J. Am. Chem. Soc. 1993, 115, 8627–8637

Transient and Matrix Photochemistry of $Fe(dmpe)_2H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$): Dynamics of C–H and H–H Activation

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Received April 15, 1993

Abstract: The transient photochemistry in solution and low-temperature matrix photochemistry of $Fe(dmpe)_2H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) are reported; this compound is uniquely effective among first-row transition metal complexes in its ability to activate C–H bonds. Pulsed laser photolysis (308 nm) of alkane solutions of $Fe(dmpe)_2H_2$ at ambient temperature generates $Fe(dmpe)_2$ (λ_{max} = 355 nm) within 30 ns. In the absence of added quenchers, the latter decays by reaction with the alkane solvent (in pentane, k_{obs} = 630 s^{-1} at 297 K, $\Delta H^{\ddagger}$ = 25.0 ± 5.9 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −125 ± 22 J K^{-1} mol^{-1}). The pseudo-first-order rate constants very with alkane by a factor of ca. 4. $Fe(dmpe)_2$ is quenched by added reagents with second-order rate constants in the range 10^9–10^4 dm^3 mol^{-1} s^{-1}, decreasing in the order CO $\gg H_2 > C_2H_4 > N_2 >$ cyclopentene $> Et_3SiH$. The activation parameters for reaction with Et_3SiH are $\Delta H^{\ddagger}$ = 22.4 ± 1.8 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −87 ± 6 J K^{-1} mol^{-1}. The product of reaction with CO is demonstrated by time-resolved IR spectroscopy to be $Fe(dmpe)_2(CO)$, which forms at the same rate as the transient decays. The reactions with arenes (benzene and toluene) in cyclohexane exhibit saturation kinetics which are interpreted in terms of reversible formation of $Fe(dmpe)_2$(arene), followed by conversion to $Fe(dmpe)_2$(aryl)H with rate constants of ca. 10^6 s^{-1}. UV irradiation of $Fe(dmpe)_2H_2$ in Ar matrices at 12 K also yields $Fe(dmpe)_2$ (UV and IR detection). The reaction may be partially reversed by selective photolysis. Irradiation in CO- or N_2-doped matrices yields $Fe(dmpe)_2L$ (L = CO, N_2); in a methane matrix the photoproduct is $Fe(dmpe)_2(CH_3)H$. $Fe(dmpe)_2$ differs drastically from $Ru(dmpe)_2$ in its absorption spectrum and its reactivity. Most notably, the rate constant for reaction with H_2 is a factor of 7500 smaller for $Fe(dmpe)_2$ than for $Ru(dmpe)_2$. In contrast, reactions of both complexes with CO are diffusion-controlled.

Introduction

Many complexes are now known to activate the C–H bonds of alkanes, and considerable progress has been made in understanding the mechanism of these reactions.[2] The early work of Chatt and Davidson[3] on reactions of the postulated intermediate "$Ru(dmpe)_2$" (dmpe = $Me_2PCH_2CH_2PMe_2$) represented the first evidence that intermolecular cleavage of a C–H bond of an arene was possible. Later, Tolman and co-workers[4] expanded the investigation of "$Ru(dmpe)_2$" and also studied the much more reactive "$Fe(dmpe)_2$" intermediate. They exploited the naphthyl hydride complexes, $M(dmpe)_2(C_{10}H_7)H$, as thermal sources of the intermediates. However, the elevated temperature required for naphthalene elimination prevented the observation of any thermally sensitive products; this problem can be circumvented by photochemical activation of the corresponding dihydride complexes, $M(dmpe)_2H_2$.

The preparation and characterization of the dihydride *cis*-$Fe(dmpe)_2H_2$ was first reported about 20 years ago.[5,6] In 1986 Bergamini et al.[7] reported that 313-nm irradiation of a toluene solution of $Fe(dmpe)_2H_2$ led to formation of the insoluble dimer $Fe_2(dmpe)_5$. Crossover experiments involving photolysis of $Fe(dmpe)_2H_2$ and $Fe(dmpe)_2D_2$ proved that loss of hydrogen was intramolecular and concerted, as little HD was evolved. Photolysis in the presence of CO led to the formation of $Fe(dmpe)_2CO$.

Baker and Field described the photochemistry of $Fe(dmpe)_2H_2$ in solutions containing arenes, alkenes, and alkanes at low temperature (Scheme I).[8,9,10a] Of particular importance was the formation of alkyl hydride complexes from alkanes, *including methane*, the only examples of homogeneous alkane C–H oxidative addition to a first-row transition metal complex. The alkyl hydride complexes proved to be very labile, decomposing rapidly at temperatures greater than −20 °C, and could not be isolated. The photochemical reactions of $Fe(dmpe)_2H_2$ in the presence of amides result in N–H bond activation.[10b]

Tolman, Field, and others presumed that the reactive intermediate responsible for the C–H bond cleavage reactions was the 16-electron species, $Fe(dmpe)_2$. Although Chatt and Watson[11] claimed initially to have synthesized this complex, no one has succeeded in detecting $Fe(dmpe)_2$ directly. Following our work on $Ru(dmpe)_2$,[12] we have studied the transient and matrix photochemistry of $Fe(dmpe)_2H_2$. Laser flash photolysis studies

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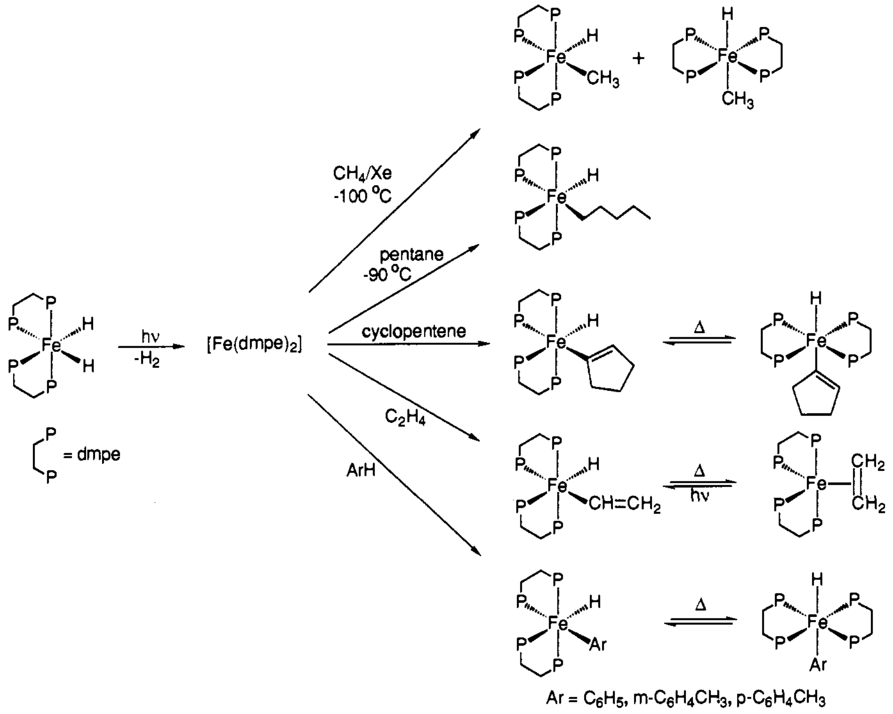
Scheme I. Solution Photochemistry of $Fe(dmpe)_2H_2$[a]



[a] After Field et al.[8-10]

with both UV/vis and infrared detection have been carried out in order to characterize $Fe(dmpe)_2$ in solution at room temperature and study the kinetics of its reactions with substrates, including CO, H_2, alkanes, and arenes. The experiments have enabled us to measure directly the rates of oxidative addition of alkanes, alkenes, and arenes. $Fe(dmpe)_2$ is found to differ dramatically from its ruthenium analogue, both in its spectroscopic properties and in its reactivity.

Results

1. Laser Flash Photolysis of $Fe(dmpe)_2H_2$. a. In Alkane Solvent. $Fe(dmpe)_2H_2$ is a yellow compound with an absorption maximum in pentane solution at 209 nm ($\epsilon = 1.66 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and two slight shoulders at 270 and 325 nm. The extinction coefficient at 308 nm (the wavelength of the laser) is ca. 2.8×10^3 dm^3 mol^{-1} cm^{-1}. All of the following flash photolysis data were recorded with excitation at 308 nm and detection at 410 nm, unless otherwise stated.

Laser flash photolysis of $Fe(dmpe)_2H_2$ in *n*-pentane solution ([Fe] = 10^{-3}–10^{-4} mol dm^{-3}) under argon results in the rapid formation (<30 ns) of a transient species which absorbs strongly at 410 nm. The transient decays with pseudo-first-order kinetics over milliseconds ($k_{obs} = 6.68 \times 10^2$ s^{-1}) to form a second species, which has a residual absorption at 410 nm (Figure 1a). In cyclohexane solution, the pseudo-first-order rate constant for the decay of the transient is about 4.4 times smaller ($k_{obs} = 1.48 \times 10^2$ s^{-1}) than in pentane. In heptane and isopentane the rate constants lie between the values for cyclohexane and *n*-pentane (Table I). A 5-fold increase in the concentration of the iron compound has no effect on the rate constant for the transient decay, thus excluding reaction of a coordinatively unsaturated product with the precursor. $Fe(dmpe)_2H_2$ is insoluble in perfluoromethylcyclohexane, which rules out the use of an "inert" fluorinated solvent to investigate the effect of alkane concentration.

The temperature dependence of the decay rate of the transient from reaction of $Fe(dmpe)_2H_2$ in *n*-pentane was measured between 252 and 297 K. Since the decay is interpreted as the rate of reaction of $Fe(dmpe)_2$ with pentane, we make use of the molarity of liquid pentane (taking changes of density with temperature into account) to convert the pseudo-first-order rate constant to a second-order rate constant, k_2 (Table II). The plot of $\ln k_2/T$ versus $1/T$ (Figure 2a) yields the activation parameters $\Delta H^\ddagger = 25.0 \pm 5.9$ kJ mol^{-1} and $\Delta S^\ddagger = -125 \pm 22$ J mol^{-1} K^{-1} (with 95% probability for error bars).

The effect of deuteration of the cyclohexane was investigated by laser flash photolysis of solutions of $Fe(dmpe)_2H_2$ in cyclohexane and cyclohexane-d_{12} under an argon atmosphere. The two measurements, conducted side-by-side for accuracy, yielded values of $k_{obs}(C_6H_{12}) = 1.48 \times 10^2$ s^{-1} and $k_{obs}(C_6D_{12}) = 1.54 \times 10^2$ s^{-1}. Since the estimated errors are ±5% or $\pm 0.08 \times 10^2$ s^{-1}, the two rates do not differ within experimental error.

Similarly, there is no significant difference between the rates of decay of the transients formed from $Fe(dmpe)_2H_2$ and $Fe(dmpe\text{-}d_{12})_2H_2$ in cyclohexane solution under an argon atmosphere. Again, the measurements were made side-by-side (errors ±5%), giving values of k_{obs}(protio) = 1.48×10^2 s^{-1} and k_{obs}(deuterio) = 1.55×10^2 s^{-1}, $k_H/k_D = 0.95$.

b. Quenching by H_2. If irradiation of $Fe(dmpe)_2H_2$ leads to the initial dissociation of H_2, the transient should be quenched by added hydrogen. Cyclohexane solutions of $Fe(dmpe)_2H_2$ were prepared under partial pressures of H_2 varying from 100 to 760 Torr, made up to a total gas pressure of 1 atm with argon where necessary. Under 1 atm of hydrogen, the transient decays with pseudo-first-order kinetics with $k_{obs} = 3.6 \times 10^3$ s^{-1} (Figure 1b; see Table III). A plot of k_{obs} vs [hydrogen] is linear and yields a second-order rate constant for the reaction of $(8.4 \pm 0.4) \times 10^5$ dm^3 mol^{-1} s^{-1} (see Table IV and Figure 3a; the solubility of H_2 in cyclohexane is taken as 3.8×10^{-3} mol dm^{-3} atm^{-1}).[13] Even under 1 atm of H_2, the absorbance still does not decay right back to the base line, suggesting that there is some residual reaction of the transient with the alkane solvent. Nevertheless, the dissociation of H_2 from $Fe(dmpe)_2H_2$ is at least partially reversible. The spectrum of the transient could not be recorded reliably under argon due to the build-up of the photoproduct, but this problem could be reduced significantly by recording the spectrum under 1 atm of hydrogen. The transient spectrum recorded 1 μs after the laser pulse in *n*-pentane is shown in Figure

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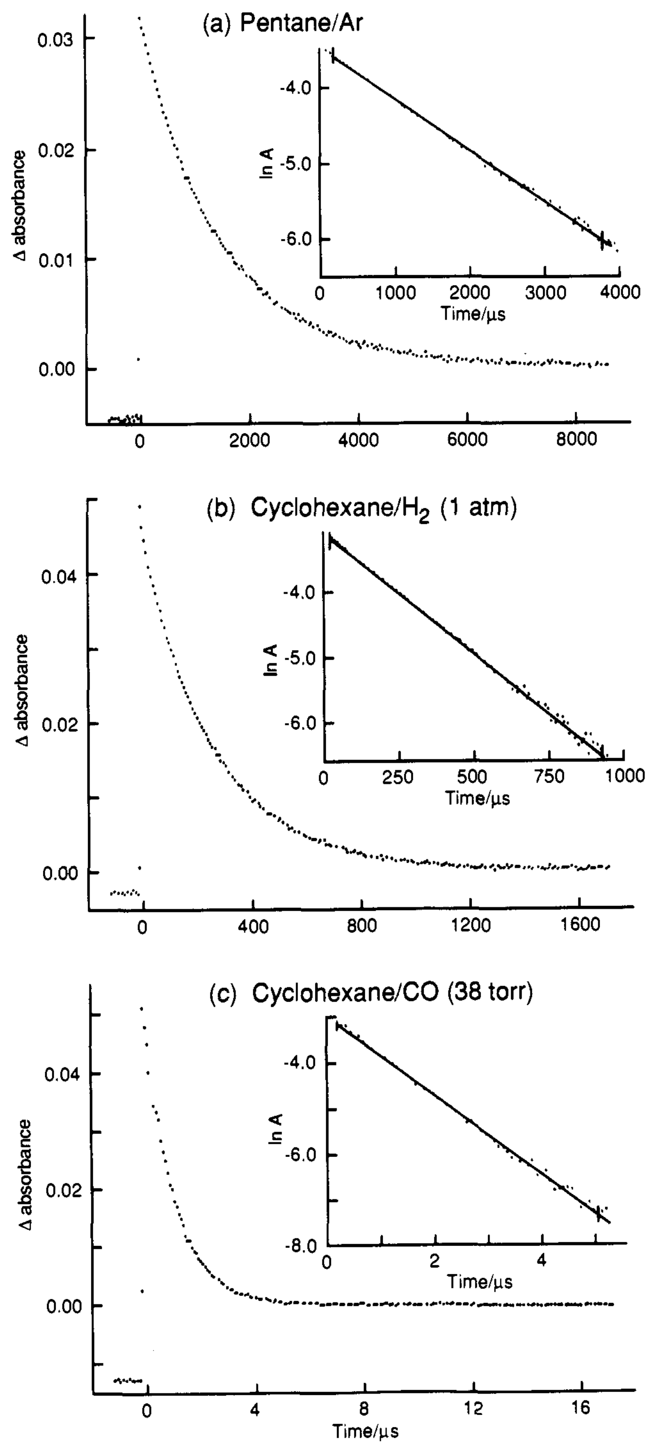

Figure 1. Transient decay following laser flash photolysis (308 nm) of Fe(dmpe)$_2$H$_2$ (ca. 3 × 10^{-4} mol dm^{-3}) at 300 K monitored at 410 nm (average of 16 shots). Each dot represents an eight-point average of the output of the digital oscilloscope. The insets show the first-order plots with a calculated line overlaying the experimental points and vertical bars to represent the limits used in the regression analysis. (a) Solution in pentane under 1 atm of argon; (b) solution in cyclohexane under 1 atm of H$_2$; (c) solution in cyclohexane under 38 Torr of CO, made up to 1 atm with argon. Notice the changes in abscissa scales between a, b, and c.

Table I. Rate Constants (±5%) for the Decay of the Transient at Ambient Temperature on Laser Flash Photolysis of Fe(dmpe)$_2$H$_2$ in Neat Alkanes and in Alkanes with Added Cyclopentene[a]

	alkane		alkane + C_5H_8	
solvent	k_{obs}/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	k_{obs}/s^{-1}	[C_5H_8]/mol dm^{-3}
cyclohexane	148	16.0	2.6 × 10^3	0.016
isopentane	296	34.5	4.2 × 10^3	0.020
heptane	476	69.8	6.1 × 10^3	0.022
n-pentane	668	77.0	7.6 × 10^3	0.022

[a] Laser wavelength 308 nm, detection wavelength 410 nm.

Table II. Temperature Dependence of the Rate Constants for the Reaction of the Transient Observed on Flash Photolysis of Fe(dmpe)$_2$H$_2$ with *n*-Pentane and with Et$_3$SiH in Cyclohexane

reaction with pentane[a]			reaction with Et$_3$SiH in cyclohexane	
temp/K	k_{obs}/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	temp/K	k_2/dm^3 mol^{-1} s^{-1}
297	6.33 × 10^2	73.7	338	6.54 × 10^4
272	2.33 × 10^2	26.1	329	5.78 × 10^4
261.5	1.58 × 10^2	17.4	322	4.56 × 10^4
258	1.08 × 10^2	11.8	315	3.57 × 10^4
252	1.01 × 10^2	11.0	309	2.77 × 10^4
			306	2.71 × 10^4
			299	2.16 × 10^4
			290	1.54 × 10^4
			284	1.34 × 10^4

[a] k_2 is derived by dividing k_{obs} by the molarity of liquid pentane at the appropriate temperature, making use of the density calculated from data in the following: *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 2, 343.

4. The spectrum shows a broad maximum centered at ca. 355 nm and is identical to that recorded in cyclohexane solution.

A change from 1 atm of H$_2$ to 1 atm of D$_2$ has little effect on the rate of decay of the transient following flash photolysis of Fe(dmpe)$_2$H$_2$ in cyclohexane. The values of the pseudo-first-order rate constants measured in side-by-side experiments were $k_{obs}(H_2)$ = 3.3 × 10^2 s^{-1} and $k_{obs}(D_2)$ = 3.03 × 10^2 s^{-1}. The resulting kinetic isotope effect, k_H/k_D, of 1.09 ± 0.07 is marginally higher than in the other deuteration studies, but is still barely significant.

c. Quenching by CO. Solutions of Fe(dmpe)$_2$H$_2$ in cyclohexane ([Fe] = 10^{-3}–10^{-4} mol dm^{-3}) were examined by flash photolysis under partial pressures of CO varying from 11 to 80 Torr. The transient decays with pseudo-first-order kinetics (Figure 1c) to give a product which is stable for at least 4 ms. A plot of k_{obs} vs [CO] (solubility of CO in cyclohexane taken as 9.2 × 10^{-3} mol dm^{-3} atm^{-1})[14] is linear (Figure 3b) and gives a second-order rate constant for the reaction of (2.2 ± 0.2) × 10^9 dm^3 mol^{-1} s^{-1}, close to the diffusion-controlled limit. Under 1 atm of CO, transient decay is too rapid to be detected; instead, an instrument-limited rise (<100 ns) in absorption is observed, which then does not decay over at least 40 ms.

The reaction of Fe(dmpe)$_2$H$_2$ with CO has also been monitored using time-resolved infrared (TRIR) spectroscopy. Laser flash photolysis of the dihydride complex in heptane solution ([Fe] = 10^{-3} mol dm^{-3}) with excitation at 308 nm under 2 atm of CO yields a species with a single carbonyl band at 1838 ± 2 cm^{-1}. This feature is at the same position within experimental error as the carbonyl band of a sample of Fe(dmpe)$_2$CO formed in isopentane solution by steady-state irradiation (1 min, λ > 200 nm) of Fe(dmpe)$_2$H$_2$ under 1 atm of CO. (The literature value of 1812 cm^{-1} was recorded in benzene.)[7]

The pseudo-first-order rate constant for the *rise* of the carbonyl complex in heptane solution was measured under a pressure of 14 Torr of CO with IR detection at 1838 cm^{-1}. The resulting value of (2.8 ± 0.3) × 10^5 s^{-1} compares favorably with the rate constant of 2.6 × 10^5 s^{-1} for the *decay* of the transient measured in the UV/vis experiments in the presence of 11 Torr of CO. These experiments confirm that the transient decays in the presence of CO to form Fe(dmpe)$_2$CO.

d. Quenching by other Gaseous Reagents: **N$_2$, CH$_4$, C$_2$H$_4$.** The quenching effects of gaseous reagents in cyclohexane and pentane are shown in Table III as rate constants for the pseudo-

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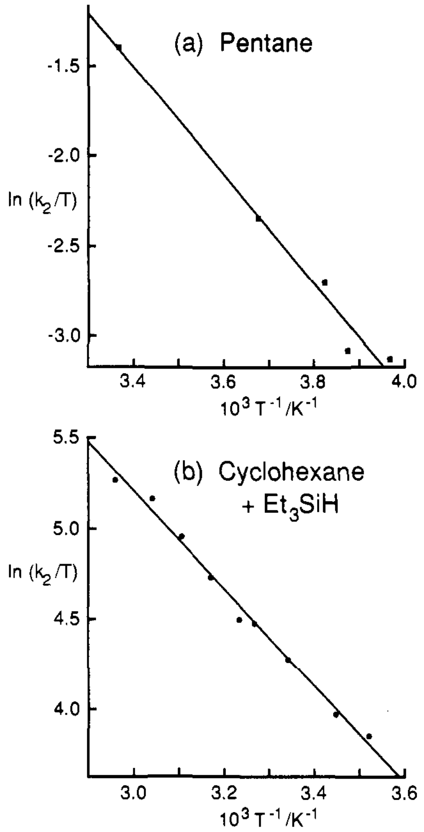

Figure 2. Eyring plots showing the temperature dependence of the second-order rate constants for reaction of the transient observed following laser flash photolysis of $Fe(dmpe)_2H_2$. (a) Reaction with solvent in neat pentane: $\Delta H^{\ddagger} = 25.0 \pm 5.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = -125 \pm 22$ J K^{-1} mol^{-1}. (b) Reaction with Et_3SiH in cyclohexane: $\Delta H^{\ddagger} = 22.4 \pm 1.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -87 \pm 6$ J K^{-1} mol^{-1}. Each point in this plot is derived from measurements at three concentrations of Et_3SiH.

Table III. Pseudo-First-Order Rate Constants for the Decay (±5%) of the Transient Following Laser Flash Photolysis of $Fe(dmpe)_2H_2$ in the Presence of 1 atm of Gas at Ambient Temperature

quenching gas	k_{obs}/s^{-1} in pentane	k_{obs}/s^{-1} in cyclohexane
argon	6.48×10^2	1.48×10^2
carbon monoxide		$>10^7$
dinitrogen	3.90×10^3	1.20×10^3
methane		1.80×10^2
dihydrogen	3.20×10^3	3.60×10^3
ethene	6.20×10^4	

Table IV. Second-Order Rate Constants for the Reaction of $Fe(dmpe)_2$ with Ligands Other Than Alkanes at Ambient Temperature in Cyclohexane Solution

ligand	k_2/dm^3 mol^{-1} s^{-1}
carbon monoxide	$(2.2 \pm 0.2) \times 10^9$
dihydrogen	$(8.4 \pm 0.4) \times 10^5$
ethene[a,c]	3.1×10^5
dinitrogen[a]	1.6×10^5
cyclopentene	$(1.48 \pm 0.05) \times 10^5$
benzene[b]	$(9.6 \pm 0.4) \times 10^5$
toluene[b]	$(9.0 \pm 0.2) \times 10^5$
triethylsilane	$(2.1 \pm 0.2) \times 10^4$

[a] Measurement at a single concentration. [b] Deduced from analysis of saturation kinetics. [c] Pentane solution.

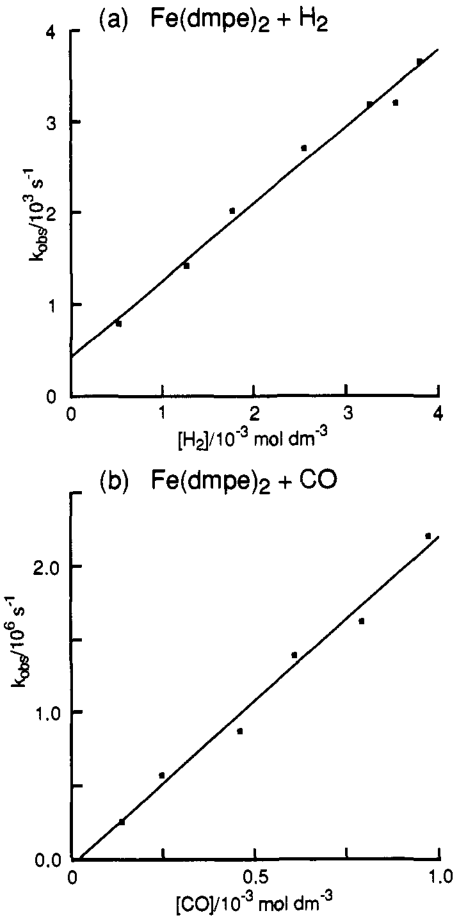

Figure 3. Plots of the pseudo-first-order rate constants for the decay of the transient observed on laser flash photolysis of $Fe(dmpe)_2H_2$ in cyclohexane (a) vs concentration of dissolved dihyrogen and (b) vs concentration of dissolved carbon monoxide. The best straight lines are shown as full lines through the experimental points.

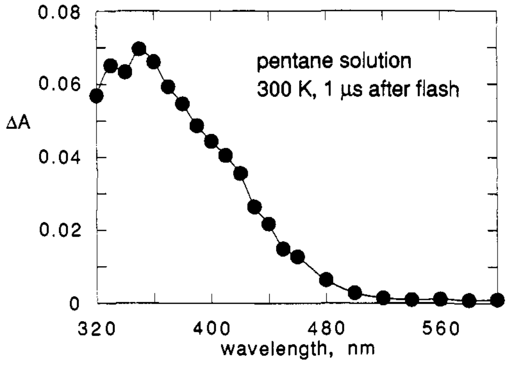

Figure 4. Transient UV/vis difference spectrum with a delay time of 1 μs relative to the laser flash (308 nm) obtained from a pentane solution of $Fe(dmpe)_2H_2$ under 1 atm of H_2 at 300 K.

first-order decay of the transient under 1 atm of gas. The presence of 1 atm of CH_4 (concentration = 3.3×10^{-2} mol dm^{-3} atm^{-1})[14] has no appreciable effect on the rate of decay of the transient in cyclohexane compared to the rate observed under argon. In contrast, the transient decay in the presence of ethene is 100 times faster than in the presence of argon. Taking a value of 2×10^{-1} mol dm^{-3} atm^{-1} for the solubility of C_2H_4 in pentane[14] gives an approximate second-order rate constant of 3.1×10^5 dm^3 mol^{-1} s^{-1} for the reaction with ethene.

In the presence of nitrogen, the transient decays in cyclohexane ($k_{obs} = 1.20 \times 10^3$ s^{-1}) to form a product which is stable over at least 10 ms. The UV/vis difference spectrum recorded on a conventional spectrometer after 200 laser shots shows the appearance of a band at 370 nm, which is probably due to $Fe(dmpe)_2N_2$. The rate of reaction with nitrogen in pentane is greater than in cyclohexane (Table III), partly because of the increased solubility of nitrogen in pentane.[14]

e. Quenching by Cyclopentene and by Triethylsilane. Flash photolysis of $Fe(dmpe)_2H_2$ in mixed cyclohexane/cyclopentene solutions ([cyclopentene] = 0.39–11.3 mol dm^{-3}) generates a

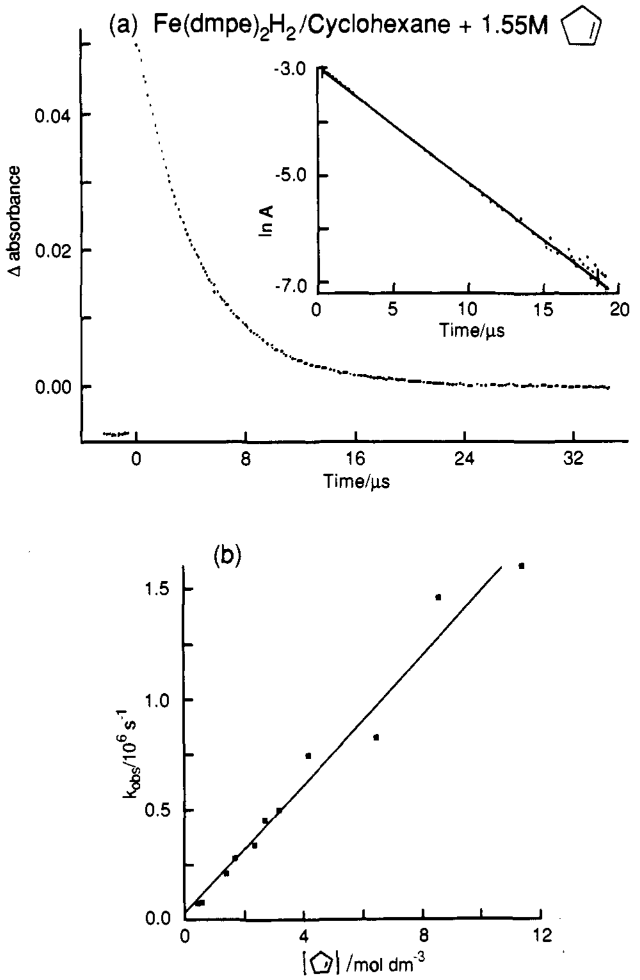

Figure 5. (a) Transient decay following laser flash photolysis of Fe(dmpe)$_2$H$_2$ in cyclohexane solution at 300 K in the presence of 1.55 mol dm^{-3} cyclopentene. (b) Plot of the pseudo-first-order rate constant for the decay of the transient vs [cyclopentene] in cyclohexane/cyclopentene mixtures ranging from 0.39 mol dm^{-3} to pure cyclopentene.

transient which decays with pseudo-first-order kinetics, but the absorbance does not return to the base line (Figure 5a). A plot of k_{obs} vs [cyclopentene] is linear right up to neat cyclopentene and gives a second-order rate constant for the reaction of (1.48 ± 0.05) × 10^5 dm^3 mol^{-1} s^{-1} (Figure 5b).

This reaction was employed to determine the magnitude of the solvent effect of different alkanes on the rate of oxidative addition to Fe(dmpe)$_2$ (see Scheme I and Discussion). Fe(dmpe)$_2$H$_2$ was studied by flash photolysis in the presence of a known concentration of cyclopentene in various alkane solvents. The results (Table I) show that the rate constants vary by a factor of ca. 2 only between the extremes of cyclohexane and *n*-pentane at almost constant cyclopentene concentration.

The quenching behavior of triethylsilane was also studied, with results similar to those for cyclopentene. The observed pseudo-first-order rate constant varied linearly with [Et$_3$SiH] up to a concentration of 2.3 mol dm^{-3}. The temperature dependence of the reaction with Et$_3$SiH was recorded between 11 and 65 °C for three different concentrations of Et$_3$SiH. The activation parameters deduced from the second-order rate constants (Table II) were as follows: $\Delta H^{\ddagger} = 22.4 \pm 1.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -87 \pm 6$ J K^{-1} mol^{-1}, $\Delta G^{\ddagger}_{298} = 48.3 \pm 2.5$ kJ mol^{-1} (Figure 2b).

f. Quenching by Benzene and Toluene. Laser flash photolysis of a solution of Fe(dmpe)$_2$H$_2$ in neat benzene ([Fe] = 10^{-3}–10^{-4} mol dm^{-3}) under argon produces a transient species (rise time < 100 ns) which decays very rapidly with pseudo-first-order kinetics (k_{obs} = 9.4 × 10^5 s^{-1}) to form a new species. A 5-fold increase in the concentration of Fe(dmpe)$_2$H$_2$ has no effect on the rate of transient decay. The transient spectrum recorded 100 ns after the flash in neat benzene under 1 atm of H$_2$ is very similar to that observed in pentane (λ_{max} ca. 350 nm).

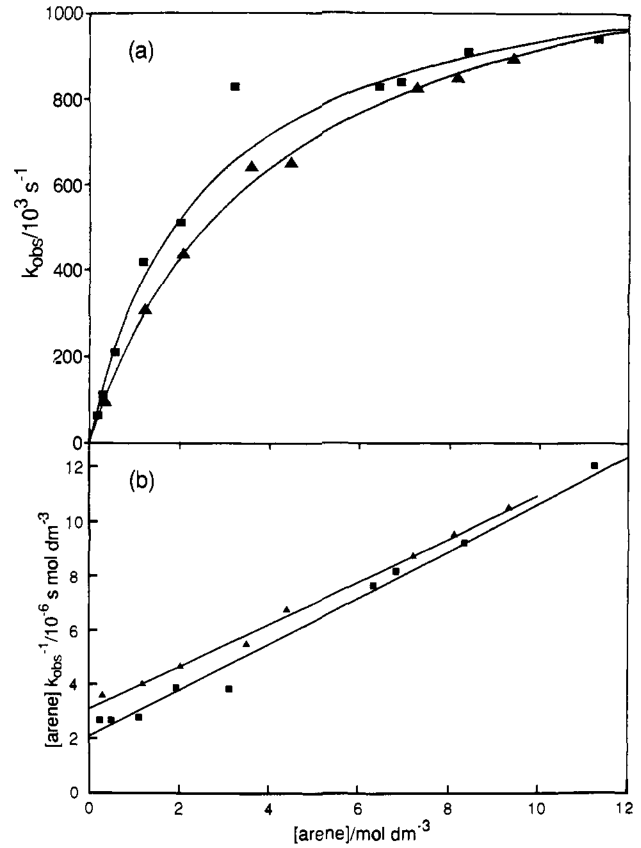

Figure 6. (a) Plot of the pseudo-first-order rate constant vs [arene] (■, arene = benzene; ▲, arene = toluene) for the decay of the transient following laser flash photolysis of Fe(dmpe)$_2$H$_2$ in arene/cyclohexane mixtures. The curve through the experimental points is calculated from the fit to the inverse plot in Figure 6b. (b) Inverse plot showing the variation of [arene]k_{obs}^{-1} with concentration of arene.

The pseudo-first-order rate constant for the decay of the transient in cyclohexane/benzene mixtures is approximately linearly dependent on [benzene] up to moderate concentrations (3 × 10^{-3} to 3 mol dm^{-3}), but tends to a limiting value at higher concentrations (Figure 6a). An inverse plot of [C$_6$H$_6$]/k_{obs} vs [C$_6$H$_6$] is linear (Figure 6b).

Solutions of Fe(dmpe)$_2$H$_2$ in cyclohexane/toluene mixtures behaved similarly (Figure 6a). The inverse plot of [toluene]/k_{obs} vs [toluene] gives a straight line (Figure 6b).

2. Photolysis of Fe(dmpe)$_2$H$_2$ in Low-Temperature Matrices. a. Photolysis in Argon Matrices. The IR spectrum of Fe(dmpe)$_2$H$_2$ in an argon matrix shows a broad band for ν(FeH) at 1780 cm^{-1} (Table V, Figure 7a, cf. 1775 cm^{-1} reported in solution) and vibrations of the dmpe ligand at lower frequency (Figure 8a).[4,5]

Filtered photolysis (25 min, 295–390 nm) leads to 35% depletion of the starting material hydride band (Figure 7a, ii). A new band at 1845 cm^{-1} is assigned to Fe(dmpe)$_2$CO, formed by the reaction of Fe(dmpe)$_2$ with traces of CO in the matrix (see below). After a total of 64 min of irradiation (295–390 nm), depletion of Fe(dmpe)$_2$H$_2$ increases to 49%, but there is little further increase in the band at 1845 cm^{-1} (Figure 7a, iii). At lower frequency, the only new band in the spectrum is at 874 cm^{-1}, although subtraction of bands due to Fe(dmpe)$_2$H$_2$ reveals further product bands which overlap with those of the starting material (Table V, Figure 8b,c). No features assignable to a new metal hydride stretching mode appear in the region 1900–1700 cm^{-1}. Long-wavelength irradiation (λ = 434 ± 5 nm, 210 min) regenerates

Table V. IR Bands of $Fe(dmpe)_2H_2$ and $Fe(dmpe)_2$ in an Argon Matrix (ν/cm^{-1})

$Fe(dmpe)_2H_2$	$Fe(dmpe)_2$	assignment[a]
2970 m		$\nu(CH)_{as}$
2906 m		$\nu(CH)_s$
1780 m		$\nu(FeH)$
1776		$\nu(FeH)$
1432 w	1433	$\delta(CH_3)_{as}$
1426 sh		$\delta(CH_3)_{as}$
1423 w		$\delta(CH_3)_{as}$
1419 w	1422	$\delta(CH_3)_{as}$
1415 w	1418	$\delta(CH_3)_{as}$
1286 w	1285	$\delta(CH_3)_s$
1282 w	1277	$\delta(CH_3)_s$
1272 w	1273	$\delta(CH_3)_s$
	1269	$\delta(CH_3)_s$
	1266	$\delta(CH_3)_s$
1262 w	1262	$\delta(CH_3)_s$
1112 vw	1111	
1081 br, w	1082 br	
1060 w	1066 sh	
933 s	926	$\rho(CH_3)$
927 m		$\rho(CH_3)$
921 s	916	$\rho(CH_3)$
903 w		
884 m	887	
	874	
846 w		
838 w		
827 m		
786 w		
717 m		$\nu(PC)_{as}$
702 m		$\nu(PC)_{as}$
684 m		
639 m		

[a] Adapted from assignments for PMe_3: Fox, P. C.; Bowen, J. P.; Allinger, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 8536.

12% of the original intensity of the ν(FeH) at 1780 cm^{-1}. Quantitative measurement shows that more product is lost than starting material recovered (Figure 8d). Less selective irradiation ($\lambda > 295$ nm to generate the product, and $\lambda > 416$ nm for subsequent photolysis) has the same effect except that conversion is increased substantially.

The UV/vis spectrum of $Fe(dmpe)_2H_2$ recorded in an argon matrix shows only a steadily increasing absorption from 500 to 200 nm with a slight shoulder at ca. 300 nm (Figure 9a). The difference spectrum, showing the spectrum after deposition subtracted from the spectrum after 64 min of photolysis (295–390 nm), shows a distinct shoulder at 388 nm and sharply rising absorption below 330 nm (Figure 9b). Long-wavelength photolysis reduces the intensities of these bands (Figure 9b). Notably, the loss of intensity in the UV band is proportionately greater than the gain in intensity of the IR bands of $Fe(dmpe)_2H_2$, a phenomenon which parallels the behavior of $Ru(dmpe)_2$. The only product bands in the 900–400-nm region are at least 10 times weaker than the 388-nm band. Their behavior on long-wavelength photolysis does not match that of the 388-nm band, implying that they represent traces of another species, perhaps a dinuclear product.

b. Photolysis in a 1% CO-Doped Argon Matrix. Pyrex-filtered photolysis ($\lambda > 285$ nm, 30 s) of $Fe(dmpe)_2H_2$ in a 1% CO/argon matrix results in depletion of the metal–hydride stretching mode and the formation of a new band at 1844 cm^{-1}, which is assigned to ν(CO) of $Fe(dmpe)_2CO$ (see section 1c). Further photolysis ($\lambda > 285$ nm) causes more depletion of ν(FeH) (56% loss of the original intensity), an increase in the intensity of the band for $Fe(dmpe)_2CO$, and the appearance of a second product band at 1899 cm^{-1}. The $Fe(dmpe)_2CO$ band is ca. 30 times more intense in these experiments than in the experiments in "pure" argon.

c. Photolysis in Nitrogen-Doped Argon Matrices. In a 1% nitrogen-doped argon matrix, 10-min Pyrex-filtered photolysis leads to 22% depletion of the band of $Fe(dmpe)_2H_2$ at 1780 cm^{-1}. A new band centered at 1991 cm^{-1} grows in with shoulders at 2001 and 1981 cm^{-1}. On further irradiation (20 min, $\lambda > 285$ nm) the 1991-cm^{-1} band continues to grow, but the shoulder at lower frequency (1981 cm^{-1}) gains in relative intensity as do other bands at 2110 and 1975 cm^{-1}.

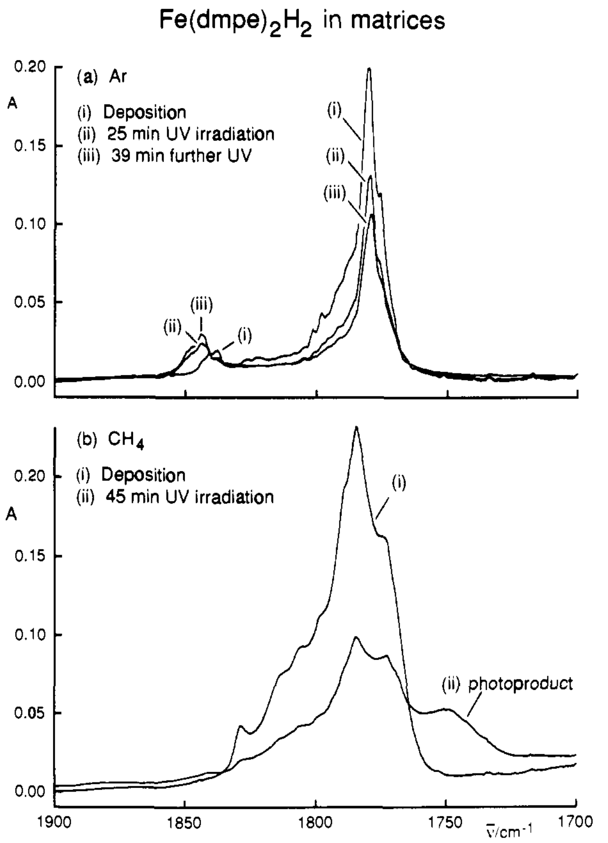

Figure 7. Matrix IR spectra of $Fe(dmpe)_2H_2$ in matrices at 12 K in the ν(FeH) region. (a) In an argon matrix: (i) after deposition; (ii) after 25 min of 295–390-nm irradiation; (iii) after 39 min of additional irradiation at the same wavelength. (b) In a methane matrix: (i) after deposition; (ii) after 45 min of irradiation ($\lambda > 295$ nm). The spectra in an argon matrix were recorded in the same experiment as for Figures 8 and 9.

In a $^{15}N_2/^{14}N_2$-doped argon matrix (1% $^{15}N_2$; 1.2% $^{14}N_2$) a band is observed at 1990 cm^{-1} (cf. 1991 cm^{-1} above), and a corresponding broad band is detected at ca. 1920 cm^{-1} for the $^{15}N_2$ analogue (calculated position 1922.7 cm^{-1}). These bands are assigned to ν(NN) of $Fe(dmpe)_2(^{14}N_2)$ and $Fe(dmpe)_2(^{15}N_2)$, respectively (cf. 1975 and 1917 cm^{-1}, respectively, in THF solution).[15] The analogous complex, $Fe(depe)_2(N_2)$ (depe = $Et_2PCH_2CH_2PEt_2$), has recently been characterized crystallographically.[16]

d. Photolysis in CH_4 Matrices. Irradiation of $Fe(dmpe)_2H_2$ in a methane matrix ($\lambda > 295$ nm, 45 min) causes 58% depletion of the ν(FeH) band at 1786 cm^{-1} and growth of a weaker feature at 1750 cm^{-1} (Figure 7b). Another product band develops at 1169 cm^{-1}. In the UV/vis spectrum a conspicuous shoulder forms at 372 nm. The complex is considerably more photosensitive in a CD_4 matrix. No product bands are observed near 1750 cm^{-1}, but bands appear at 1298 and 1289 cm^{-1} in the region expected for ν(FeD) modes. Additional product bands are formed at 1202, 1163, 1140, and 866 cm^{-1}.

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(15) Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862.

(16) The complex $Fe(depe)_2N_2$ has recently been characterized crystallographically, $\nu_{(NN)}$ = 1956 cm^{-1}, in KBr disk; the molecule adopts a trigonal bipyramidal structure analogous to that of $Ru(dmpe)_2CO$: Perthuisot, C.; Jones, W. D. Private communication. The same structure is reported in the following: Omiya, S.; Akita, M.; Yoza, A.; Kasuga, N.; Fukuoka, A.; Kai, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 787.

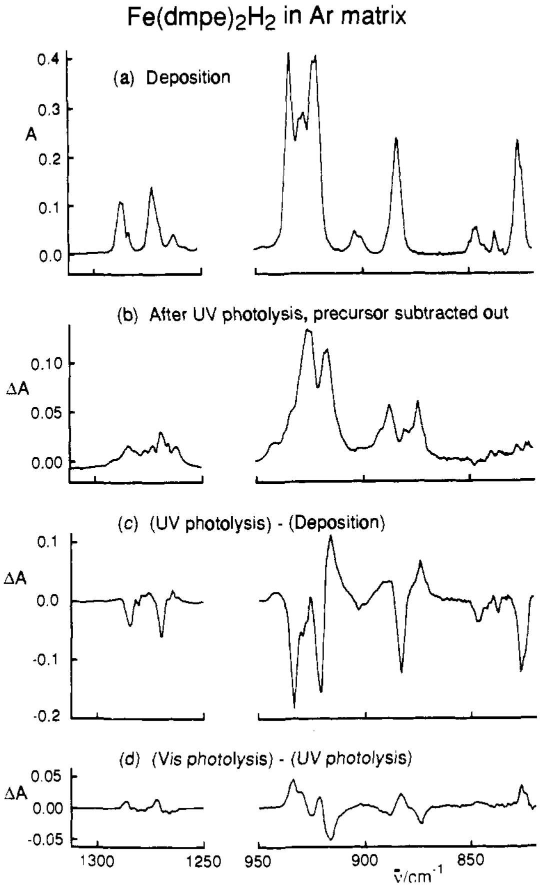


Figure 8. IR spectra of Fe(dmpe)$_2$H$_2$ in an argon matrix at 12 K in the regions 1330–1250 and 950–820 cm^{-1}. Spectra were *recorded* (i) after deposition; (ii) after 64 min of irradiation at 295–390 nm; (iii) after an additional 210 min of irradiation at 434 nm. The spectra *illustrated* are (a) spectrum i; (b) spectrum ii with remaining contribution from Fe(dmpe)$_2$H$_2$ subtracted out; (c) spectrum ii minus spectrum i, showing growth of product bands; (d) spectrum iii minus spectrum ii, showing partial regeneration of precursor.

Discussion

Sections 1 and 2 of the Discussion principally concern the evidence that the primary photoproduct both in transient solution experiments and in the argon matrix experiments is Fe(dmpe)$_2$. Reactivity toward alkanes and H$_2$ is included in section 2, reactivity toward other substrates and solvation in sections 3 and 4. Finally, we compare Fe(dmpe)$_2$ and Ru(dmpe)$_2$.

1. The Identity of the Matrix Photoproducts from Fe(dmpe)$_2$H$_2$. The matrix isolation work shows that photolysis of Fe(dmpe)$_2$H$_2$ in an argon matrix gives a photoproduct with a shoulder at ca. 380 nm but with no iron hydride absorptions in the IR. The matrix photoreaction is partially reversed by long-wavelength photolysis, behavior typical of a reaction which generates a coordinatively unsaturated product such as Fe(dmpe)$_2$. The alternative assignment of a cyclometallated structure is excluded by the absence of ν(FeH) bands for the product. Photochemical elimination of H$_2$ from iron dihydrides in matrices has been observed previously for FeH$_2$[17] and for Fe(CO)$_4$H$_2$; in the latter case the reaction is reversible.[18a] The electronic states involved in the photochemical reaction of Fe(CO)$_4$H$_2$ and the pathway for H$_2$ elimination have been identified by calculation of potential energy curves via contracted configuration interaction methods.[18b]

Photolysis in CO- or N$_2$-doped matrices leads to the formation of Fe(dmpe)$_2$CO and Fe(dmpe)$_2$N$_2$, respectively. This is perhaps the best evidence for the loss of H$_2$ and the formation of the 16-electron intermediate, Fe(dmpe)$_2$, in the matrix.

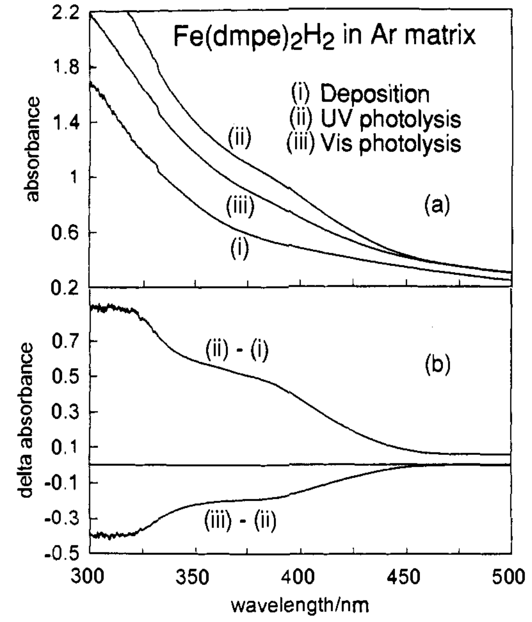
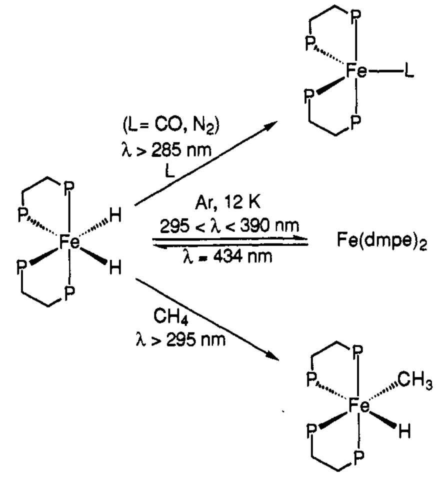


Figure 9. UV/vis spectra of Fe(dmpe)$_2$H$_2$ in an argon matrix at 12 K recorded in the same experiment as for Figure 8. The symbols i, ii, and iii refer to the same stages of the experiment as for Figure 8.

Scheme II. Matrix Photochemistry of Fe(dmpe)$_2$H$_2$



The methane matrix experiments provide evidence for insertion into a C–H bond of methane, as has been observed conclusively in solution.[10] It has also been established that photolysis of iron atoms in a methane matrix leads to (CH$_3$)FeH.[19] Several other organometallics have been found to react with methane photochemically in matrices.[20,21] The matrix photochemistry of Fe(dmpe)$_2$H$_2$ is summarized in Scheme II.

2. The Identity of the Transient Photoproduct from Fe(dmpe)$_2$H$_2$ and Its Reactions with Alkanes and Dihydrogen. Laser flash photolysis of Fe(dmpe)$_2$H$_2$ in alkane solution under an H$_2$ atmosphere generates a primary transient with a spectrum which

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[17] Ozin, G. A.; McCaffrey, J. G. *J. Phys. Chem.* **1984**, *88*, 645. See also: Rubinovitz, R. L.; Nixon, E. R. *Ibid.* **1986**, *90*, 1940.

[18] (a) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410. (b) Daniel, C. *J. Phys. Chem.* **1991**, *95*, 2394.

[19] Billups, W. E.; Konarski, M. M.; Hague, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.

[20] (a) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624. (b) Bloyce, P. E.; Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* **1988**, 846. (c) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181. (d) Bloyce, P. E.; Rest, A. J.; Whitwell, I. *J. Chem. Soc., Dalton Trans.* **1991**, 813.

[21] (a) McCamley, A.; Perutz, R. N.; Stahl, S.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1690. (b) Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810.

is the same whether recorded in cyclohexane or in pentane solution and which shows a broad maximum in the UV region at 355 nm (cf. 388 nm in argon matrix). In the absence of added reagents, the transient decays by pseudo-first-order kinetics over hundreds of milliseconds. It reacts with added dihydrogen with a second-order rate constant of 8.5×10^5 dm^3 mol^{-1} s^{-1}. We consider four possible assignments for the transient: (a) $Fe(dmpe)_2(\eta^2\text{-}H_2)$, (b) $Fe(dmpe)_2(alkyl)H$, (c) the cyclometalated product $HFe[CH_2(Me)PCH_2CH_2PMe_2](dmpe)$, and (d) $Fe(dmpe)_2$ [or a solvent adduct $Fe(dmpe)_2(alkane)$].

As 18-electron complexes, none of the possibilities a–c would be expected to show such a high reactivity toward H_2. Additionally, we know that $Fe(dmpe)_2(pentyl)H$ is stable enough at −30 °C for NMR observation.[9] The low-temperature flash experiments in pentane can be extrapolated to give an estimated lifetime of the transient of ca. 17 ms at −30 °C. Thus, it is much too short-lived to be an alkyl hydride complex. Intramolecular cyclometalation is established for $Fe(depe)_2$ but is unknown for $Fe(dmpe)_2$ complexes.[22] In contrast, all the evidence fits assignment d: the transient is $Fe(dmpe)_2$ or a solvent adduct $Fe(dmpe)_2(alkane)$.

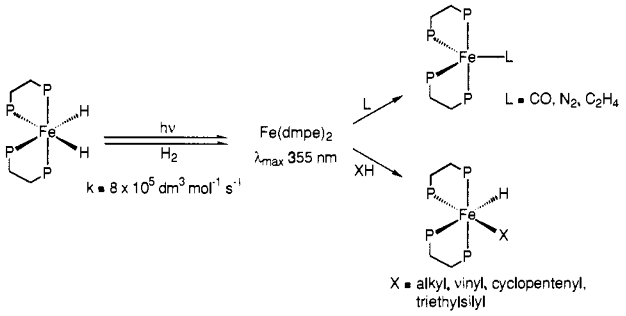
The major pathway for the decay of the transient in the absence of added H_2 fits reaction of $Fe(dmpe)_2$ with alkane solvent *to form* $Fe(dmpe)_2(alkyl)H$.[23] Second-order rate constants for this reaction, calculated with the aid of the solvent molarity (Table I), lie in the range $10\text{–}10^2$ dm^3 mol^{-1} s^{-1}. The observation of first-order kinetics excludes recombination of $Fe(dmpe)_2$ with photoejected H_2 as the *major* process since that would give second-order kinetics as for $Ru(dmpe)_2$.[12] However, there may be a contribution to the decay from the back-reaction with hydrogen. If so, the second-order rate constants in Table I would represent upper-limiting values for reactivity toward alkanes.

The variable temperature studies in pentane yield values for the enthalpy of activation for alkane C–H oxidative addition of 25.0 ± 5.7 kJ mol^{-1} and $\Delta S^{\ddagger} = -125 \pm 22$ J K^{-1} mol^{-1}, i.e. a major entropic contribution to the barrier. There are very few reports in the literature of such data, although Bergman and co-workers have reported an activation energy of 20.1 ± 0.8 kJ mol^{-1} for the activation of the C–H bond in cyclohexane by $(\eta^5\text{-}C_5Me_5)Rh(CO)$.[24]

No significant effect upon the rate of decay of the transient in alkane solution is observed on changing from $Fe(dmpe)_2H_2$ to the deuterated complex $Fe(dmpe\text{-}d_{12})_2H_2$. Significant kinetic isotope effects have been reported elsewhere for the cleavage of agostic M···CH bonds.[25a] The absence of such a kinetic isotope effect for $Fe(dmpe)_2$ cannot be taken to exclude agostic interaction with the dmpe methyl group, but it certainly does not support such an effect. There is also barely any kinetic isotope effect when substrate H_2 is replaced by D_2 or C_6H_{12} by C_6D_{12}. These experiments indicate that there is very little H–H or C–H bond extension in the transition state for oxidative addition of H_2 or cyclohexane to $Fe(dmpe)_2$.

3. The Reactions of Fe(dmpe)₂ with CO, N₂, Alkenes, and Triethylsilane. Reaction of $Fe(dmpe)_2$ with CO proceeds extremely rapidly, and the second-order rate constant of 2×10^9 dm^3 mol^{-1} s^{-1} is a factor of ca. 13 below the diffusion-controlled limit (the experimental value in cyclohexane is 2.81×10^{10} dm^3 mol^{-1} s^{-1}).[25b] Since the carbonyl complex $Fe(dmpe)_2CO$ has a singlet ground state, the rate constant for reaction with CO favors a singlet ground state for $Fe(dmpe)_2$ but is not large enough to be decisive. $Ru(CO)_4$, $Os(CO)_4$, and $Ru(dmpe)_2$ have singlet ground states,[12,26] whereas the triplet ground state of $Fe(CO)_4$ results in a much slower reaction with CO ($k_2 = 3.5 \times 10^7$ dm^3 mol^{-1} s^{-1}).[26] The reaction of $Fe(dmpe)_2$ with CO has been investigated using laser flash photolysis with both UV/vis and IR detection. The rate constants found for loss of $Fe(dmpe)_2$ in the UV/vis studies and the growth of the carbonyl complex by IR are in very close agreement. The time-resolved IR spectrum demonstrates conclusively that $Fe(dmpe)_2CO$ is formed directly from transient $Fe(dmpe)_2$. The same photoproduct is also observed in CO-doped matrices.

Scheme III. Transient Photochemistry of $Fe(dmpe)_2H_2$: Reactivity toward H_2, CO, N_2, Alkanes, Alkenes, and Triethylsilane



The rate of reaction of $Fe(dmpe)_2$ with N_2 is much smaller than with CO (Table IV). The formation of $Fe(dmpe)_2N_2$ in the reaction is demonstrated by the IR evidence from N_2-doped matrix experiments.

The transient is quenched by cyclopentene with a second-order rate constant of ca. 10^5 dm^3 mol^{-1} s^{-1}. Previous NMR studies have shown that photolysis of $Fe(dmpe)_2H_2$ in the presence of cyclopentene yields $Fe(dmpe)_2(cyclopentenyl)H$. The quenching of the transient with ethene occurs with a rate constant similar to that for cyclopentene, although it is probably composed of the sum of the rate constants for coordination of the alkene to form a π-complex and oxidative addition to form the vinyl hydride complex, $Fe(dmpe)_2(CH{=}CH_2)H$.[8]

The reaction of $Fe(dmpe)_2$ with Et_3SiH is also rapid. By comparison with the thermal reaction of $Fe(dmpe)_2(naphthyl)H$ with Me_3SiH,[4b] we presume formation of the oxidative addition product *cis*-$Fe(dmpe)_2(SiEt_3)H$. When compared to the C–H activation reaction in pentane, the activation parameters reveal a similar value of $\Delta H^{\ddagger}$ but a substantial decrease in $\Delta S^{\ddagger}$. The transient photochemistry of $Fe(dmpe)_2H_2$ is summarized in Scheme III.

4. Role of Solvation in the Reactions of Fe(dmpe)₂: Reactions with Arenes. It is now well established that specific solvent coordination is crucial to the chemistry of $Cr(CO)_5$ and related complexes even in alkane solvents.[27–34] There is also substantial

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[22] Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821.

[23] Ultimately, $Fe(dmpe)_2(alkyl)$ H must decay, but this process will occur on a slower time scale than can be measured by laser flash photolysis.

[24] Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimentel, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288. Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315.

[25] (a) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429. Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Inorg. Chem.* **1989**, *28*, 4285. (b) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1.

[26] (a) Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1983**, *79*, 1089. (b) Seder, T. A.; Ouderkirk, A. J.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 1977. (c) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1989**, *111*, 3163. (d) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1990**, *112*, 639. (e) Ryther, R. J.; Weitz, E. *J. Phys. Chem.* **1991**, *95*, 9841. (f) Hayes, D. M.; Weitz, E. *Ibid.* **1991**, *95*, 2723. The kinetic data could be reconciled with a triplet ground state for $Fe(dmpe)_2$ with a transmission coefficient close to unity for reaction with CO. In contrast, transmission coefficients for all other reactions would be less than 1.

[27] Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

[28] Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

[29] Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 2530.

[30] Sprague, J. R.; Arrivo, S. M.; Spears, K. G. *J. Phys. Chem.* **1991**, *95*, 10528.

[31] Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

[32] Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344. Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751. Joly, A. G.; Nelson, K. K. *Chem. Phys.* **1991**, *152*, 69.

evidence that alkane complexes are formed prior to the C–H insertion reactions of (η^5-C$_5$Me$_5$)Rh(PMe$_3$) and (η^5-C$_5$R$_5$)Rh(CO) (R = H, Me).[24,35] We can define three overall types of solvent effects which may be important in reactions of Fe(dmpe)$_2$: (i) general solvation, (ii) specific solvation, and (iii) oxidative addition of the solvent.

The third effect can be separated from the first two by comparing the rates of reaction of Fe(dmpe)$_2$ with pure alkanes to the rates of reaction with cyclopentene dissolved in the same alkanes (Table I). The rate constant for the reaction of Fe(dmpe)$_2$ with cyclopentene in *n*-pentane is 2.1 times faster than that for reaction with cyclopentene in cyclohexane. The rate of direct reaction with *n*-pentane is 4.7 times faster than that with cyclohexane. Thus, the general and specific solvent effects can account for the factor of 2.1 in the sensitivity of rate constants to alkanes, leaving a factor of 2.2 for effects of oxidative addition. The effects of specific solvation and general solvation are not distinguishable kinetically, but a factor of 2.1 (<2 kJ mol^{-1}) is well within the bounds of general solvent effects. The matrix UV spectra of Fe(dmpe)$_2$ do not provide clear evidence regarding specific solvation. The absorption maximum determined by flash photolysis is the same in cyclohexane, pentane, or even benzene.

The reaction of Fe(dmpe)$_2$ with arenes appears to be quite complex. The saturation behavior in cyclohexane/benzene and cyclohexane/toluene solutions implies the presence of a rapid preequilibrium step. The reaction kinetics with benzene or toluene can be explained if Fe(dmpe)$_2$, or a weak Fe(dmpe)$_2$(alkane) complex, reacts with the arene to yield an arene complex, which then goes on to form an aryl hydride species. In Scheme IV we have assumed the involvement of Fe(dmpe)$_2$(alkane). Kinetic analysis of Scheme IV may be simplified since the reaction with benzene overwhelms reaction with the alkane even at a concentration of benzene as low as 5 × 10^{-2} mol dm^{-3}. We therefore neglect the role of k_1 in Scheme IV.

$$\text{rate of product formation} = k_2[\mathrm{B}] \tag{1}$$

$$K = [\mathrm{B}][\mathrm{C_6H_{12}}]/\{[\mathrm{A}][\text{arene}]\} \tag{2}$$

We define a mole fraction term X, where

$$X = [\text{arene}]/\{[\text{arene}] + [\mathrm{C_6H_{12}}]\}$$

so

$$[\mathrm{C_6H_{12}}]/[\text{arene}] = (1 - X)/X$$

Substituting this expression into eq 2 and rearranging gives

$$[\mathrm{B}] = K[\mathrm{A}]X/\{1 - X\} \tag{3}$$

If [Fe$_{\text{tot}}$] = [A] + [B], substituting into eq 3 and rearranging gives

$$[\mathrm{B}] = [\mathrm{Fe_{tot}}]KX/(1 + \{K - 1\}X)$$

Hence,

$$k_{\text{obs}} = k_2KX/\{1 + (K - 1)X\} \tag{4}$$

and

$$X/k_{\text{obs}} = \{1 + (K - 1)X\}/k_2K \tag{5}$$

Thus, a plot of X/k_{obs} against X should give a straight line with a slope of $(K - 1)/(k_2K)$ and an intercept of $1/(k_2K)$. The equilibrium constant, K, can thus be found from the ratio of slope to intercept:

	benzene	toluene
K	4.75 ± 0.65	3.32 ± 0.2
k_2, s^{-1}	(9.56 ± 0.35) × 10^5	(8.99 ± 0.15) × 10^5

The analysis of rates of reaction in cyclopentene/alkane solutions and the values of K derived here suggest that Fe(dmpe)$_2$ is very weakly solvated in either alkane or arene solution. It is possible to analyze the kinetics assuming Fe(dmpe)$_2$ in place of Fe(dmpe)$_2$(alkane) without affecting the principal conclusions. Carbon monoxide is able to react with the iron complex with a rate constant of 10^9 dm^3 mol^{-1} s^{-1}, regardless of the presence of any weakly coordinating alkane ligand. The lack of kinetic impact of such specific solvation may reflect both its weakness and the fact that a Fe(dmpe)$_2$(solvent) molecule is still only 5-coordinate and hence vulnerable to attack.[36] It is also apparent that any M(η^2-arene) species plays a much more minor role as an intermediate en route to the aryl hydride product than is the case for (η^5-C$_5$H$_5$)Rh and (η^5-C$_5$Me$_5$)Rh half-sandwich systems.[37,38]

5. Comparison of Ru(dmpe)$_2$ and Fe(dmpe)$_2$. We showed previously that Ru(dmpe)$_2$ has a UV/vis spectrum with *three prominent bands* ranging from 750 to 450 nm.[12] It reacts with H$_2$ and CO at rates close to the diffusion-controlled limit and with N$_2$, cyclopentene, PMe$_3$, Et$_3$SiH, and Me$_3$CNC with second-order rate constants in the range 10^9–10^7 dm^3 mol^{-1} s^{-1}. No reaction with benzene could be observed, apparently because of the failure to complete with the rapid back-reaction with hydrogen. There was no evidence for reaction of Ru(dmpe)$_2$ with alkanes. The spectrum of Ru(dmpe)$_2$ was tentatively interpreted in terms of a square-planar ground state.[12]

The complex Fe(dmpe)$_2$ contrasts sharply with Ru(dmpe)$_2$ both spectroscopically and in its reactivity (Scheme V). Fe(dmpe)$_2$ has only one UV/vis band, and it is at very short wavelength (355 nm in solution, 388 nm in Ar matrix). The rate constant for reaction with hydrogen is *ca. 7500 times smaller* than that for Ru(dmpe)$_2$. The rate constant for reaction of Fe(dmpe)$_2$ with Et$_3$SiH is reduced by a similar factor. The activation parameters for this reaction reveal a substantial increase in enthalpy and a larger loss in entropy in the transition state for iron when compared to ruthenium (Ru(dmpe)$_2$: $\Delta H^{\ddagger}$ = 8.9 ± 1.1 kJ mol^{-1}, $\Delta S^{\ddagger}$ = –53 ± 4 J K^{-1} mol^{-1}. Fe(dmpe)$_2$: $\Delta H^{\ddagger}$ = 22.4 ± 1.8 kJ mol^{-1}, $\Delta S^{\ddagger}$ = –87 ± 6 J K^{-1} mol^{-1}). The resultant value of $\Delta G^{\ddagger}{}_{298}$ is twice as large for iron as for ruthenium. The reactions with benzene and toluene are readily observed and have rate constants of ca. 10^6 dm^3 mol^{-1} s^{-1}. Fe(dmpe)$_2$ also reacts with alkanes with second-order rate constants in the range 10–10^2 dm^3 mol^{-1} s^{-1}. Perhaps the only common feature is the near-diffusion-controlled reaction with CO. The rate constants for the reactions of Fe(dmpe)$_2$ span 7 orders of magnitude, indicating considerable selectivity in spite of its high reactivity; those of Ru(dmpe)$_2$ span less than 3 orders of magnitude.

These differences lead us to conclude that Fe(dmpe)$_2$ must have a different geometry from Ru(dmpe)$_2$, although the spectra

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[36] In contrast, Cr(CO)$_5$(C$_6$H$_{12}$) shows much reduced reactivity toward CO compared to Cr(CO)$_5$ in C$_7$F$_{14}$.[32]

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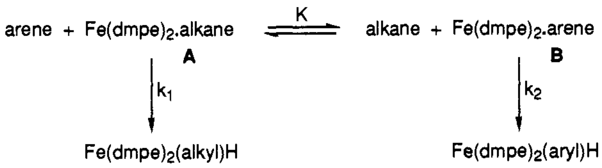
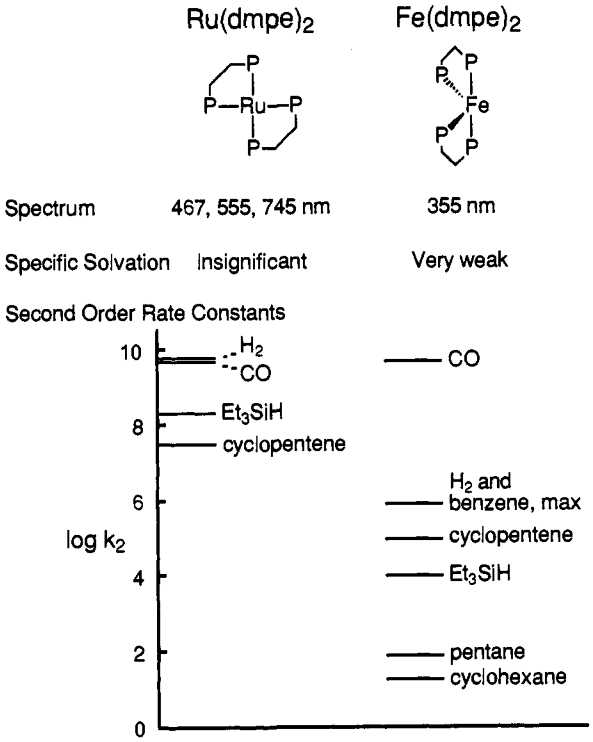
Scheme IV. Kinetic Scheme for Reactions of Fe(dmpe)$_2$ in Arene/Alkane Mixtures



Scheme V. Comparison of Reactivity and Spectra of Fe(dmpe)$_2$ and Ru(dmpe)$_2$



provide no direct evidence as to the exact structure. A singlet electronic ground state is compatible with a D_{4h} square-planar geometry, a D_{2d} geometry, or a C_{2v} geometry as proposed by Ziegler et al. for Ru(CO)$_4$.[39] A C_{2v} or D_{2d} structure could also be associated with a triplet ground state. A C_{2v} structure would differ from that of Ru(dmpe)$_2$, allowing weak solvation and rapid attack by CO possibly from the back side. "Naked" Fe(CO)$_4$ has a C_{2v} structure with a triplet ground state, but the solvent-stabilized S···Fe(CO)$_4$ (S = Xe, CH$_4$) probably has a singlet ground state with bond angles of 125° and 175°, resembling that postulated for Fe(dmpe)$_2$.[40] Theoretical investigations also suggest that a C_{2v} intermediate is needed for alkane activation.[41]

Conclusions

1. Laser flash photolysis of Fe(dmpe)$_2$H$_2$ in alkane solution at room temperature generates a single transient, which is demonstrated to be Fe(dmpe)$_2$. The evidence indicates that any specific solvation has a minimal kinetic effect. The same Fe(dmpe)$_2$ fragment is formed in argon matrices. The UV/vis spectrum of the transient shows a broad maximum at 355 nm in solution and a similar spectrum in an argon matrix. Fe(dmpe)$_2$ reacts with alkanes in solution and in matrices to yield Fe(dmpe)$_2$(alkyl)H.

2. The experiments have enabled us to measure the rates of binding of a coordinatively unsaturated fragment in solution to N$_2$ and CO, and the rates of oxidative addition of H$_2$, alkenes, arenes, alkanes, and triethylsilane to the same species. The activation parameters are reported for the last two reactions. The entropy of activation makes a major contribution to the barrier to the reaction with pentane.

3. The transient shows saturation kinetics in mixed arene/alkane solutions (arene = benzene or toluene). The kinetic behavior is interpreted in terms of a rapid preequilibrium between Fe(dmpe)$_2$ or Fe(dmpe)$_2$(alkane) and a loosely bound arene complex. The arene complex then reacts to form an aryl hydride complex in the slow step.

4. Reaction with CO proceeds at a near-diffusion-controlled rate. The rate constant for reaction with H$_2$ is a factor of 10^4 lower than that with CO. The product of reaction with CO is identified as Fe(dmpe)$_2$CO both by time-resolved IR spectroscopy in solution and by matrix isolation.

5. Fe(dmpe)$_2$ differs from Ru(dmpe)$_2$ drastically in its spectra and reactivity.

Experimental Section

Materials. Gases for matrix isolation and flash photolysis experiments were of research grade (BOC). Deuterium was obtained from the same source with isotopic purity 99.7%. Solvents for flash photolysis (Aldrich HPLC grade) were dried over CaH$_2$ under argon. Cyclopentene (Fluka, Puriss >99.5%) and triethylsilane (Fluka >99%) were distilled under nitrogen and stored over grade 3A molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. Iodomethane-*d*$_3$ (Aldrich, 99.5%) was used without further purification.

Synthesis of *cis*-Fe(dmpe)$_2$H$_2$ and Isotopically Labeled Analogues. *trans*-Fe(dmpe)$_2$Cl$_2$ and Cl$_2$PCH$_2$CH$_2$PCl$_2$ were synthesized by literature methods.[42,43]

***cis*-Fe(dmpe)$_2$H$_2$ and *cis*-Fe(dmpe)$_2$D$_2$.** A solution of *trans*-Fe(dmpe)$_2$Cl$_2$ (0.1 g, 0.26 mmol) in THF (15 cm^3) was added via a cannula to a suspension of an excess of LiAlH$_4$ in THF. The mixture was stirred under H$_2$ for 1 h. The THF was removed in vacuo and the residue extracted exhaustively with warm pentane. The solvent was removed from the combined extracts, and the residue was sublimed at 40–50 °C (10^{-4} mbar) onto a finger kept at 0 °C to yield *cis*-Fe(dmpe)$_2$H$_2$ as a pale yellow solid. The purity was checked by comparison with published ^{1}H and ^{31}P NMR data.[6] Fe(dmpe)$_2$D$_2$ was synthesized by shaking Fe(dmpe)$_2$H$_2$ (0.02 g, 0.06 mmol) with CD$_3$OD (3 × 5 cm^3). The solvent was removed in vacuo and the dideuteride purified as above.

Dmpe-*d*$_{12}$. Dmpe-*d*$_{12}$ was synthesized by a procedure analogous to that for dmpe.[43] A solution of iodomethane-*d*$_3$ (25 g, 170 mmol) in dry ether (40 cm^3) was added slowly to a suspension of magnesium filings (5 g, 210 mmol) in dry ether (80 cm^3) at a rate sufficient to maintain reflux. The solution was cooled to -10 °C, and Cl$_2$PCH$_2$CH$_2$PCl$_2$ (7 g, 30 mmol) was added while the temperature was maintained between -10 and -5 °C. The mixture was allowed to warm to room temperature, stirred for 16 h, and cooled to 10 °C and the excess Grignard reagent hydrolyzed with saturated ammonium chloride solution, until all of the precipitate dissolved. The product was extracted into ether (3 × 50 cm^3), dried over sodium sulfate, and concentrated to a volume of 5–10 cm^3 by distillation of the ether at atmospheric pressure.

***trans*-Fe(dmpe-*d*$_{12}$)$_2$Cl$_2$.** *trans*-Fe(dmpe-*d*$_{12}$)$_2$Cl$_2$ was synthesized by adding the ethereal solution of dmpe-*d*$_{12}$ dropwise over 5 min to a stirred suspension of anhydrous iron(II) chloride (1.0 g, 8 mmol) in benzene (50 cm^3) at room temperature. A further portion of benzene (20 cm^3) was added and the mixture stirred overnight. The dark green mixture was filtered and the solvent removed in vacuo. The crude product was recrystallized from benzene to give *trans*-Fe(dmpe-*d*$_{12}$)$_2$Cl$_2$ as a green crystalline solid (2.3 g, 34% based on starting Cl$_2$PCH$_2$CH$_2$PCl$_2$): mp 280–285 °C dec; NMR ^{1}H (C$_6$D$_6$) δ 1.95 (m, 4 × CH$_2$), 1.48 (s, <1%, CH$_3$); ^{31}P δ 57.4 (cf. δ 58.6 for undeuterated analogue); MS *m/z* 450 (M$^+$, 40), 144 (85), 134 (92), 116 (98), 69 (85), 67 (94), 63 (95), 59 (72), 49 (67), 47 (100).

***cis*-Fe(dmpe-*d*$_{12}$)$_2$H$_2$.** A saturated solution of lithium aluminum hydride (0.35 mol dm^{-3} in THF) was added in small portions to a solution of *trans*-Fe(dmpe-*d*$_{12}$)$_2$Cl$_2$ (1.0 g, 2 mmol) in THF (50 cm^3). The reaction was monitored by ^{31}P NMR and the addition continued until no starting

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material or *trans*-Fe(dmpe-d_{12})$_2$(H)Cl remained. The solvent was removed in vacuo and the residue extracted exhaustively with hot pentane. The combined extracts were stripped of solvent in vacuo, and the resultant residue was sublimed (60 °C, 10^{-5} mmHg) onto a cold finger (−78 °C) to give *cis*-Fe(dmpe-d_{12})$_2$H$_2$ as a pale yellow powder (0.41 g, 49%): NMR ^{31}P (THF) δ 76.6 (apparent triplet, splitting 25.4 Hz), 67.7 (apparent triplet, splitting 25.4 Hz) (cf. δ 78.0 and 69.0 for undeuterated analogue); ^{1}H (C$_6$D$_6$) δ −13.95 (m, 2H, FeH) (cf. δ −13.93 for undeuterated analogue).

Laser Flash Photolysis. The apparatus for laser flash photolysis has been described previously.[12,44] In brief, a XeCl laser (308 nm, 30 ns pulse width, 40 mJ pulse^{-1}) is used as the exciting source, and a pulsed Xe arc is used as the monitoring source. The spectrometer is linked to a digital oscilloscope, and the entire system is controlled by a microcomputer. Transient signals are usually collected as 16-shot averages. The rise time of the apparatus is 50–100 ns. Some transient spectra including Figure 4 were recorded on a very similar apparatus in Ottawa, which had a shorter rise time (ca. 30 ns).[12]

Samples for flash experiments were sublimed immediately before use and, in a glovebox, loaded into a quartz cuvette (1-, 2-, or 10-mm path length) fitted with a PTFE stopcock and degassing bulb. Solvent was added via a cannula on a Schlenk line evacuated by a diffusion pump to 10^{-4} mbar and filled with argon. The sample was degassed by three freeze–pump–thaw cycles before back-filling to 1 atm with the appropriate gas. Gas mixtures were made up manometrically in 1-L bulbs, so that the pressure in the flash cell was typically 700 Torr. Solutions with liquid quenchers were made up by addition of quencher to the cuvette with a microliter syringe. The absorbances of the solutions were in the range 0.5–1.0 at 308 nm. Variable temperature measurements were made with an insulated sample holder through which thermostated water was circulated.

Time-Resolved Infrared Spectroscopy. Time-resolved infrared experiments were performed with the Nottingham apparatus, which has been described previously. The sample was flowed through the IR cell under a CO atmosphere. The pump beam came from an excimer laser (308 nm, Lumonics Hyper-Ex 440). The sample was probed with infrared radiation from a CO laser (Edinburgh Instruments PL3) and detected by an MCT detector (Laser Monitorings S-0025).[45]

Matrix Isolation Methods. The matrix isolation apparatus has been described previously.[21b] Samples were deposited onto a BaF$_2$ window cooled by an Air Products CS202 closed-cycle refrigerator to 12–25 K. The outer windows were also of BaF$_2$, enabling UV/vis spectra (Perkin-Elmer Lambda 7G with data station) or IR spectra (Mattson Sirius or Mattson RS, 1-cm^{-1} resolution, 4000–800 cm^{-1}) to be recorded on the same sample. IR spectra were recorded down to 400 cm^{-1} with CsI outer and inner windows. Matrices were photolyzed with a Philips HPK 125-W mercury arc equipped with a quartz focusing lens, a water filter, and appropriate cutoff or interference filters. For deposition, the side arm with Fe(dmpe)$_2$H$_2$ was held at ca. 317 K with the central window maintained at 20 K for Ar matrices and 25 K for methane matrices. The window was cooled to 12 K before recording spectra or irradiation. A typical deposition time was 2 h with matrix gas deposited at ca. 1.7 mmol h^{-1}.

Acknowledgment. We are grateful to Prof. W. D. Jones for helpful discussions and a gift of Fe(dmpe)$_2$Cl$_2$. We also acknowledge the support of The Royal Society, SERC, NATO, British Gas, and the EC Commission.

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