond length is altered little, so the CO carries away relatively little vibrational energy leaving much of the excess of energy in the photoproduct. When H_2 is dissociated from a metal dihydride, the H···H distance is necessarily compressed with the result that much of the excess of energy may be removed by vibrational excitation of expelled H_2 (*cf.* CH_2O).[16] Almost all of the excess of energy would be removed if H_2 leaves in its v = 7 state.** In reality, some of the excess of energy will go into rotation of H_2 and translation of the photofragments, as well as vibrations of [Ru(PPh$_3$)$_3$(CO)]. However, the lack of observable vibrational relaxation of [Ru(PPh$_3$)$_3$(CO)] is understandable.

The ultrafast experiments provide unambiguous evidence for removal of **1** and formation of [Ru(PPh$_3$)$_3$(CO)] within the experimental time-scale. The use of IR detection has removed any possibility that the signals are due to excited states of precursor or photoproducts. We conclude that photoelimination of H_2 from **1** is a process in which H–H bond formation, Ru–H bond cleavage and any reorganisation of the co-ordination geometry at ruthenium occur within 6 ps.

Acknowledgements

We are grateful to EPSRC for support for equipment, studentships and an Advanced Fellowship (to J. N. M.). We also acknowledge the support of the European Commission and British Gas.

References

1 M. Berry, K. Elmitt, M. L. H. Green and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1979, 1950; P. Grebenik, R. Grinter and R. N. Perutz, *Chem. Soc. Rev.*, 1988, **17**, 453.
2 W. D. Jones and F. J. Feher, *Acc. Chem. Res.*, 1989, **22**, 91; R. M. Chin, L. Dong, S. B. Duckett, M. G. Partridge, W. D. Jones and R. N. Perutz, *ibid.*, 1993, **115**, 7685; A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929; J. M. Buchanan, J. M. Stryker and R. G. Bergman, *ibid.*, 1986, **108**, 1537; B. M. Sponsler, B. H. Weiller, P. O. Stoutland and R. G. Bergman, *ibid.*, 1989, **111**, 6841; P. E. Bloyce, A. J. Rest and I. Whitwell, *J. Chem. Soc., Dalton Trans.*, 1990, 813; M. G. Partridge, A. McCamley and R. N. Perutz, *ibid.*, 1994, 3519; W. A. Kiel, R. G. Ball and W. A. G. Graham, *J. Organomet. Chem.*, 1990, **383**, 481; S. A. Brough, C. Hall, A. McCamley, R. N. Perutz, S. Stahl, U. Wecker and H. Werner, *ibid.*, 1995, **504**, 33; H. Azizian and R. H. Morris, *Inorg. Chem.*, 1983, **22**, 6.
3 R. N. Perutz, *Chem. Soc. Rev.*, 1993, 361; R. Osman, D. I. Pattison, R. N. Perutz, C. Bianchini and M. Peruzzini, *J. Chem. Soc., Chem. Commun.*, 1994, 513.
4 L. Cronin, M. C. Nicasio, R. N. Perutz, R. G. Peters, D. M. Roddick and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1995, **117**, 10 047.
5 C. Hall, W. D. Jones, R. J. Mawby, R. Osman, R. N. Perutz and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1992, **114**, 7425.
6 R. Osman, R. N. Perutz, A. D. Rooney and A. J. Langley, *J. Phys. Chem.*, 1994, **98**, 3562.
7 T. Q. Ye, C. J. Arnold, D. I. Pattison, C. L. Anderton, D. Dukic, R. N. Perutz, R. E. Hester and J. N. Moore, *Appl. Spectrosc.*, 1996, **50**, 597.
8 G. L. Geoffroy and M. G. Bradley, *Inorg. Chem.*, 1977, **16**, 744.
9 F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 62 and refs. therein.
10 M. Sonoda, F. Kakiuchi, A. Kamatani and S. Murai, *Chem. Lett.*, 1996, 109.
11 B. M. Trost, K. Imi and I. W. Davies, *J. Am. Chem. Soc.*, 1995, **117**, 5371; F. Kakiuchi, Y. Tanaka, T. Sato, N. Chatani and S. Murai, *Chem. Lett.*, 1995, 679.
12 (*a*) E. Wilhelm and R. Battino, *Chem. Rev.*, 1973, **73**, 1; (*b*) P. G. T. Fogg and W. Gerrard, *Solubility of Gases in Liquids*, Wiley, Chichester, 1991.
13 R. J. Mawby, R. N. Perutz and M. K. Whittlesey, *Organometallics*, 1995, **14**, 3268.
14 M. K. Whittlesey, R. N. Perutz, I. G. Virrels and M. W. George, *Organometallics*, 1997, **16**, 268.
15 M. Lee and C. B. Harris, *J. Am. Chem. Soc.*, 1989, **111**, 8963; J. C. King, J. Z. Zhang, B. J. Schwartz and C. B. Harris, *J. Chem. Phys.*, 1993, **99**, 7595; T. P. Dougherty and E. J. Heilweil, *Chem. Phys. Lett.*, 1994, **227**, 19; S. M. Arrivo, T. P. Dougherty, W. T. Grubbs and E. J. Heilweil, *Chem. Phys. Lett.*, 1995, **235**, 247.
16 C. B. Moore, *Ann. Rev. Phys. Chem.*, 1983, **34**, 525.
17 S. T. Belt, J. C. Scaiano and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1993, **115**, 1921.
18 G. Herzberg and L. L. Howe, *Can. J. Phys.*, 1959, **37**, 636.

Received 25*th June* 1997; *Communication* 7/04484D

** At 304 nm, $h\nu = 393$ kJ mol^{-1}. Enthalpy[17] of [Ru(dmpe)$_2$H$_2$] $\longrightarrow$ [Ru(dmpe)$_2$] + H_2 = 95 kJ mol^{-1}. If enthalpy change for **1** $\longrightarrow$ [Ru(PPh$_3$)$_3$(CO)] + H_2 is the same, excess of energy = 298 kJ mol^{-1}. Energy of H_2 (v = 7) ≈ 290 kJ mol^{-1}.[18]