Laser Flash Photolysis and Matrix Isolation Studies of 
Ru[R2PCH2CH2PR2]2H2 (R = C2H5, C6H5, C2F5): Control of 
Oxidative Addition Rates by Phosphine Substituents

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Abstract: The photochemistry of ruthenium hydrides Ru(depe)2H2, cis-Ru(dppe)2H2 and cis-Ru(dfepe)2H2 [depe = Et3PCH2CH2PEt2, dppe = Ph3PCH2CH2PPh2, dfepe = (C6F5)2PCH2CH2P(C6F5)2] has been studied by matrix isolation at 12 K and laser flash photolysis at ambient temperature. Both techniques yield the 4-coordinate 16-electron Ru4 species. The ethyl and phenyl species, Ru(depe)2 and Ru(dppe)2, exhibit very similar UV—visible spectra to Ru(dmpe)2 [Ru(depe)2 475, 580, 735 nm; Ru(dppe)2 465, 550, 760 nm in solution]. The spectrum of Ru(dfepe)2 is blue-shifted relative to the others (380, 450, 620 nm). The comparison of the spectra with that of [Rh(dppe)2]+ conclusively establishes a square-planar structure for Ru(depe)2 and Ru(dppe)2. The rates of reaction with added ligands are extremely sensitive to substituent. The rate constants for reaction with H2 are Ru(dfepe)2 2.0 × 108, Ru(dppe)2 2.4(2) × 108, Ru(depe)2 4.0(4) × 108 dm3 mol−1 s−1 compared to 6.8 × 109 dm3 mol−1 s−1 for Ru(dmpe)2. For reaction with CO, the rate constants are Ru(dppe)2 1.1 × 104, Ru(dppe)2 1.0(2) × 105, Ru(depe)2 9.1(7) × 103 dm3 mol−1 s−1 compared to 4.6 × 105 dm3 mol−1 s−1 for Ru(dmpe)2. Thus reactivity increases in the order Ru(dppe)2 < Ru(depe)2 < Ru(dppe)2 < Ru(dmpe)2 with an overall span of a factor of 34 000 for reaction with H2 and 418 000 for reaction with CO. The rate constants for reaction of Ru(dppe)2 with C2H4 and Et3SiH, and for reaction of Ru(dppe)2 with C2H4 have also been determined.

Introduction

The oxidative addition of hydrogen by transition metal phosphine complexes represents a key step in many homogeneous catalytic reaction pathways, such as hydrogenation and hydroformylation. Numerous mechanistic studies have been reported for H2 addition to square planar d8 complexes, particularly derivatives of Vaska’s complex, IrX(CO)L2 (X = halide, L = tertiary phosphine).

\[
\text{IrX(CO)L}_2 + \text{H}_2 \stackrel{k_1}{\rightleftharpoons} \text{IrX(CO)L}_2 \text{H}_2
\]

Kinetic studies have revealed that both the rate of the forward step \(k_1\) and reverse step \(k_2\) are sensitive to the nature of the halide.\(^1\) The rate of H2 addition decreases in the order \(P(p\text{-MeOC}_6\text{H}_4) > P\text{Ph}_3 > P\text{E}_2 > P\text{Cy}_3\); the rates depend on both steric and electronic properties of the substituent.

Studies of H2 addition by conventional methods are necessarily limited to less reactive complexes. If the coordinately unsaturated complex is formed only as a reactive intermediate, other techniques are required.\(^4\) It is such species which exhibit the highest reactivity and are capable, for instance, of inserting into C–H bonds. We have recently employed laser flash photolysis to determine\(^1\) rate constants for the oxidative addition of H2 to the coordinatively unsaturated d8 species, Fe(dpme)2 and Ru(dmpe)2 (dpme = Me2PCH2CH2PMe2), which are produced upon photolysis of the dihydride precursors cis-M(dpme)2H2. The rate constant for the ruthenium species is close to the diffusion-controlled limit and, more remarkably, is 7500 times faster than for the iron species. Ru(dmpe)2 has a striking three-band visible spectrum, which we associated with a square-planar geometry, whereas Fe(dpme)2 is postulated to have a butterfly structure. Both species are known to react with C–H bonds in solution; other group 8 metal complexes of the form ML4 (L = phosphine) are known to undergo similar reactions.\(^5\)

In an effort to probe the influence of the bidentate phosphine ligand on the structure and reactivity of the ruthenium center, we now report studies on the \(\text{[C(C}_2\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(C}_2\text{H}_5)_2]}\)
The Intensity of the Metal Hydride Stretch in the IR Spectrum.

The positions of the UV-visible bands of the Ru-H stretching mode and bands at lower frequency associated with cyclometalation of the depe ligand. The UV-visible spectrum recorded after photolysis showed new absorption bands at 286, 1457 m, 1417 m, 1046 m, 1039 m, 1027 m, 998 w, 975 w, 965 w, 883 w, 823 w.

The spectra were obtained by subtraction of the deposition spectra from those recorded after photolysis.

(abbreviated to “depe”), [(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}] (“dppe”), and [(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}] (“dfepe”) analogues of Ru(dmpe\textsubscript{2})H\textsubscript{2}. This choice of ligands allows us to change the electronic properties from an electron-rich metal center (dmpe/depe) to an electron-poor case (dfepe) and also to alter the steric bulk (cone angles: dmpe = 107°, depe = 115°, dppe = 125°, dfepe = 129°). The results provide strong evidence that all the Ru(dppe\textsubscript{2}) (dppe = dmpe, depe, dppe, dfepe) complexes have structures close to planar and demonstrate remarkable changes in rates of reaction according to substituent.

**Results**

1. Matrix Photochemistry.

   **a. Ru(dppe\textsubscript{2})H\textsubscript{2} in Inert Matrices.** A sample of Ru(dppe\textsubscript{2})H\textsubscript{2} (3:1 cis/trans mixture by 1H NMR) was cocondensed with argon. The IR spectrum recorded at 12 K showed a broad band at 1825 cm\textsuperscript{-1} for the Ru-H stretching mode and bands at lower frequency associated with the depe ligand. The UV-visible spectrum of this white compound was broad and featureless.

   Broad-band UV photolysis of the matrix (15 min) resulted in a 63% depletion of the hydride band and the appearance of no new features in the same region, therefore, excluding cyclometalation of the depe ligand. The UV-visible spectrum recorded after photolysis showed new absorption bands at 286, 476, 573, and 757 nm (Figure 1a, Table 1). Long wavelength photolysis design to irradiate selectively on the red side of the band at 476 nm (\(\lambda = 940-509 \text{ nm, } 60 \text{ min}\)) resulted in a small depletion of all the UV-visible bands and a growth in the intensity of the metal hydride stretch in the IR spectrum. We therefore associate all the UV-visible bands with a single product. The positions of the UV-visible bands of the photoproduct were identical when the matrix host was changed from argon to methane (Table 1).

   **b. cis-Ru(dfepe\textsubscript{2})H\textsubscript{2} in Inert Matrices.** The IR spectrum of cis-Ru(dfepe\textsubscript{2})H\textsubscript{2} in an argon matrix at 12 K displayed a broad, weak band for \(\nu(\text{Ru-H})\) at 1980 cm\textsuperscript{-1} (cf. 1990 cm\textsuperscript{-1} in nujol\textsuperscript{(9)} and vibrations due to the dfepe ligand at lower frequency.\textsuperscript{(9)} The UV-visible spectrum recorded in the same matrix showed bands at 272 and 235 nm.

   Filtered UV photolysis (\(\lambda = 234-376 \text{ nm, } 30 \text{ min}\)) resulted in 60% depletion of the hydride band of the starting material. No new Ru-H bands were observed in the IR spectrum and very little change was observed at lower frequency. Interactive subtraction indicated the presence of new product bands overlapping with starting material bands in the lower frequency region of the IR spectrum associated with the dfepe modes. The UV-visible spectrum recorded after photolysis showed depletion of the two bands at 272 and 235 nm and the appearance of new bands at 251, 297, 375, 461, and 611 nm (Figure 1b, Table 1). Visible photolysis (either \(\lambda = 420-450 \text{ nm or } \lambda = 475-508 \text{ nm, } 150 \text{ min}\)) resulted in slight shifts in all of the visible bands. No regeneration of intensity in the Ru-H stretching mode of the starting material was observed in the IR spectrum.

   A change of the matrix host from argon to methane resulted in the parallel observations with virtually no difference in \(\lambda_{\text{max}}\) for the absorption bands of the photoproduce.

   **c. Photolysis of Ru(dppe\textsubscript{2})H\textsubscript{2} and Ru(dppe\textsubscript{2})H\textsubscript{2} in CO-Doped Matrices.** Photolysis of the depe complex in a 1.7% CO/Ar matrix (\(\lambda > 200 \text{ nm, } 5 \text{ min}\)) resulted in the formation of a new band at 1850 cm\textsuperscript{-1}, which was assigned to \(\nu(\text{CO})\) of Ru(dppe\textsubscript{2})CO by comparison with solution IR data (see section 3) and Ru(dmpe\textsubscript{2})CO (1844 cm\textsuperscript{-1}).\textsuperscript{(6)} Photolysis of Ru(dppe\textsubscript{2})H\textsubscript{2} in a 5% CO/Ar matrix (\(\lambda = 234-376 \text{ nm, } 35 \text{ min}\)) did not result in the formation of any new carboxyl bands. The same five-band UV-visible spectrum observed in argon and methane was found, implying that no reaction takes place at all with CO under these conditions. No changes were observed on annealing the matrix to 30 K.

2. Laser Flash Photolysis in Solution at Room Temperature.

   a. In the Presence of Hydrogen. Laser flash photolysis experiments with Ru(dmpe\textsubscript{2})H\textsubscript{2} demonstrated that Ru(dmpe\textsubscript{2}) reacts with hydrogen with a second-order rate constant of 6.8 \(\times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) at ambient temperature.\textsuperscript{(5)}

   Laser flash photolysis (\(\lambda_{\text{exc}} = 308 \text{ nm, pulse width ca. } 30 \text{ ns, pulse energy ca. } 30 \text{ mJ}\)) of Ru(dppe\textsubscript{2})H\textsubscript{2} in heptane (ca. 1.5 \(\times 10^{-3} \text{ mol dm}^{-3}\)) at 295 K under 79 Torr of hydrogen (made up to a total pressure of 750 Torr with argon) resulted in the rapid formation (<100 ns) of a transient species at 470 nm. The transient decayed with pseudo-first-order kinetics (Figure 2a) on a microsecond time scale (\(k_{\text{obs}} = 1.71 \times 10^8 \text{ s}^{-1}\)) restoring the original absorbance. Additional heptane solutions of the complex were made up under partial pressures of hydrogen ranging from 14 to 270 Torr with the total pressure made up to 750 Torr with argon. In all cases, the decay of the transient followed pseudo-first-order behavior and the absorbance returned to the baseline. A plot of \(k_{\text{obs}}\) versus [H\textsubscript{2}]\textsuperscript{(10)} was linear (Figure 3a) and gave a second order rate constant for the reaction of (4.0 \pm 0.4) \(\times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (Table 2).

   A similar series of experiments was carried out on benzene solutions of cis-Ru(dppe\textsubscript{2})H\textsubscript{2} (ca. 6 \(\times 10^{-4} \text{ mol dm}^{-3}\)) in the presence of hydrogen, for which a transient was observed at 460 nm. The transient decayed back to the baseline with

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(8) IR bands for Ru(dppe\textsubscript{2})H\textsubscript{2} in an argon matrix at 12 K (\(\nu, \text{ cm}^{-1}\)): 2965 m, 2939 m, 2909 m, 2883 m, 2838 m, 1825 m, 1816 m, 1465 m, 1457 m, 1417 m, 1046 m, 1039 m, 1027 m, 998 w, 975 w, 869 w, 807 m, 762 m, 755 m, 736 m, 695 m.

(9) IR bands for Ru(dppe\textsubscript{2})H\textsubscript{2} in an argon matrix at 12 K (\(\nu, \text{ cm}^{-1}\)): 1980 w, 1423 w, 1317 w, 1299 m, 1235 x, 1219 m, 1211 m, 1201 m, 1160 w, 1120 w, 1103 m, 983 w, 975 w, 965 w, 883 w, 823 w.

(10) Wilhelm, E.; Batino, R. Chem. Rev. 1973, 73, 1. Gas solubilities were taken as follows: H\textsubscript{2} (heptane, 4.7 \(\times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}\); benzene, 2.9 \(\times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}\)); CO (heptane, 1.2 \(\times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}\); benzene, 7.5 \(\times 10^{-6} \text{ mol dm}^{-3} \text{ atm}^{-1}\); ethene (heptane, 1.2 \(\times 10^{-4} \text{ mol dm}^{-3} \text{ atm}^{-1}\); benzene, 1.4 \(\times 10^{-1} \text{ mol dm}^{-3} \text{ atm}^{-1}\)).
Laser Flash Photolysis and Matrix Isolation Studies

Table 1. UV–Visible Band Maxima for Transient Species in Matrices and in Solution (λ, nm (ε, dm³ mol⁻¹ cm⁻¹))a

<table>
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<tr>
<th>transient</th>
<th>argon matrix</th>
<th>methane matrix</th>
<th>solution</th>
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<tr>
<td>Ru(dmpe)₂⁺</td>
<td>--, 287, 463, 559, 747</td>
<td>--, --, 451, 543, 734</td>
<td>467 (2400), 555 (1700), 745⁺ (1900)</td>
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<td>Ru(dppe)₂⁺</td>
<td>--, 286, 476, 573, 757</td>
<td>246, 286, 476, 571, 756</td>
<td>475 (2500), 580 (1200), 735⁺ (630)</td>
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<tr>
<td>Ru(dppe)₂⁻</td>
<td>251, 297, 375, 461, 611</td>
<td>251, 297, 375, 462, 616</td>
<td>465, 550, 760⁺</td>
</tr>
<tr>
<td>Ru(dfepe)₂⁻</td>
<td>380, 450, 620⁺</td>
<td></td>
<td></td>
</tr>
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</table>

a Estimated from the kinetics in the absence of added H₂ and from the relative intensities of the bands. b Matrix values for Ru(dmpe)₂ for the "reversible species" taken from ref 5a. The matrix spectra also show shoulders at 365, 666 nm (Ar) and 365, 610 nm (methane). c Transient spectrum obtained in cyclohexane. d The matrix spectra show shoulders at 316, 354, 375, 665 (Ar), and 371, 665 nm (methane). e Transient spectrum obtained in heptane.

Figure 2. (a) Transient decay following laser flash photolysis (308 nm) of Ru(dppe)₂H₂ in heptane solution under 79 Torr of hydrogen made up to 750 Torr with argon (the inset shows the corresponding first-order plot); (b) Transient decay and first-order plot from a similar experiment with Ru(dppe)₂H₂ in benzene solution under 760 Torr of hydrogen; (c) transient decay and second-order plot from Ru(dppe)₂H₂ in heptane solution under 760 Torr of argon; (d) transient decay and first-order plot from a similar experiment with Ru(dppe)₂H₂ in benzene solution under 760 Torr of argon.

pseudo-first-order kinetics (Figure 2b) over a hydrogen partial pressure range from 80 to 760 Torr. A plot of kobs versus [H₂]¹⁰ (Figure 3a) gave a second-order rate constant of (2.4 ± 0.2) × 10⁷ dm³ mol⁻¹ s⁻¹ (Table 2).

In the case of Ru(dfepe)₂H₂, flash photolysis of a benzene solution (ca. 8 × 10⁻⁴ mol dm⁻³) under 760 Torr of hydrogen resulted in the decay of a transient at 460 nm back to the baseline with pseudo-first-order kinetics over hundreds of microseconds (kobs = 5.9 × 10² s⁻¹).

b. Transient Spectra. The spectra of the transient species formed from all three ruthenium hydride complexes were recorded under a partial pressure of hydrogen (for depe, under 11 Torr of H₂, and for dppe and dfepe, under 760 Torr of H₂) to ensure complete reversibility and prevent the build up of any stable photoproducts. For all three complexes, the transient spectra exhibited three absorption maxima between 350 and 800 nm (Figure 4, Table 1), although the central band for dppe overlapped to some extent with the highest energy band. Figure 4a shows the spectrum of Ru(dppe)₂⁺ for comparison. The decay kinetics of the transients were measured at each of the maxima with the same result showing that only a single intermediate was produced from each precursor. No effect of solvent (heptane, cyclohexane or benzene) was found for the transients derived from depe or dppe. Similarly the spectrum produced from Ru(dfepe)₂H₂ was the same in heptane, benzene, and perfluorohexane.

c. Flash Photolysis under Argon. Laser flash photolysis of Ru(dppe)₂H₂ in heptane under argon resulted in the formation of the transient species at 470 nm, which decayed with second-order kinetics returning back to the baseline over hundreds of microseconds (slope = k₁/ε₁ = 2.0 × 10⁵ s⁻¹) (Figure 2c). The same second-order decay was observed upon changing the solvent to either cyclohexane or benzene. An increase in the concentration of precursor by a factor of 2 or 5 (achieved with different path length cuvettes but constant precursor absorbance) resulted in a more rapid decay of the transient that could not be fitted to either second-order or first-order kinetics and which no longer returned to the baseline.

Flash photolysis of a benzene solution of Ru(dfepe)₂H₂ under argon yielded a transient (at 460 nm) which also decayed with second order kinetics back to the baseline, but over a period of seconds (k₂/ε₂ = 1.0 × 10⁸ s⁻¹).

In the case of Ru(dppe)₂H₂, flash photolysis of a benzene solution under argon produced a transient species at 470 nm which decayed with pseudo-first-order kinetics over a millisecond time scale (kobs = 1.5 × 10⁵ s⁻¹, Figure 2d). The same observed rate constant, kobs, was found upon changing the solvent to either THF or cyclohexane. The ground-state UV-visible spectrum of the solution in all solvents was changed after 200 laser shots with a new absorption band present at 375 nm. When different path length cuvettes were used in order to
benzene was removed and the residue was redissolved in transient kinetics was investigated for the depe and dppe CO followed pseudo-first-order kinetics though still over the transient in benzene solution at 460 nm under 760 Torr of heptane.

The effect of ethene on the concentration of Ru(dppe)$_2$H$_2$ by a factor of 10, an increase in $k_{obs}$ resulted.

d. Addition of Quenching Ligands. i. Carbon Monoxide. Flash photolysis in the presence of CO resulted in rapid quenching of the transients from both depe (in heptane) and dppe (in benzene) and traces which no longer returned back to the baseline. Plots of $k_{obs}$ against [CO] were linear$^0$ (Figure 3a) and gave second-order rate constants for Ru(depe)$_2$H$_2$ of (9.1 $\pm$ 0.7) x 10$^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ and (1.0 $\pm$ 0.2) x 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ for Ru(dppe)$_2$H$_2$ (Table 2). For dppe, the decay of the transient in benzene solution at 460 nm under 760 Torr of CO followed pseudo-first-order kinetics though still over hundreds of microseconds ($k_{obs}$ = 8.0 x 10$^4$ s$^{-1}$). From this measurement at a single CO pressure, the estimated second-order rate constant was 1.1 x 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$. Exposure of the sample to 100 laser shots resulted in a significant change in the baseline. Plots of $k_{obs}$ versus [CO] were linear$^0$ (Figure 5a) with a value of second-order rate constant of (1.1 $\pm$ 0.2) x 10$^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ for Ru(dppe)$_2$H$_2$ resulting in quenching of the transient as monitored at 470 nm. A plot of $k_{obs}$ versus [Et$_3$SiH] showed a linear dependence (Figure 5a) with a value of second-order rate constant of (1.1 $\pm$ 0.2) x 10$^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Table 2). The temperature dependence for the pseudo-first-order rate constant was measured over the range 303-338 K with a concentration of Et$_3$SiH of 0.41 mol dm$^{-3}$ (Figure 5b). The activation parameters obtained were as follows: $E_a$ = 13.3 $\pm$ 1.2 kJ mol$^{-1}$, $\Delta H^\circ$ = 10.6 $\pm$ 1.3 kJ mol$^{-1}$, and $\Delta S^\circ$ = -112 $\pm$ 4 J mol$^{-1}$ K$^{-1}$ (Figure 5b).

Addition of Et$_3$SiH (up to 1.41 mol dm$^{-3}$) to benzene solutions of Ru(dppe)$_2$H$_2$ did not result in any increase in the rate of decay of the transient. Ru(dppe)$_2$H$_2$ showed a remarkable lack of reactivity toward any added ligands. High concentrations of Et$_3$SiH (3.8 mol dm$^{-3}$) or cyclopentene (3 mol dm$^{-3}$) had no effect. Flash photolysis of a benzene solution of dppe under 760 Torr of N$_2$ showed no evidence for reaction with nitrogen.

ii. Other Quenching Ligands. The effect of ethene on the transient kinetics was investigated for the depe and dppe complexes. Similar results were obtained to both the H$_2$ and CO quenching data with values of second-order rate constants for depe and dppe with ethene$^0$ of (2.0 $\pm$ 0.7) x 10$^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ and (5.9 $\pm$ 1.9) x 10$^4$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively (Figure 3b, Table 2). Addition of Et$_3$SiH (2.4 x 10$^{-2}$ - 2.4 mol dm$^{-3}$) to heptane solutions of Ru(depe)$_2$H$_2$ resulted in quenching of the transient as monitored at 470 nm. A plot of $k_{obs}$ versus [Et$_3$SiH] showed a linear dependence (Figure 5a) with a value of second-order rate constant of (1.1 $\pm$ 0.2) x 10$^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Table 2). The temperature dependence for the pseudo-first-order rate constant was measured over the range 303-338 K with a concentration of Et$_3$SiH of 0.41 mol dm$^{-3}$ (Table 3). The activation parameters obtained were as follows: $E_a$ = 13.3 $\pm$ 1.2 kJ mol$^{-1}$, $\Delta H^\circ$ = 10.6 $\pm$ 1.3 kJ mol$^{-1}$, and $\Delta S^\circ$ = -112 $\pm$ 4 J mol$^{-1}$ K$^{-1}$ (Figure 5b).

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3. Solution Photochemistry of Ru(depe)$_2$H$_2$, Ru(dppe)$_2$H$_2$, and Ru(dppe)$_2$H$_2$. In order to interpret the results of the laser flash photolysis experiments, the photochemistry of the three complexes was probed in solution using NMR and IR studies. Steady-state photolysis of Ru(depe)$_2$H$_2$ in benzene-$d_6$ in an ampule ($\lambda > 285$ nm, 14 h) at room temperature yielded no

![Figure 3. Plots of pseudo-first-order rate constants for the decays of the transients obtained upon laser flash photolysis of Ru(depe)$_2$H$_2$ and Ru(dppe)$_2$H$_2$ vs the concentration of added quenching gas for (a) H$_2$ and (b) C$_2$H$_4$. The best straight lines are shown as full lines through the experimental points.](image)

![Figure 4. Transient UV-visible spectra measured at 295 K obtained 400 ns after laser flash photolysis: (a) spectrum of Ru(dmpe)$_2$ in cyclohexane from ref 19b; (b) spectrum after photolysis of Ru(depe)$_2$H$_2$ in heptane under 11 Torr of hydrogen (made up to 750 Torr with argon); (c) spectrum after photolysis Ru(dppe)$_2$H$_2$ in cyclohexane under 760 Torr of hydrogen; (d) spectrum after photolysis of Ru(dppe)$_2$H$_2$ in heptane under 760 Torr of hydrogen.](image)

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<th>Ru(dppe)$_2$H$_2$</th>
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<td>H$_2$</td>
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<td>CO</td>
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<td>Et$_3$SiH</td>
<td>(1.1 $\pm$ 0.2) x 10$^5$</td>
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*Errors are shown as 95% confidence limits. Data recorded in heptane. Measurement at only one gas pressure in benzene.

Exposure of Ru(dppe)$_2$H$_2$ with nitrogen. High concentrations of Et$_3$SiH (3.8 mol dm$^{-3}$) or cyclopentene (3 mol dm$^{-3}$) had no effect. Flash photolysis of a benzene solution of dppe under 760 Torr of N$_2$ showed no evidence for reaction with nitrogen.

Steady-state photolysis of Ru(depe)$_2$H$_2$ in benzene-$d_6$ in an ampule ($\lambda > 285$ nm, 14 h) at room temperature yielded no
Laser Flash Photolysis and Matrix Isolation Studies

The reaction of Ru(depe)₂ with Et₃SiH (0.41 mol dm⁻³) in heptane photolysis in C₆H₆ or heptane was equally unproductive.

New band at 1835 cm⁻¹ in the IR spectrum, which is assigned to v(CO) of Ru(depe)₂CO (eq 1).

The ¹H NMR spectrum recorded following photolysis of Ru(depe)₂H₂ in benzene-‑d₆ (λ > 285 nm, 5 days) resulted in the appearance of only minor new peaks in the ¹H and ³¹P{¹H} NMR spectra. Both Traverso and co-workers and Azizian and Morris have reported that irradiation of Fe(dppe)₂H₂ in toluene solution for 3 h resulted in formation of the previously characterized cyclometalated complex, Fe(dppe)₂(Ph)C₆H₄PPh₂H₂. In order to confirm the photochemical loss of hydrogen from Ru(dppe)₂H₂, a CO- saturated toluene solution was photolyzed in an IR cell for 2 min. The IR spectrum showed depletion of the metal–hydroxide stretch at 1880 cm⁻¹ and formation of a new, more intense band at 1847 cm⁻¹ resulting from Ru(dppe)₂CO.

Photolysis of Ru(dppe)₂H₂ in THF-‑d₆ (λ > 285 nm, 4 h, -78 °C) yielded no new peaks in the ¹H or ³¹P{¹H} NMR spectra.

### Discussion

The photochemistry of Ru(dppe)₂H₂, Ru(dppe)₂H₂ and Ru(dppe)₂H₂ has been studied in solution at room temperature (12) under nitrogen and under reduced pressure.

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**Table 3. Temperature Dependence of the Rate Constants for the Reaction of Ru(dppe)₂ with Et₃SiH (0.41 mol dm⁻³) in heptane**

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<th>Temp. K</th>
<th>kₐ dm⁻³ mol⁻¹ s⁻¹</th>
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<td>338</td>
<td>2.24 x 10⁸</td>
</tr>
<tr>
<td>328</td>
<td>1.92 x 10⁸</td>
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<tr>
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</tr>
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</tr>
<tr>
<td>303</td>
<td>1.31 x 10⁸</td>
</tr>
</tbody>
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**Figure 5.** (a) Plot of the pseudo-first-order rate constants for the decay of the transient obtained upon laser flash photolysis of Ru(dppe)₂H₂ in heptane solution vs concentration of added triethylsilane and (b) Eyring plot of the pseudo-first-order rate constants for the same reaction in the presence of 0.41 mol dm⁻³ Et₃SiH: ΔH° = 10.6 ± 1.3 kJ mol⁻¹, ΔS° = -112 ± 4 J mol⁻¹ K⁻¹.
by laser flash photolysis and in low temperature matrices. The results parallel those obtained earlier on Ru(dmpe)\textsubscript{2}H\textsubscript{2}, and are fully consistent with the formation of the 4-coordinate Ru(dmpe)\textsubscript{2}: (dmpe = depe, dppe, dfepe) species in the primary photochemical step (eq 4).

\[
\text{Ru(dmpe)}_2\text{H}_2 \xrightleftharpoons{hv} \text{Ru(dmpe)}_2 + \text{H}_2 \tag{4}
\]

The reductive elimination of H\textsubscript{2} is complete well within the instrumental risetime (<100 ns). In the presence of added H\textsubscript{2}, the Ru(dmpe)\textsubscript{2} species react readily to reform the precursor. Alternatively the 16-electron intermediate may be trapped with other reagents. There are two very striking deductions from these results. Firstly, the multiband UV-visible spectrum is characteristic of all four 16-electron complexes, indicating a common molecular and electronic structure. Since detailed evidence of the electronic structure and electronic spectra are available for the isoelectronic rhodium cations, we can make very firm deductions about Ru(dmpe)\textsubscript{2}. Secondly, comparisons of rate constants for the four complexes show that rates of oxidative addition and ligand coordination are highly sensitive to substituent.

**Spectra and Structure.** All four Ru(dmpe)\textsubscript{2} species show multiband UV-visible spectra. For Ru(dmpe)\textsubscript{2} and Ru(depe)\textsubscript{2}, there are three prominent bands between 400 and 800 nm. In Ru(dppe)\textsubscript{2}, the central band lies close to the high energy band and is not well resolved. The spectrum of Ru(dfepe)\textsubscript{2} is conspicuously blue-shifted compared to all the others, so the three bands lie in the region 350–700 nm. Comparisons of the solution spectra show that the long wavelength band follows the trend in \( \lambda_{\text{max}} \): Ph > Me > Et > C\textsubscript{2}F\textsubscript{5} with small shifts between the first three complexes and 2500 cm\textsuperscript{-1} between Ru(dppe)\textsubscript{2} and Ru(dfepe)\textsubscript{2}. The short-wavelength band and the central band follow the trend in \( \lambda_{\text{max}} \): Et > Me > Ph > C\textsubscript{2}F\textsubscript{5}.

We have shown previously\textsuperscript{2a} that there are two forms of Ru(dmpe)\textsubscript{2}, present in an argon matrix with slightly different visible spectra, a “reversible” form in which expelled H\textsubscript{2} is held close by in the matrix cage, and an “irreversible” form in which the hydrogen molecule has diffused out of the cage. In the case of Ru(dppe)\textsubscript{2}, we only observed a reversible form whereas Ru(dfepe)\textsubscript{2} failed to recombine with H\textsubscript{2} altogether.

We postulated previously that the multiband spectrum of Ru(dmpe)\textsubscript{2} is characteristic of a square-planar geometry and that the lowest energy band should be assigned to a metal-centered \( d_\pi^0-p_\pi \) transition. We were hampered in comparisons with the literature because there are few spectra of square-planar complexes with \( d \)-bonding ligands only, and those did not show a comparable pattern of bands. The present results demonstrate that Ru(dppe)\textsubscript{2} and, most importantly, Ru(dmpe)\textsubscript{2}, must have the same electronic and molecular structure as Ru(dmpe)\textsubscript{2}. The isoelectronic ion, [Rh(dmpe)\textsubscript{2})\textsuperscript{2+}, has been shown crystallographically to adopt a structure close to square planar.\textsuperscript{16a} Geoffroy et al.\textsuperscript{17} carried out a thorough investigation of the UV-visible and MCD spectra of salts of [M(dmpe)\textsubscript{2}]\textsuperscript{2+} (M = Rh, Ir) and found three bands for each salt with extinction coefficients above 4000 dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1} between 22 000 and 32 000 cm\textsuperscript{-1} (the central rhodium band required MCD in order to pick it out from the high energy band). The longest wavelength band was assigned to a \( A_{2g} \) excited state on the basis of the sign of the dichroism.

In the Rh complex, complications from spin-orbit coupling are very firm deductions about Ru(dmpe)\textsubscript{2}. Secondly, comparisons of solution spectra show that the long wavelength band follows the trend in \( \lambda_{\text{max}} \): Ph > Me > Et > C\textsubscript{2}F\textsubscript{5} to a IA\textsubscript{2}" excited state on the basis of the sign of the dichroism.

The deviations of the RhP\textsubscript{4} atoms from the mean plane are ca. 0.04 \textAA. The mean interligand PRhP angles are 82.7°. The mean PRhP (trans) angles are 176.9°.

(16) Hall, M. C.; Kilbourn, B. T.; Taylor, K. A. J. Chem. Soc. (A) 1970, 2539. The deviations of the RhP\textsubscript{4} atoms from the mean plane are ca. 0.04 \textAA. The mean interligand PRhP angles are 82.7°. The mean PRhP (trans) angles are 176.9°.

dfepe between PCl₂Ph and PF₃ in acceptor ability, substantially below CO.²⁵

Reactivity. The similarity in structure of Ru(drpe)₂ (drpe = depe, dppe, and dfepe) to Ru(dmpe)₂ contrasts with the reactivity of these species toward added ligands (Scheme 1). The variation in rate constants for reaction with H₂, CO, and C₂H₄ is illustrated in Figure 6. The rate constants for the oxidative addition of hydrogen vary remarkably 4 orders of magnitude from Ru(dmpe)₂ to Ru(dfepe)₂ (k₂ = 6.8 × 10⁹ dm³ mol⁻¹ s⁻¹ for dmpe, 2.0 × 10⁶ dm³ mol⁻¹ s⁻¹ for dfepe). This range of rate constants for the oxidative addition of hydrogen upon changing the chelating phosphine ligand is much larger than that found upon changing the phosphine substituents in IrCl(CO)(PR₃)₂. For the latter, the rate constants for H₂ addition are the same for PEt₃ and PPh₃, and a maximum rate constant ratio of 1200 has been found between R = P- MeOPh and R = C₆H₁₁. No data are available for bidentate phosphines such as dppe or dppe. Wilson et al.²⁶ have attempted to analyze these rate constants in terms of a series of ligand effect parameters correlating both steric and electronic effects. Although an electronic factor χ and the cone angle of the phosphine θ show a correlation with rate, an additional parameter has to be included once aryl substituents are placed on the phosphine.

As for Ru(dmpe)₂, the rate constants for quenching of the depe, dppe, and dfepe complexes by CO, C₂H₄, and Et₃SiH are all lower than for the reaction with H₂. The rate constants for reaction with CO span 5 orders of magnitude between dmpe and dfepe. The large rate constant for reaction of Ru(dmpe)₂ with CO (ca. 5 × 10⁹ dm³ mol⁻¹ s⁻¹) was taken to imply that the fragment possessed a singlet ground state; density functional calculations have now confirmed this.²⁰ The lower rate constants observed for Ru(dppe)₂ do not necessarily imply a change in spin state, but, in general, reflect the much lower reactivity than depe, dppe or dmpe.³⁷ The failure to react in a CO-doped argon matrix or to re-form starting material in a neat argon matrix upon long wavelength irradiation is unusual for a coordinatively unsaturated species²⁸ and raises the possibility that the ruthenium centre may interact with a C₂F₅ group on the ligand to block the vacant reaction site. Such a M-F-C interaction has been cited for one of the photoproducts produced on irradiation of (dfepe)Cr(CO)₅.²⁹ The similarity of the absorption maxima to that of Cr(CO)₅CF₃ in argon or methane matrices.³⁵ The assignment of the species was based principally upon the similarity of the absorption maxima to that of Cr(CO)₅CF₃.²⁹ In the present study, we have not been able to obtain conclusive evidence for or against F coordination.³⁰

Scheme 1. Transient Photochemistry of Ru(drpe)₂H₂ in Solution at Ambient Temperature

![Scheme 1](image)

Conclusions

1. The primary photoproducts of Ru(drpe)₂H₂ (drpe = depe, dppe and dfepe) are the 4-coordinate complexes Ru(dppe)₂.
2. Each of the complexes Ru(dppe)₂ exhibits a multiband UV-visible spectrum resembling that of Ru(dmpe)₂ including a long-wavelength band assigned to a M(d)-M(p) transition which appears between 700 and 800 nm for Ru(dppe)₂ and Ru(dppe)₂ and at 620 nm for Ru(dfepe)₂.
3. The spectra are characteristic of a structure close to square planar for Ru(dppe)₂, Ru(dppe)₂, and Ru(dppe)₂. The structure of Ru(dppe)₂ may be slightly distorted or may be stabilized by F coordination.
4. The reactivity of the complexes increases in the order Ru(dppe)₂ < Ru(dppe)₂ < Ru(dppe)₂ < Ru(dppe)₂. The rate constants for reaction with H₂ are much more sensitive to variation of phosphine than those of more stable d⁰ square-planar complexes studied previously.
5. The rate constants of each Ru(dppe)₂ complex increases with substrate in the order C₂H₄ < CO < H₂, but the selectivity toward substrates is far greater for Ru(dppe)₂ and Ru(dppe)₂ than for Ru(dmpe)₂.

²⁷ In contrast to the low reactivity of Ru(dppe)₂, Ru(dppe)₂H₂ is thermally reactive and dehydrogenates cyclic alkanes upon heating. See ref. ²⁶.

Experimental Section

General Methods and Materials. Ruthenium trichloride, depe, and dppe were obtained from Aldrich. Compounds were synthesized and handled using standard Schlenk, high-vacuum, and glovebox techniques. Solvents for synthesis (AR Grade) were dried by refluxing over sodium/benzophenone and then distilled under an argon atmosphere while those for flash photolysis (Aldrich HPLC Grade) were refluxed over calcium hydride under argon. Perfluorohexane (Aldrich, 95%) was distilled from CaH2 under argon. Benzene-d6 and THF-d8 (Goss Scientific Instruments Ltd.) were dried by stirring over potassium/benzophenone and then vacuum transferred. Hydrogen used in synthesis was BOC standard grade (99.9% purity). Gases used for the matrix experiments (Ar, CH4, CO) and for flash experiments (Ar, H2, CO, N2, C2H2) were BOC research grade (99.999% purity). Hydrogen used in synthesis was BOC standard grade (99.9% purity). Gases used for the matrix experiments (Ar, CH4, CO) and for flash experiments (Ar, H2, CO, N2, C2H2) were BOC research grade (99.999% purity). Triethylsilane was stored over activated 3 A molecular sieves.

Matrix Isolation Experiments. The matrix isolation apparatus is described in detail elsewhere. Samples for IR spectroscopy alone were deposited onto a CsI window cooled by an Air Products CS202 closed-cycle refrigerator to 12–35 K. A BaF2 window was used for combined IR and UV-visible spectroscopy. The outer windows of the vacuum shroud were chosen to match. Ru(depe)2H2 and Ru(dppe)2H2 were sublimed from right-angled glass tubes (at 388 and 358 K, respectively) at the same time as a gas stream entered the vacuum shroud through a separate inlet. Typical deposition temperatures and rates were 20 K for Ar (2 mmol h⁻¹) and 25 K for CH4 (2 mmol h⁻¹). The samples were then cooled to 12 K before recording IR spectra on a Mattson Research Series FTIR spectrophotometer fitted with a TGS detector and KBr beam splitter, which was continuously purged with dry CO2-free air. Spectra were recorded at 1 cm⁻¹ resolution with 128 scans coaveraged (25K data points with two-times zero filling). UV-visible spectra were recorded on the same sample at the same temperature on a Perkin-Elmer Lambda 7G spectrophotometer. Matrices were photolyzed through a quartz window with a Philips HPK 125-W medium-pressure mercury arc, quartz focusing lens and water filter or with an ILC 302UV 300 W Xe arc equipped with either UV-reflecting (240–400 nm) or with visible-reflecting (400–800 nm) mirrors and a water filter. Photolysis wavelengths were selected with cutoff or interference filters.

Laser Flash Photolysis. The apparatus for flash photolysis experiments has been described in detail elsewhere. Briefly, a XeCl excimer laser (308 nm) is used as the excitation source and a pulsed Xe arc lamp is used as the monitoring source. The spectrometer is linked to a digital oscilloscope, and the system is controlled by a PC. Transient signals are usually collected as 12- or 16-shot averages. Some of the data for Ru(depe)2H2 were collected on a similar apparatus at the University of Ottawa.

Samples of Ru(depe)2H2 for flash experiments were sublimed immediately before use, and Ru(dppe)2H2 and Ru(dppe)2H2 were freshly recrystallized. Samples of the depe complex were handled in the glovebox exclusively. The samples were loaded into a quartz cuvette (1-, 2-, or 10-mm pathlength) fitted with a Young’s PTFE stopcock and degassing bulb. Solvent was added via a cannula under argon on a Schlenk line fitted with a diffusion pump. The sample was degassed three times by freeze–pump–thaw cycles before being back-filled to 760 Torr with the appropriate gas. Gas mixtures were made up manometrically in 1-L bulbs such that the total pressure in the cell was typically 750 Torr. Liquid quenchers were added with a microliter syringe. The absorbances of the samples were typically 0.5–1.0 at 308 nm. Variable-temperature measurements were made by replacing the standard cell holder by an insulated holder mounted on a block through which thermostated water was passed.

NMR Spectroscopy. The NMR spectra were recorded with either Bruker MSL300 or AMX500 spectrometers. The 1H NMR chemical shifts were referenced to residual CDCl3 at δ 7.13 ppm. The 31P{1H} NMR chemical shifts were referenced externally to H3PO4 at δ = 0.

Synthesis. trans-Ru(depe)2Cl2,34 Ru(dppe)2H2 and Ru(dppe)2H4 were prepared by literature methods.

cis-Ru(depe)2H2. trans-Ru(depe)2Cl2 (300 mg, 0.51 mmol) was dissolved in 20 mL of THF. Freshly cut Na (300 mg) was added, and the mixture was stirred under 760 Torr of H2 in an ampule for 24 h at room temperature. The solvent was then removed from the resulting gray suspension and the residue extracted exhaustively with hexane (3 × 20 mL) and filtered through Celite to yield a colorless solution. After the solution was cooled to −20 °C overnight, white crystals of Ru(depe)2H2 were obtained; yield 200 mg (84%). The NMR data were consistent with the literature. The 31P{1H} NMR spectrum showed a 3:1 ratio of cis/trans species.

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