ChemComm

Two photochemical pathways in competition: matrix isolation, time-resolved and NMR studies of *cis*-$[Ru(PMe_3)_4(H)_2]$†

Virginia Montiel-Palma,[a] Robin N. Perutz,*[a] Michael W. George,[b] Omar S. Jina[b] and Sylviane Sabo-Etienne[c]

[a] *University of York, Heslington, York, UK YO10 5DD. E-mail: rnp1@york.ac.uk*
[b] *University of Nottingham, University Park, Nottingham, UK NG7 2RD*
[c] *Laboratoire de Chimie de Coordination du C. N. R. S., 205 Route de Narbonne, 31077 Toulouse Cedex 04, France*

Received (in Basel, Switzerland) 20th March 2000, Accepted 8th May 2000

***cis*-$[Ru(PMe_3)_4(H)_2]$ (1) reacts by two distinct photochemical pathways resulting in the formation of $[Ru(PMe_3)_4]$ and $[Ru(PMe_3)_3(H)_2]$; derivatives of these intermediates are generated in the presence of CO and Ph_2SiH_2.**

Photochemical loss of H_2 from *cis*-metal dihydride complexes is a general phenomenon widely employed to generate reactive unsaturated species.[1] We have demonstrated by laser flash photolysis, matrix isolation and steady state photolysis of the complexes $[Ru(R_2PCH_2CH_2PR_2)_2H_2]$ (R = Me, Et, Ph, C_2F_5) that irradiation induces efficient loss of H_2 and formation of square-planar $[Ru(R_2PCH_2CH_2PR_2)_2]$ intermediates.[2] It is therefore puzzling that UV irradiation of *cis*-$[Ru(PMe_3)_4(H)_2]$ (**1**) in the presence of R_3SiH (R = Me, Ph) results in quantitative loss of PMe_3 and formation of $[Ru(PMe_3)_3(SiR_3)(H)_3]$.[3,4] Here we present an investigation of the low-temperature matrix, transient-solution and steady-state photochemistry of **1**. We show that the reaction with R_3SiH creates the illusion of a single pathway. Our evidence reveals two photochemical pathways involving 16-electron intermediates, one gives rise to $[Ru(PMe_3)_4]$ (**2**) and the other to $[Ru(PMe_3)_3(H)_2]$ (**3**).

When **1** was irradiated under CO in $[^2H_6]$benzene (or $[^2H_8]$toluene), two monocarbonyls *cis, mer*-$[Ru(PMe_3)_3(CO)(H)_2]$ (**4**)[5] and $[Ru(PMe_3)_4(CO)]$ (**5**)[6] and two dicarbonyls $[Ru(PMe_3)_2(CO)_2(H)_2]$ (**6**)[7] and $[Ru(PMe_3)_3(CO)_2]$ (**7**),[8,9] were identified by their characteristic ^1H and ^{31}P NMR as well as their solution IR spectra (ESI†). The number of CO groups in each species was counted *via* the ^{31}P NMR spectrum with ^{13}CO labelled material.[10] The identity of the products obtained by steady-state solution photolysis suggests the occurrence of photochemical loss of H_2 in competition with the loss of PMe_3 established previously.[3,4] In order to test this hypothesis, we turned to matrix isolation in conjunction with time-resolved spectroscopy in solution.

Complex **1** was isolated in an Ar matrix at 12 K.[11] After UV irradiation (17 min, $273 < \lambda < 400$ nm), the originally colourless matrix turned purple and the area of the ν(Ru–H) bands (1820 cm^{-1}) decreased by 11%. A weak new band in the ν(Ru–H) region was observed at *ca.* 1790 cm^{-1}. The UV–VIS spectrum showed new bands at 543 and *ca.* 304 nm (Fig. 1). Subsequent selective photolysis ($\lambda > 520$ nm) depleted the principal initial photoproduct leaving bands of another species with λ_{max} = 503, *ca.* 610 nm. UV irradiation ($273 < \lambda < 400$ nm, 30 min) of **1** in an Ar + 1.5% CO matrix, resulted in new bands in the ν(CO) region assigned to **4**, **5** and **7** (Table 1, ESI†).

Laser flash photolysis (308 nm)[12] of **1** in cyclohexane solution under argon generated a transient within the instrumental response time, which decayed by second order kinetics ($k_2/\varepsilon l = 2.9 \times 10^5\ s^{-1}$). The spectrum under 400 Torr of H_2 recorded by this method ($\lambda_{max} = 550 \pm 5$ nm) greatly resembled the one obtained after photolysis in inert matrices (Fig. 1). The transient reacted with a variety of reagents giving pseudo-first order rate constants which varied linearly with the concentration of added quencher (Fig. S1, ESI†). The resulting second order rate constants are: $k(CO) = (8.9 \pm 0.4) \times 10^8 > k(H_2) = (5.6 \pm 0.4) \times 10^8 > k(Et_2SiH_2) = (2.2 \pm 0.1) \times 10^7 > k(PMe_3) = (1.1 \pm 0.1) \times 10^6 > k(Et_3SiH) = (2.8 \pm 0.1) \times 10^5 > k(PEt_3) = (2.7 \pm 0.8) \times 10^5 > k(C_2H_4) = (1.8 \pm 0.1) \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$.[13]

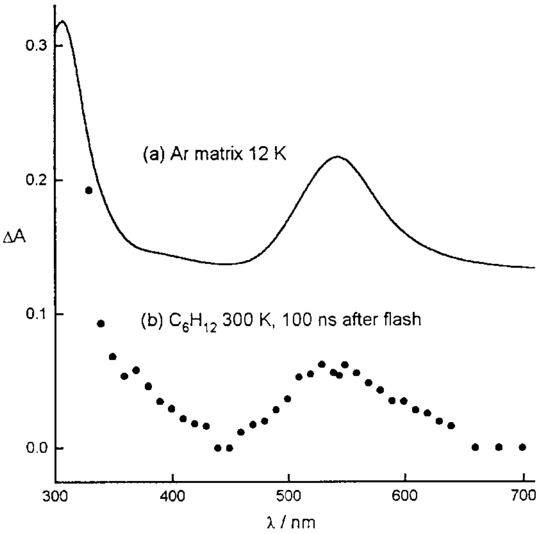

Fig. 1 (*a*) UV–VIS spectrum following photolysis of **1** in an argon matrix at 12 K (17 min, $273 < \lambda < 400$ nm). (*b*) Point-by-point transient spectrum at 300 K measured 100 ns after laser flash photolysis (308 nm) of **1** in cyclohexane under 400 Torr H_2.

When the decay of the transient generated under H_2 was complete, no net change in absorbance was observed at any wavelength from 350 to 800 nm. In contrast, a high net change in absorbance at 350 nm in the presence of PMe_3 (< 0.1 mol dm^{-3}) implicated a longer-lived photoproduct.[14] This behaviour can be understood if the extinction coefficient in the visible region of **2** greatly exceeds that of **3**. The principal transient species observed by UV–VIS spectroscopy is then **2**. Reaction of **2** with H_2 would regenerate **1**, while treatment with PMe_3 would result in $[Ru(PMe_3)_5]$ (probably unstable).

Further kinetic information was obtained by time-resolved infrared (TRIR) spectroscopy. A cyclohexane solution of **1** under CO was irradiated with a pulsed laser (266 nm) and the IR spectrum measured in a point-by-point fashion.[15] The TRIR spectrum showed a well-defined band at 1929 cm^{-1} due to **4** (Fig. 2). The second order rate constant for formation of **4** was determined [p(CO) = 150 to 760 Torr] as $k_2 = (5.1 \pm 0.6) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$. Since this value is about 17 times smaller than the rate constant for reaction of the UV–VIS transient with CO (see above), we postulate that **2** is the only transient *observable* by flash photolysis with UV–VIS detection.[16]

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† Electronic supplementary information (ESI) available: IR spectral data for **4**–**7** (Table 1) and kinetic data (Fig. S1). See http://www.rsc.org/suppdata/cc/b0/b002297g/

DOI: 10.1039/b002297g

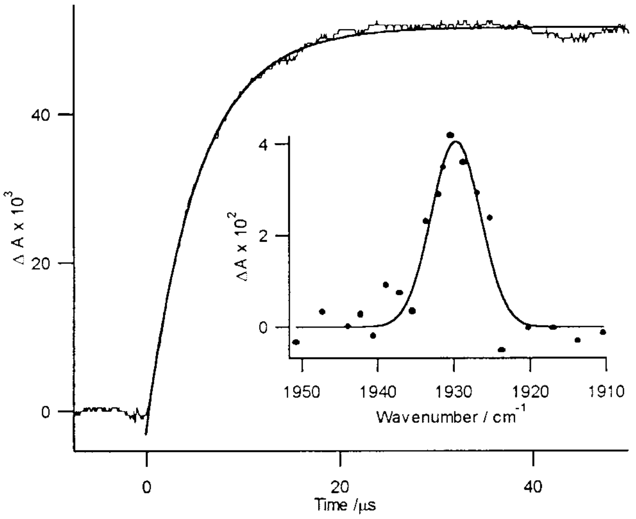
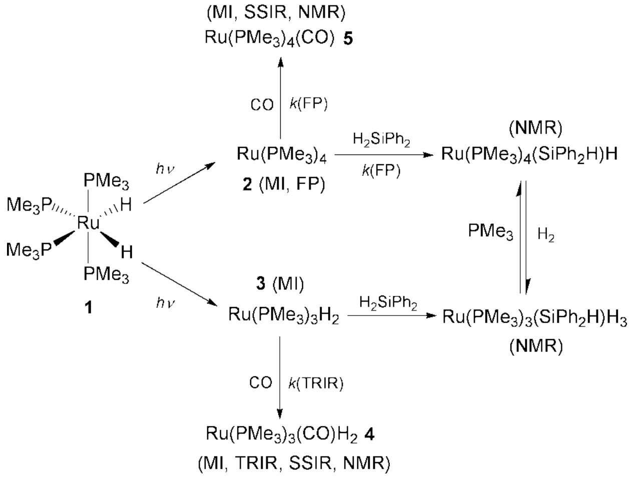


Fig. 2 Growth of ν(CO) band at 1929 cm^{-1} of **4** measured by TRIR spectroscopy after flash photolysis (266 nm) of **1** in cyclohexane under 300 Torr CO. Inset shows partial spectrum 23 μs after flash.

At this stage, we knew that laser flash photolysis of **1** generates **2** which reacts with Et$_3$SiH, presumably to give [Ru(PMe$_3$)$_4$(SiEt$_3$)H]. In apparent contradiction, steady state photolysis of **1** with Me$_3$SiH or Ph$_3$SiH only gives [Ru(PMe$_3$)$_3$(SiR$_3$)(H)$_3$] (R = Me, Ph), derived from loss of PMe$_3$.[3,4] We therefore investigated the products of irradiating **1** with silanes by NMR spectroscopy. Low temperature photolysis in [^{2}H$_8$]toluene at 195 K in the presence of HSiMe$_3$ or HSiEt$_3$ generated the trihydrides but did not reveal the anticipated H$_2$-loss products. Reasoning that silanes with a smaller cone angle would stabilise [Ru(PMe$_3$)$_4$(SiR$_3$)H], we irradiated **1** in the presence of dihydridosilanes. Photolysis of **1** with Ph$_2$SiH$_2$ yielded *cis*-[Ru(PMe$_3$)$_4$(SiPh$_2$H)H] and [Ru(PMe$_3$)$_3$(SiPh$_2$H)(H)$_3$][17] with an initial ratio of quantum yields of *ca.* 1:4.5 respectively.[18] Similar results were obtained with Et$_2$SiH$_2$, HSi(OMe)$_2$(allyl) and HSiMe$_2$(allyl).

Our evidence from a variety of methods now provides a consistent view of the photochemistry of **1** (Scheme 1). Two photochemical pathways act in competition: loss of PMe$_3$ occurs with a quantum yield *ca.* 4.5 times that for loss of H$_2$ in solution. We postulate that the H$_2$-loss products, *cis*-[Ru(PMe$_3$)$_4$(SiR$_3$)H], are generated initially with all silanes, but if the silane is bulky (R = Me, Et, Ph), these products are labile and are converted to [Ru(PMe$_3$)$_3$(SiR$_3$)(H)$_3$]. Rapid displacement of PMe$_3$ by H$_2$ from *cis*-[Ru(PMe$_3$)$_4$(SiR$_3$)H] has also been observed by Berry.[19] Competitive photodissociation of dihydrogen and phosphine has been encountered in the tetrahydride system [Os(H)$_4$(PMe$_2$Ph)$_3$],[20] but H$_2$ photodissociation is the sole pathway in [Ir(η^5-C$_5$Me$_5$)(PMe$_3$)(H)$_2$].[21]



Scheme 1 The photoreactivity of **1** showing the reactions of the primary photoproducts with CO and Ph$_2$SiH$_2$. The methods employed for detection are indicated: MI = matrix isolation, FP = flash photolysis, TRIR = time resolved IR, SSIR = IR spectroscopy following steady-state irradiation and NMR = NMR spectroscopy following steady-state irradiation.

We are grateful for support from CONACYT (México), ORS Awards, The British Council-Alliance Programme and to Professor D. H. Berry, Dr J. N. Moore and Dr S. B. Duckett for helpful discussions.

Notes and references

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2 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.

3 (*a*) D. H. Berry and L. J. Procopio, *J. Am. Chem. Soc.*, 1991, **113**, 8627; (*b*) J. A. Reichl and D. H. Berry, *Adv. Organomet. Chem.*, 1998, **43**, 197.

4 M. J. Burn and R. G. Bergman, *J. Organomet. Chem.*, 1994, **472**, 43.

5 W. Kohlmann and H. A. Werner, *Naturforsch, Teil B*, 1993, **48**, 1499 ($\nu_{(CO)}$ of **4** (C$_6$H$_6$) = 1940 cm^{-1} is inconsistent with our measurements).

6 **5**: ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 300 K): δ −10.1 (s). IR ν(^{13}CO) (C$_6$D$_6$): 1760 cm^{-1}.

7 R. J. Mawby, R. N. Perutz and M. K. Whittlesey, *Organometallics*, 1995, **14**, 3268.

8 R. Boese, W. B. Tolman and K. P. C. Vollhardt, *Organometallics*, 1986, **5**, 582. Note that **7** adopts a fluxional C_{2v} structure.[9]

9 M. Ogasawara, F. Maseras, N. Gallego-Planas, K. Kawamura, K. Ito, K. Toyota, W. E. Streib, S. Komiya, O. Eisenstein and K. G. Caulton, *Organometallics*, 1997, **16**, 1979.

10 ^{31}P{^{1}H} NMR (121.5 MHz, [^{2}H$_8$]toluene, 300 K). [Ru(PMe$_3$)$_3$(^{13}CO)(H)$_2$]: δ 1.0 (dd, $^2J_{PP}$ 25.4 and $^2J_{PC}$ 10.5 Hz), δ −9.3 (td, $^2J_{PP}$ 24.7 and $^2J_{PC}$ 9 Hz); [Ru(PMe$_3$)$_2$(^{13}CO)$_2$(H)$_2$]: δ −0.8 (t, $^2J_{PC}$ 9.5 Hz); [Ru(PMe$_3$)$_3$(^{13}CO)$_2$]: δ −4.3 (t, $^2J_{PC}$ 8.4 Hz); [Ru(PMe$_3$)$_4$(^{13}CO)]: δ −9.8 (d, $^2J_{PC}$ 2.9 Hz).

11 Compound **1** was sublimed at 328 K and cocondensed with argon onto a window cooled to 20 K. The matrix was cooled to 12 K, see D. M. Haddleton, A. McCamley and R. N. Perutz, *J. Am. Chem. Soc.*, 1988 **110**, 1810.

12 Laser flash photolysis experiments were performed using a XeCl excimer laser (λ_{exc} = 308 nm, pulse width *ca.* 50 ns).[2]

13 E. Wilhelm and R. Battino, *Chem. Rev.*, 1973, **73**, 1. The solubilities of CO, H$_2$ and C$_2$H$_4$ in cyclohexane were taken as 9.3×10^{-3}, 3.8×10^{-3} and 1.4×10^{-1} mol dm^{-3} atm^{-1} respectively. Errors in rate constants are quoted to 95% confidence limits.

14 The rate constant for reaction with PMe$_3$ did not vary significantly with the wavelength of measurement.

15 Nd:YAG laser (λ_{exc} = 266 nm, detection with diode IR laser, CaF$_2$ windows, 1 mm pathlength), see M. W. George, M. Poliakoff and J. J. Turner, *Analyst*, 1994, **119**, 551.

16 The detection of the ν(CO) band of **5** by TRIR spectroscopy proved difficult due to overlap with the Ru–H stretching mode of **1** and its low IR extinction coefficient. To our surprise, bands were observed at 1828 and 1881 cm^{-1} (rise time < 1 μs) which correspond to the multiple substitution product **7** even when using an open-flow system. They were confirmed to result from a single-photon process. This species may be derived from hot **2** (full details will be published elsewhere).

17 Selected NMR data [^{2}H$_8$]toluene, 294 K. [Ru(PMe$_3$)$_4$H(SiPh$_2$H)] ^{1}H NMR (400.1 MHz): δ −10.3 (dq, 1 H, $^2J_{HP}$ 67, 22.5 Hz, RuH), 5.9 (tt, 1H, $^3J_{PH}$ 14.6, 4.7 Hz, SiPh$_2$H). ^{31}P NMR (162 MHz): ABX$_2$ δ -0.1 (m, $^2J_{PP}$ 25, 23.7 Hz, X$_2$), −10.2 (m, $^2J_{PP}$ 25, 16 Hz, A) and −10.7 (m, $^2J_{PP}$ 25, 16 Hz, B. [Ru(PMe$_3$)$_3$(H)$_3$(SiPh$_2$H)] ^{1}H NMR: δ −9.5 (m, 3 H, RuH$_3$), 6.7 (m, 1 H, SiPh$_2$*H*). ^{31}P NMR: δ −10.4 (br s) J_{SiH} by ^{29}Si filtered ^{1}H{^{31}P} spectroscopy: 64.5 Hz.

18 Relative quantum yields were calculated from the integrations of the dangling Si–H protons of both products in the ^{1}H NMR spectra recorded after short photolysis times in the presence of 3 equiv. of silane. On more prolonged photolysis, the ratio of the yields approaches unity, as a result of thermal/photochemical interconversion of the products.

19 (*a*) D. H. Berry, personal communication; V. K. Dioumaev, K. Plössl, P. J. Carroll and D. H. Berry, *J. Am. Chem. Soc.*, 1999, **121**, 8391; (*b*) We further tested this hypothesis by placing a 1:1 solution of *cis*-[Ru(PMe$_3$)$_4$(SiPh$_2$H)H] and [Ru(PMe$_3$)$_3$(SiPh$_2$H)(H)$_3$] under dihydrogen and heating to 80 °C. After 2 h the ratio of the products changed to 1:3.9 respectively.

20 J. W. Bruno, J. C. Huffman, M. A. Green, J. D. Zubkowski, W. E. Hatfield and K. G. Caulton, *Organometallics*, 1990, **9**, 2556.

21 A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154.