Photochemistry of $Ru(etp)(CO)H_2$ (etp = $PhP(CH_2CH_2PPh_2)_2$): Fast Oxidative Addition and Coordination Following Exclusive Dihydrogen Loss

Virginia Montiel-Palma,[†] David I. Pattison,[‡] Robin N. Perutz,*[,‡] and Claire Turner[‡]

Department of Chemistry, University of York, York, YO10 5DD, U.K., and Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, Col Chamilpa, Cuernavaca, Morelos, 62210 México

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The photochemistry of $Ru(etp)(CO)H_2$ (**1**, etp = $PhP(CH_2CH_2PPh_2)_2$) has been studied by UV/vis spectroscopy following nanosecond laser flash photolysis and by NMR and IR spectroscopy following steady-state irradiation. Steady-state irradiation under CO, C_2H_4, and Et_3SiH yields $Ru(etp)(CO)_2$, $Ru(etp)(CO)(C_2H_4)$, and $Ru(etp)(CO)(SiEt_3)H$, respectively. Laser flash photolysis (laser wavelength 308 nm) of **1** in cyclohexane generates the 16-electron transient Ru(etp)(CO). In the absence of additional ligands, Ru(etp)(CO) decays by reaction with photoejected dihydrogen, regenerating **1**. When flash photolysis was performed in the presence of added ligands, the transient decays by pseudo-first-order kinetics with second-order rate constants on the order of 10^8 dm^3 mol^{-1} s^{-1}. However, the fastest reaction rate (H_2) is only a factor of ca. 4 greater than the slowest (Et_3SiH). Activation parameters for the reaction of **1** with Et_3SiH were determined as $\Delta G_{298}{}^{\ddagger} = 25.7 \pm 0.1$ kJ mol^{-1}, $\Delta H^{\ddagger} = 11 \pm 1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -49 \pm 4$ J mol^{-1} K^{-1}. The evidence from the UV/vis spectrum of the transient and from the structures of the stable photoproducts indicates that Ru(etp)(CO) adopts a nonplanar geometry.

Introduction

Multidentate phosphines are widely employed as ligands in catalysis because of their ability to control the coordination number and molecular geometry of the complex. The multiple binding sites also may prevent complete dissociation of the phosphine, which leads to deactivation of the catalyst.[1,2] Transition metal complexes of polyphosphines have attracted attention as catalysts in homogeneous reactions[3] such as the hydrogenation,[4−7] hydroformylation, and isomerization of alkenes[5−7] and the functionalization, hydroamination, and polymerization of alkynes.[8,9]

In previous papers, we reported the photochemistry of a series of iron and ruthenium phosphine dihydride complexes and showed that the reactivity of the photogenerated 16-electron intermediate is strongly dependent on the nature of the phosphine.[10,11b] For instance, $Ru(PP_3)$ [PP_3 = $P(CH_2CH_2PPh_2)_3$] reacts rapidly with benzene, whereas $Ru(dppe)_2$ (dppe = $Ph_2CH_2CH_2PPh_2$) shows no sign of such a C−H activation reaction. In these systems, the switch from a tetradentate to a bidentate phosphine alters the reactivity substantially, although the phenyl substituent at phosphorus and the ethane backbone are retained. The most extreme reactivity toward dihydrogen or CO is observed with $Ru(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[11] The behavior of the complex $Ru(PMe_3)_4(H)_2$ contrasts with the reactivity of the other complexes that we have studied in this series. This complex is the only one to exhibit two photochemical pathways, one involving loss of H_2, the other loss of phosphine.[12]

The introduction of a CO group into the ligand sphere introduces a very useful structural reporter through the CO-stretching vibration. It also raises the possibility of photochemical loss of CO competing with loss of H_2. It has long been known that $Ru(PPh_3)_3(CO)H_2$ undergoes selective photodissociation of H_2,[13] a feature we exploited to show that H_2 photodissociation occurs within ca. 10^{-11} s of the initial laser flash.[14] Since our studies of $Ru(PPh_3)_3(CO)H_2$ were hampered by its lack of

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[†] Universidad Autónoma del Estado de Morelos.

[‡] University of York.

(1) Osborn, J. A.; Young, J. F.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1965**, 17.

(2) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239.

(3) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramírez, J. A. *Organometallics* **1990**, *9*, 226.

(4) Dubois, D. L.; Meek, D. W. *Inorg. Chim. Acta* **1976**, *19*, L29.

(5) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

(6) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 210.

(7) Bianchini, C.; Laschi, F.; Meli, A.; Peruzzini, M.; Zanello, P.; Frediani, P. *Organometallics* **1988**, *7*, 2575.

(8) Bianchini, C.; Frediani, P.; Meli, A.; Vizza, F.; Peruzzini, M.; Zanobini, F. *Organometallics* **1989**, *8*, 2080.

(9) Muller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y.-K. *Organometallics* **2000**, *19*, 170.

(10) Whittlesey, M. K.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Field, L. D.; Wilkinson, M. P.; George, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 8627.

(11) (a) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425. (b) Cronin, L.; Nicasio, M. C.; Perutz, R. N.; Peters, R. G.; Roddick, D. M.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1995**, *117*, 10047.

(12) Montiel-Palma, V.; Perutz, R. N.; George, M. W.; Jina, O. S.; Sabo-Etienne, S. *Chem. Commun.* **2000**, 1175.

(13) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744.

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solubility in alkane solvents, we sought an alternative ruthenium carbonyl phosphine dihydride complex for further experiments.

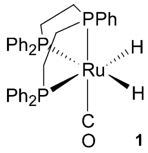
The work described in this paper concerns the photochemistry of Ru(etp)(CO)H_2 (**1**) (etp = [PhP($CH_2CH_2PPh_2$)$_2$])[15] in solution as studied by time-resolved and steady-state methods. In principle, the relatively constrained geometry of **1** should prevent a dimerization pathway analogous to that proposed for Ru(PPh_3)$_3$(CO)H_2.[14] The investigation by time-resolved UV/vis spectroscopy demonstrates that **1** undergoes reductive elimination of dihydrogen within the instrumental response time and establishes the rate constants for reaction of the transient Ru(etp)(CO). Studies by NMR and IR spectroscopy prove that only dihydrogen-loss products are generated when reactions are performed in the presence of ligands such as CO, C_2H_4, and Et_3SiH.

Results

1. Synthesis and Characterization of 1 and 2. The only report of complex **1** describes its synthesis by $NaBH_4$ reduction of Ru(etp)(CO)Cl_2.[15] We preferred to synthesize **1** by photolysis of Ru(etp)(CO)$_2$ (**2**) under dihydrogen. A saturated THF solution of **2**, synthesized according to literature methods,[16] was photolyzed with broad band UV radiation ($\lambda > 200$ nm) under a vigorous stream of dihydrogen. The reaction was monitored periodically by IR spectroscopy in the CO-stretching region until negligible starting material (**2**) remained.

The structure of **1** has been established previously:[15] the etp ligand coordinates facially on the octahedron with CO *trans* to the central phosphorus atom, generating a structure with C_s symmetry (see below). Other ruthenium complexes of etp also show a facial arrangement for the phosphine ligand.[17] Complex **1** is soluble in THF and to a lesser extent in benzene and toluene; in THF it exhibits a carbonyl band in the IR spectrum at 1938 cm^{-1}. Its $^{31}P\{^1H\}$ NMR spectrum is characteristic of an AX_2 spin system, with a triplet at δ 105.5 and a doublet at δ 69.1 ($^2J_{PP}$ 16.2 Hz). The ^1H NMR spectrum shows a hydride resonance as a symmetrical second-order multiplet centered at δ −8.02, indicative of the presence of a mirror plane. We employed the software *gNMR* to estimate the coupling constants as *cis* $^2J_{PH}$ −16.5 and −22.0 and *trans* $^2J_{PH}$ 67.0 and $^2J_{HH}$ 3.3 Hz.[18] Relevant NMR data are listed in Table 1. Complex **1** is a pale yellow solid; its UV/vis spectrum shows an absorption that increases into the UV with a resolved shoulder at 300 nm.

The IR spectrum of **2** shows bands of almost equal relative intensity at 1948 and 1884 cm^{-1} in THF. The $^{31}P\{^1H\}$ NMR spectrum in [$^2H_8$]-THF displays a doublet at δ 76.4 and a triplet at δ 190 with coupling constants ($^2J_{PP}$) of 32 Hz. The IR relative intensities were used to calculate an angle between the carbonyl groups of 92°.[19] The most likely structure of **2** is shown below.



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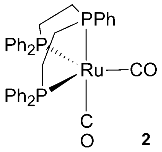

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Table 1. Principal NMR Data δ (multiplicity, J/Hz) in [$^2H_8$]-THF

complex, temp/K	^1H	$^{31}P^a$
1, 300 K	−8.06 (m, see text, hydride)	105.5 (t, $^2J_{PP} = 16.2$, bridge) 69.1 (d, $^2J_{PP} = 16.2$, term)
2, 300 K		109.4 (t, $^2J_{PP} = 32.5$, bridge) 76.4 (d, $^2J_{PP} = 32.5$, term)
3, 286 K	0.71 (broad, C_2H_4) 1.47 (broad, C_2H_4)	97.5 (t, $^2J_{PP} = 25$, bridge) 74.6 (d, $^2J_{PP} = 25$, term)
4, 257 K	−8.00 (ddd, $^2J_{PH}$ 61.0, 21.8, 17.4, hydride)	94.3 (apparent t, $^2J_{PP}$ 17.2, bridge) 66.0 (d, 17.2 term) 62.1 (d, 17.2 term)

[a] Bridge = bridgehead phosphorus, term = terminal phosphorus.

2. Laser Flash Photolysis. We studied the photochemistry of **1** by laser flash photolysis in cyclohexane solution. At the laser wavelength of 308 nm, it has an absorption coefficient of 1.04×10^3 dm^3 mol^{-1} cm^{-1}.

a. Under Argon. A transient species was generated within the instrumental response time on laser flash photolysis ($\lambda_{exc} = 308$ nm) of **1** in cyclohexane at 295 K. A plot of ΔA^{-1} versus time was linear, consistent with second-order kinetics. The slope of the line yielded $k_2/\epsilon l = 7.28 \times 10^5$ s^{-1} where ΔA is the change in absorbance, k_2 is the second-order rate constant, ϵ is the molar absorption coefficient, and l is the path length (1 cm). Such behavior is typical of a photodissociation reaction that generates equal concentrations of transient and dissolved H_2 and is followed by thermal recombination.[11] At 390 nm, the original absorbance was not restored even after a period of hundreds of microseconds, indicating that the back-reaction was incomplete in that period and that permanent photoproducts may also have been formed. Nevertheless, the UV/vis spectrum recorded after flash photolysis (ca. 50 laser shots) was found to be essentially unchanged.

b. Transient Spectrum under H_2. The UV/vis transient spectrum was recorded under a partial pressure of dihydrogen (700 Torr) in order to ensure the reversibility of the system and prevent the buildup of any stable photoproducts. The spectrum measured point-by-point 200 ns after the flash from 800 to 360 nm shows increasing absorbance toward the UV with a maximum at 390 nm (Figure 1). This spectrum resembles those of species such as Ru(PPh_3)$_3$(CO)[14] and Fe(dmpe)$_2$,[10] which also show broad maxima in the near UV region.

c. Addition of Quenching Ligands. (i) Dihydrogen. Addition of a small pressure of dihydrogen caused an increase in the rate of decay of the transient species, which decayed obeying pseudo-first-order kinetics. When using partial pressures of H_2 > 600 Torr, no residual

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(14) Colombo, M.; George, M. W.; Moore, J. N.; Pattison, D. I.; Perutz, R. N.; Virrels, I. G.; Ye, T.-Q. *J. Chem. Soc., Dalton Trans.* **1997**, 2857.

(15) Michos, D.; Luo, X.-L. Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245.

(16) Jia, G.; Meek, D. W. *Inorg. Chim. Acta* **1990**, *178*, 195.

(17) (a) Delgado, G.; Rivera, A. V.; Suárez, T.; Fontal, B. *Inorg. Chim. Acta* **1995**, *233*, 145. (b) Sheldrick, W. S.; Brandt, K. *Inorg. Chim. Acta* **1994**, *217*, 51. (c) Albinati, A.; Jiang, Q. Z.; Ruegger, H.; Venanzi, L. M. *Inorg. Chem.* **1993**, *32*, 4940.

(18) Budzelaar, P. H. M. *g-NMR*, version 4; Cherwell Scientific Publishing Limited: Oxford, 1995−1997.

(19) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

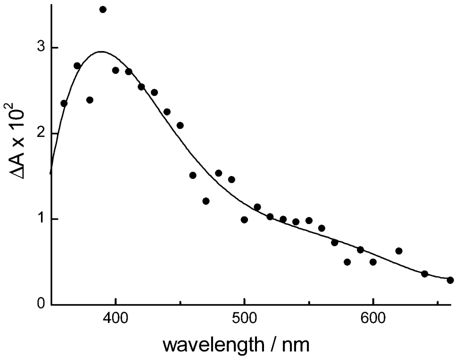

Figure 1. Point-by-point transient spectrum measured 100 ns after laser flash photolysis of Ru(etp)(CO)H_2 (**1**) in cyclohexane under 700 Torr of dihydrogen. The line is a fit to the points with a polynomial of order 6.

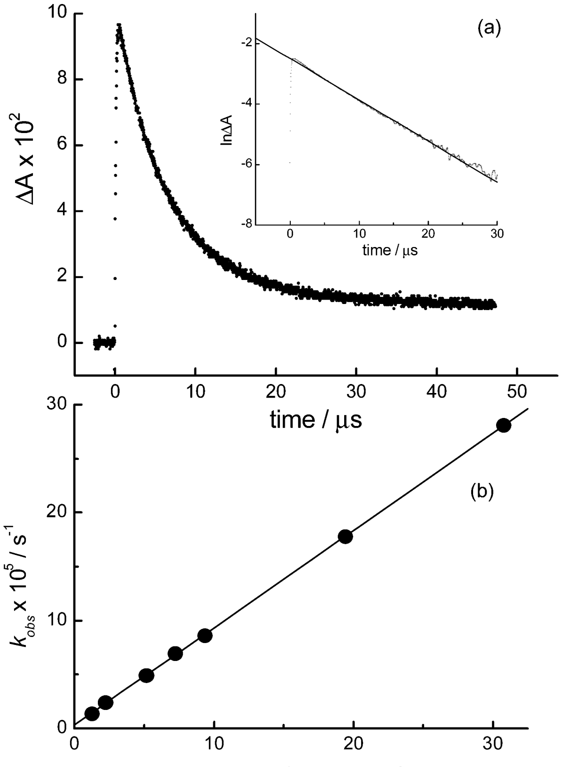

Figure 2. (a) Decay of the transient (monitoring wavelength, $\lambda = 390$ nm) generated upon laser flash photolysis (excitation wavelength, $\lambda = 308$ nm) of **1** in cyclohexane at 295 K under a partial pressure of 30 Torr of H_2. The inset plot shows the fitting to pseudo-first-order behavior. (b) Plot of k_{obs} versus concentration of dissolved H_2, yielding, from the slope, the second-order rate constant for reaction of the transient with added H_2.

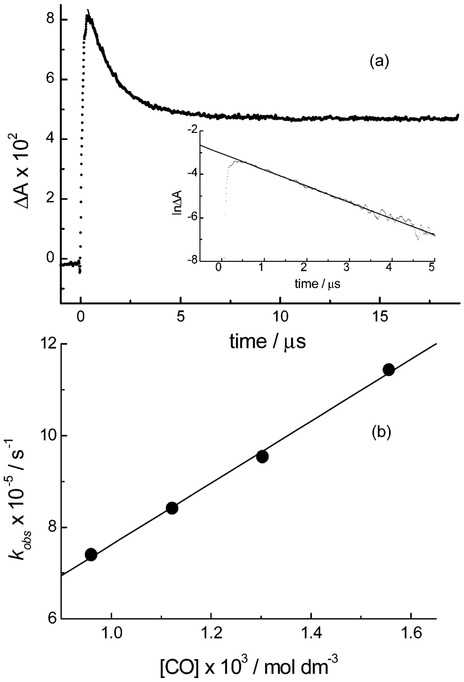

Figure 3. (a) Kinetic trace obtained upon flash photolysis of **1** in cyclohexane in the presence of CO (0.96×10^{-3} mol dm^{-3}). The inset plot shows the fitting to pseudo-first-order behavior. (b) Plot of k_{obs} versus [CO] ($\lambda_{exc} = 308$ nm, $\lambda_{mon} = 390$ nm).

Table 2. Second-Order Rate Constants for Reaction of Ru(etp)CO with Added Quenchers

quencher	k_2 ($dm^3\ mol^{-1}\ s^{-1}$)
H_2	$(9.0 \pm 0.1) \times 10^8$
C_2H_4	$(8.4 \pm 0.5) \times 10^8$
CO	$(6.8 \pm 0.8) \times 10^8$
Et_3SiH	$(2.1 \pm 0.5) \times 10^8$

change in absorbance remained at the end of the decay (Figure 2a). The rate of the reaction of the transient with dihydrogen was measured over a range of partial pressures of H_2 that corresponded to concentrations of dissolved dihydrogen from 1.3 to 19.4×10^{-4} mol dm^{-3}.[20] A plot of k_{obs} versus [H_2] was linear (Figure 2b) and gave a second-order rate constant $k_2 = (9.0 \pm 0.1) \times 10^8$ dm^3 mol^{-1} s^{-1}. No significant variation in the rate constant was found when monitoring at different wavelengths. Second-order rate constants are collected in Table 2.

(ii) Carbon Monoxide. When flash photolysis of a cyclohexane solution of **1** was carried out in the presence of dissolved CO and monitored at 390 nm, the kinetic data fitted pseudo-first-order behavior. The formation of a long-lived photoproduct was indicated by high residual absorbance, which increased to shorter wavelengths (Figure 3a). A plot of k_{obs} versus [CO] was linear (Figure 3b) and gave a second-order rate constant of $(6.8 \pm 0.8) \times 10^8$ dm^3 mol^{-1} s^{-1} at 390 nm; no significant variation was found when monitoring at other wavelengths.

(iii) Ethene and Triethylsilane. The reactions of the transient with ethene and triethylsilane were investigated at several wavelengths and with different concentrations of the added reagents. Addition of C_2H_4 or Et_3SiH to cyclohexane solutions of **1** resulted in quenching of the transient, which decayed over a period of microseconds. Plots of k_{obs} versus [quencher] showed linear dependence on the quencher concentration (Figure 4a). No significant variation in the rate constants was found in either case when monitoring at different wavelengths.

d. Activation Parameters for Reaction with Et_3SiH. Pulsed laser flash photolysis of **1** in cyclohexane in the presence of Et_3SiH (2.5×10^{-3} mol dm^{-3}) was carried out at seven different temperatures in the range

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[20] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. Gas solubilities in cyclohexane were taken as follows: H_2 (3.8×10^{-3} mol dm^{-3} atm^{-1}); CO (9.3×10^{-3} mol dm^{-3} atm^{-1}); ethene (1.4×10^{-1} mol dm^{-3} atm^{-1}).

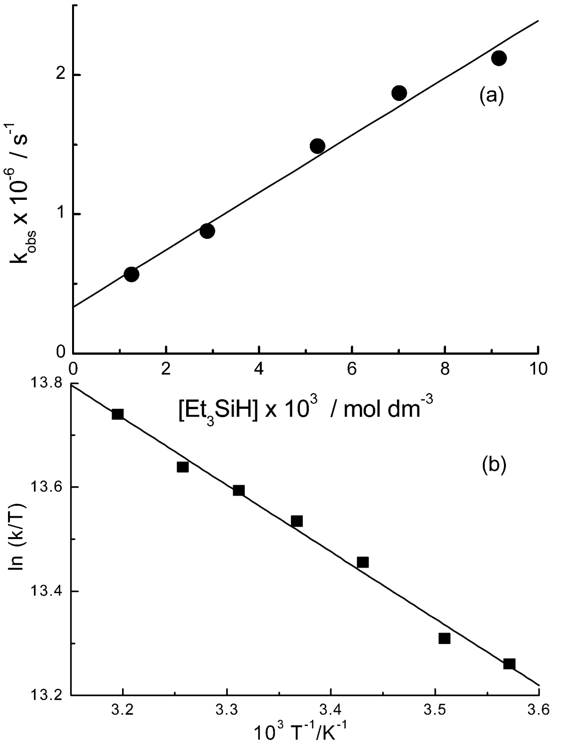


Figure 4. (a) Plot of k_{obs} versus [Et_3SiH] ($\lambda_{exc} = 308$ nm, $\lambda_{mon} = 390$ nm). (b) Eyring plot showing the temperature variation of the second-order rate constant for reaction with Et_3SiH.

Table 3. Temperature Dependence of Second-Order Rate Constant for Reaction of Ru(etp)CO with Et$_3$SiH

T (K)	k_2 (10^8 dm^3 mol^{-1} s^{-1})	T (K)	k_2 (10^8 dm^3 mol^{-1} s^{-1})
280	1.61	302	2.42
285	1.72	307	2.57
291.5	2.04	313	2.90
297	2.24		

280−313 K (Table 3). Plots of ln(k_2/T) against 1/T and ln k_2 versus 1/T were used to calculate the activation parameters for the formation of product Ru(etp)(CO)(H)(SiEt$_3$) from the intermediate (Figure 4b). The resulting parameters were determined as $\Delta G_{298}^{\ddagger} = 25.7 \pm 0.1$ kJ mol^{-1}, $\Delta H^{\ddagger} = 11 \pm 1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -49 \pm 4$ J mol^{-1} K^{-1}.

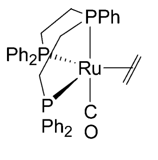
3. Steady-State Photolysis. The solution photochemistry of **1** was probed in order to interpret the results of the time-resolved experiments and identify the ultimate photoproducts.

a. Reaction with CO. A sample of **1** dissolved in [$^2H_8$]-THF was rigorously degassed and placed under an atmosphere of CO. The sample was irradiated ($\lambda >$ 290 nm) for 2 h, and IR and NMR spectra were acquired. The spectra allowed unambiguous assignment of the photoproduct as **2**.[16]

b. Reaction with C$_2$H$_4$. Complex **1** was found to react with ethene over a period of hours to yield Ru(etp)(CO)(C_2H_4) (**3**) quantitatively on irradiation ($\lambda >$ 290 nm) in THF. The reaction was followed conveniently by $^{31}P\{^1H\}$ NMR spectroscopy. Depletion of the resonances for **1** was accompanied by growth of a new triplet at δ 97.5 and a doublet at δ 74.6 ($^2J_{PP}$ 25 Hz), indicative of an AX_2 spin system. In the ^1H NMR spectrum measured at 286 K, new broad resonances were observed at δ 0.71 and 1.47, which sharpened at lower temperature (220 K, δ 0.59 and 1.43). The IR spectrum recorded in [$^2H_8$]-THF displays a strong carbonyl band at 1910 cm^{-1}. In marked contrast with Ru(dmpe)$_2$H$_2$ and Ru(depe)$_2$H$_2$, no hydride resonances attributable to vinyl hydride products were observed in the ^1H NMR spectrum.[10,11]

Insights into the geometry of **3** can be obtained from the ab initio calculations carried out by Ogasawara et al. on the model compound Ru(PH_3)$_4$(C_2H_4), which showed a preference for the ethene ligand to lie in the equatorial position due to stronger back-donation of the metal into its π^* orbital.[21,22] On the other hand, there is little energy difference between isomers of Ru(PH_3)$_4$(CO) having CO in axial or equatorial sites. The etp ligand is almost certain to adopt a facial geometry like the isoelectronic complexes [Co(etp)(CO)L]X (L = CO, P(OMe)$_3$, PPh$_2$H, PEt$_3$, PPh$_2$Me; X = BF$_4$, PF$_6$).[23] We therefore conclude that **3** probably adopts the structure shown below.

c. Reaction with Et$_3$SiH. Photolysis of **1** with $\lambda >$ 290 nm in the presence of 20 equiv of Et$_3$SiH yielded a new hydride multiplet centered at δ −8.00. Alternatively, the same product could be generated by photolysis of **3** in the presence of excess Et$_3$SiH in [$^2H_8$]-THF. The integrations of the resonances in the ^1H NMR spectrum are consistent with the formation of a product of the formula Ru(etp)(CO)(H)(SiEt$_3$) (**4**). The room-temperature $^{29}Si\{^1H\}$ NMR spectrum of **4** shows a doublet of triplets resonance at δ 18.1 with coupling constants $^2J_{SiP}$ 79.2 and 16.0 Hz. In the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature, complex **4** shows a triplet resonance at δ 94.3 with $^2J_{PP}$ 17.2 Hz and two broad signals at δ 66.0 and 62.1. At 257 K, the hydride resonance of the ^1H NMR spectrum resolves into a doublet of doublets of doublets ($^2J_{PH}$ = 61.0, 21.8, and 17.4 Hz), and the two highest field resonances (δ 66.0 and 62.1) in the $^{31}P\{^1H\}$ NMR spectrum resolve into doublets ($^2J_{PP}$ = 17.2 Hz). A selective heteronuclear decoupling experiment was also performed at 257 K. Decoupling of the ^{31}P signal at δ 49.3 removed a doublet coupling from the hydride multiplet in the ^1H NMR spectrum, leaving a doublet of doublets resonance with coupling constants 61.0 and 17.4 Hz. The retention of the large *trans* coupling indicated that the central phosphorus atom is not *trans* to the hydride. Decoupling of the other two phosphorus signals provided less precise information due to their proximity. However, the similarity of the chemical shift of the triplet resonance of the product in the $^{31}P\{^1H\}$ NMR spectrum when compared to that of **1** prompts us to postulate that the bridgehead phosphorus atom lies *trans* to CO. We also note that the fluxional behavior may be associated with an η^2-H-SiEt$_3$ intermediate that allows exchange of the two terminal phosphorus ligands. We therefore assign the structure of **4** as shown below.



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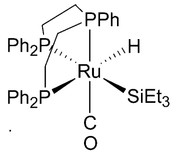

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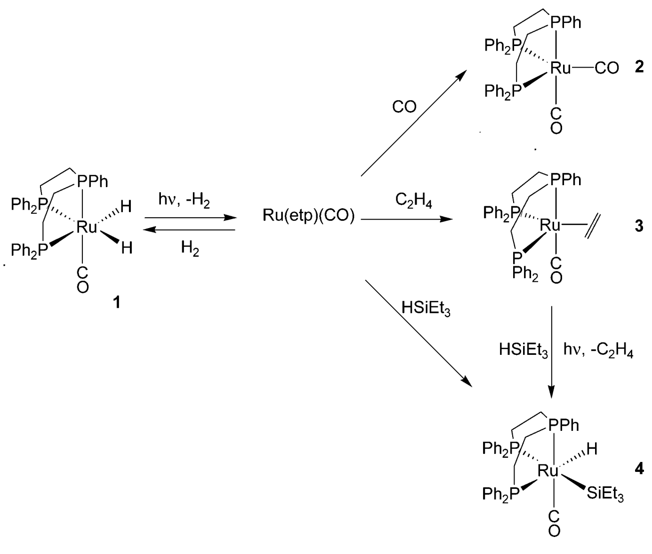
Scheme 1. Photochemical Reactions of Ru(etp)(CO)(H)$_2$ (1)



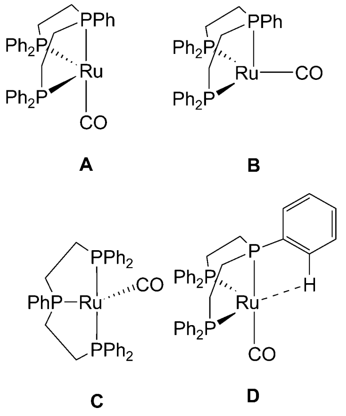
Discussion

The results from our investigations on the solution photochemistry of **1** are summarized in Scheme 1.

Flash Photolysis. Transient Identification and Structural Implications. The primary transient formed upon flash photolysis of **1** in cyclohexane solution is demonstrated from the following arguments to be 16-electron Ru(etp)(CO). First, reaction with H_2 (>600 Torr) results in complete regeneration of the dihydride precursor as indicated by the absence of residual absorbance. Second, the stable products formed upon steady-state photolysis all result from dihydrogen loss. Third, the transient reacts with other quenchers with second-order kinetics. The occurrence of a cyclometalation reaction with a phosphine phenyl group can be ruled out since it would result in first-order kinetics and the kinetics would be independent of added quenchers.

The UV/vis spectrum of the transient generated upon flash photolysis of **1** in cyclohexane shows a steadily increasing absorbance toward the UV with a maximum at 390 nm. The spectrum contrasts with the multiband UV/vis spectra of complexes Ru(dmpe)$_2$ and related square-planar complexes with two bidentate ligands.[11] However, it resembles the UV/vis spectra of fragments M(PP$_3$) (M = Ru, Os), which show broad maxima at 395 and 390 nm, respectively. In these cases, the constraint imposed by the PP$_3$ phosphine prevents the fragments from adopting a square planar geometry. Three structures have been proposed for the M(PP$_3$) intermediates: C_{3v}, C_s, and one with an agostic interaction of the phenyl ligand to the metal center. Of these, the agostic structure offers the most satisfactory explanation of the observed behavior of such species.[24] In the case of Ru(etp)(CO), the UV/vis spectral evidence prompts us to disregard a square planar structure and consider the three structural possibilities (**A**, **B**, **C**) of C_s symmetry and the agostic structure (**D**) shown in Scheme 2.

Scheme 2. Possible Structures for Ru(etp)(CO)



Transient Reactivity and Structural Implications. In the absence of quenchers, Ru(etp)(CO) reacted back with dihydrogen, decaying over a period of hundreds of milliseconds (390 nm) and obeying second-order kinetic behavior. This can be understood by considering the recombination of the Ru(etp)(CO) and H$_2$, which are generated in equal concentrations, giving a second-order rate law.[11] This reaction probably competes with other pathways when the reaction is carried out under an argon atmosphere. The transient Ru(etp)(CO) reacted with quenchers H$_2$, CO, Et$_3$SiH, and C$_2$H$_4$ following pseudo-first-order kinetics with rate constants that followed the trend $H_2 > C_2H_4 > CO > Et_3SiH$ (Table 2). The plots of observed rate constant versus quencher concentration were linear for a wide range of quencher concentrations. On the basis of its very high rate constants for reaction with a variety of quenchers, we deduce that Ru(etp)(CO) is a "naked" fragment as opposed to Ru(etp)(CO)···S (S = solvent). Solvation would be expected to reduce the rate constants significantly.[25,26]

The very high value of k_2 for the reaction of Ru(etp)(CO) with CO can also be used to argue against the formation of a triplet ground-state intermediate. It is well documented that spin-forbidden reactions of triplet-state complexes with singlet CO to form singlet photoproducts proceed at a lower rate than for singlet-state complexes as has been demonstrated for $^3Fe(CO)_4$.[27] Additionally, high-spin ground states are highly unusual for ruthenium and osmium compounds. Recently it has been shown through parahydrogen-induced polarization of NMR spectra that Ru(dppe)(CO)$_2$ has a singlet ground state.[28]

The second-order rate constants of Ru(etp)(CO) vary only by a factor of ca. 4 (k_2(H$_2$)/k_2(Et$_3$SiH)) and are ca. 100 times faster than those of Ru(PP$_3$);[24] we have found

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(21) Ogasawara, M.; Maseras, F.; Gallego-Planas, N.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 7468.

(22) Ogasawara, M.; Maseras, F.; Gallego-Planas, N.; Toyota, K.; Streib, W. E.; Komiya, S.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 1979.

(23) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

(24) Osman, R.; Pattison, D. I.; Perutz, R. N.; Bianchini, C.; Casares, J. A.; Peruzzini, M. *J. Am. Chem. Soc.* **1997**, *119*, 8459.

(25) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125.

(26) (a) Kelly, J. M.; Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 1220. (b) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

(27) (a) Weitz, E. *J. Phys. Chem.* **1987**, *91*, 3945. (b) Barton, T. J.; Grinter, R.; Thomson, A. J.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1977**, 841. (c) Poliakoff, M.; Weitz, E. *Acc. Chem. Res.* **1987**, *20*, 408. (d) Harvey, J. N.; Aschi, M. *Faraday Discuss.* **2003**, *124*, 129. (e) Poliakoff, M.; Turner, J. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 2809. (f) Snee, P. T. Payne, C. K.; Mebane, S. D.; Kotz, K. T.; Harris, C. B. *J. Am. Chem. Soc.* **2001**, *123*, 6909. (g) Ihee, H.; Cao, J.; Zewail, A. H. *Angew. Chem. Int. Ed.* **2001**, *40*, 1532.

(28) Schott, D.; Sleigh, C. J.; Lowe, J. P.; Duckett, S. B.; Mawby, R. J.; Partridge, M. G. *Inorg. Chem.* **2002**, *41*, 2960.

Table 4. Comparison of log k_2/dm^3 mol^{-1} s^{-1} for Reaction of Ruthenium Phosphine Transients with Quenchers, Q

	transient, reference				
Q	Ru(dmpe)$_2$, 10	Ru(depe)$_2$, 11	Ru(PP$_3$), 24	Ru(PPh$_3$)$_3$-(CO), 14	Ru(etp)(CO), this work
H_2	9.79	8.60	6.30	7.92	8.96
CO	9.66	7.96	6.00	8.49	8.83
Et_3SiH	8.32	5.04	5.73	7.95	8.32
C_2H_4	8.34	5.30	5.88		8.93

no evidence for reaction of Ru(etp)(CO) with benzene. The rate constants are, however, similar to those of Ru-(PPh$_3$)$_3$(CO) (see Table 4). The transient Ru(etp)(CO) is less discriminating in its reactivity than Ru(dmpe)$_2$ or Ru(depe)$_2$. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the reaction of Ru(etp)(CO) with Et_3SiH are similar to those of Ru-(dmpe)$_2$ with a significant entropic component to the barrier. In the case of Ru(PP$_3$) the small variation in rate constants and the small value of $\Delta S^\ddagger$ were associated with an agostic interaction similar to **D**.[24] The higher value of the rate constants and the more negative value of $\Delta S^\ddagger$ in Ru(etp)(CO) indicate that any agostic stabilization of the transient is kinetically insignificant. Although we favor structure **A** on the basis of the arguments presented above and the geometry of the final products, we cannot rigorously exclude the other structures (Scheme 2).

Conclusions

Reductive elimination of dihydrogen from Ru(etp)-(CO)H_2 occurs within the instrument response time (<100 ns) upon laser flash irradiation. The resulting transient species, assigned as 16-electron Ru(etp)(CO), is rapidly quenched by coordination or oxidative addition of a variety of reagents. The second-order rate constants decrease in the order $k_2(H_2) > k_2(C_2H_4) > k_2(CO) > k_2(Et_3SiH)$, but there is little selectivity toward these reagents. Product studies confirmed that dihydrogen loss is the only photochemical pathway.

Experimental Methods

General Procedures. All syntheses and manipulations were carried out under argon using standard Schlenk, high-vacuum line, or glovebox techniques. Solvents for general use were dried by refluxing for several hours over sodium/benzophenone transferred by cannula and stored under argon in ampules fitted with Young's taps. [$^2H_8$]-THF was dried over potassium and distilled under high vacuum directly into the NMR tubes before use. Cyclohexane for laser flash photolysis experiments was obtained from Sigma-Aldrich (99.9+% HPLC grade) and dried by refluxing over calcium hydride under argon, distilled, and collected. Gases used for flash photolysis were BOC research grade 99.999% purity. All NMR tubes (Wilmad 528-PP) were fitted with Young's taps. $Ru_3(CO)_{12}$ (Aldrich) and bis(2-diphenylphosphinoethyl)phenylphosphine (etp, Strem) were used without further purification. NMR spectra were recorded either on a Bruker MSL300 operating at 300.13 MHz (^{1}H), 121.49 MHz (^{31}P), or 75.47 MHz (^{13}C) or on a Bruker DRX400 operating at 400.13 MHz (^{1}H), 161.97 MHz (^{31}P), or 79.49 MHz (^{29}Si).

Synthesis of 2. Complex **2** was synthesized by a modification of a literature route.[16] $Ru_3(CO)_{12}$ (0.18 g, 0.3 mmol) and etp (0.49 g, 0.9 mmol) in toluene (50 mL) were refluxed in a three-necked round-bottomed flask for 4.5 h, forming a yellow-orange solution. The solvent was reduced until a precipitate started to appear; hexane (5 mL) was added and the mixture left to crystallize overnight at 273 K. Filtration of the mixture yielded yellow crystals of **2** that were washed three times with hexane (10 mL) and dried in vacuo (yield 0.62 g, 70%).

Synthesis of 1. A saturated solution of **2** (100 mg, 0.14 mmol) in THF was placed in a cylindrical Pyrex cell (20 mm path length, 50 mm diameter) fitted with a greaseless cone and a tubing connection. The solution was irradiated ($\lambda > 290$ nm, 150 W mercury arc) while stirring continuously and bubbling dihydrogen vigorously via a needle introduced through a silicone septum. The reaction was monitored by IR spectroscopy. After 12 h, little starting material remained and the solution was carefully decanted from the cell and evaporated under vacuum. The residue was extracted with benzene and the volume reduced until some solid started to precipitate. Hexane (2 mL) was added and the solution left to crystallize at 273 K. The resulting yellow solid was pure according to IR and NMR spectroscopy (yield 70 mg, 73%).

Laser Flash Photolysis. The laser flash photolysis equipment for excitation with 308 nm[29,30] has been described in detail elsewhere. In brief, a XeCl excimer laser (energy 35 mJ pulse^{-1}, 30 ns pulse width, 32.5 kV supply voltage) was used as excitation source for photolysis with 308 nm, and a pulsed Xe arc lamp acted as the monitoring source. All measurements were made at 295 ± 1 K unless otherwise stated. Samples for temperature measurements above ambient were equilibrated in a thermostated bath for a few minutes prior to flash photolysis. To avoid thermal reactions and inaccuracies caused by sample degradation in the determination of activation parameters, the temperature was not raised above 313 K and the samples were changed every two to three readings.

Steady-State Photolysis. Steady-state photolysis was performed with samples contained in Pyrex ampules or Pyrex NMR tubes (cutoff ca. 290 nm) fitted with a Young's stopcock. The photolysis source was either a Xe arc (ILC, 300 W) or a medium-pressure Hg arc (Philips HPK, 125 W). In both cases, a water filter (10 cm path) was placed between the arc and the sample to remove heat.

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[29] Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810.

[30] Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425.