Low-Temperature-Matrix and Room-Temperature-Solution Photochemistry of Ru(CO)₃(dmpe) (dmpe = Me₂PCH₂CH₂PMe₂)[†]

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The photochemistry of Ru(CO)₃(dmpe) (**II**; dmpe = Me₂PCH₂CH₂PMe₂), has been studied by matrix isolation at 12 K and laser flash photolysis with UV–visible and IR detection at ambient temperature. UV photolysis in a matrix results in the formation of Ru(CO)₂(dmpe)·S (S = matrix host), which shows two distinctive UV–visible bands with λ_{max} dependent on S (Ar, 410, 600 nm; CH₄, 357, 500 nm; Xe, 345, 457 nm). These shifts are the largest yet observed for any matrix-solvated species. The reactions are partially reversed by long-wavelength ($\lambda > 420$ nm) photolysis. Laser flash photolysis in heptane solution ($\lambda_{exc} = 266$ or 308 nm) with IR or UV–visible detection reveals that Ru(CO)₂(dmpe)·heptane is a short-lived fragment which decays rapidly by reaction with Ru(CO)₃(dmpe) ($k_2 \approx 1 \times 10^9$ dm³ mol⁻¹ s⁻¹). Steady-state photolysis of **II** in heptane in the presence of hydrogen or triethylsilane yields Ru(CO)₂(dmpe)H₂ and Ru(CO)₂(dmpe)(SiEt₃)H, respectively, which have been characterized by IR and NMR spectroscopy.

Introduction

The interaction of coordinatively unsaturated transition-metal complexes with H–H, Si–H and C–H bonds to give σ complexes is well established.[1] Following isolation of dihydrogen[2] and silane[3] complexes, we and others have searched for alkane complexes which are stable at room temperature. Until this goal is achieved, the direct observation of such species will require low-temperature matrix isolation and time-resolved spectroscopic methods (either solution or gas phase).[4] The application of both of these techniques to the same problem provides a very powerful tool and has allowed the initial observations on the first known example of an alkane complex, Cr(CO)₅(CH₄),[4a] to be extended from a matrix to solution to yield values for the rate of

reaction of naked Cr(CO)₅ with alkane[5] and also the Cr–alkane bond energy.[6] The use of time-resolved spectroscopy in conjunction with liquefied noble gases and supercritical fluids has allowed kinetic measurements to be made on M–alkane together with M–Xe and M–Kr complexes.[7]

We have recently reported[8] that photolysis of Ru(CO)₂(PMe₃)₂H₂ or Ru(CO)₃(PMe₃)₂ in matrices resulted in loss of CO and the formation of the 16-electron complex Ru(CO)₂(PMe₃)₂ (**I**). The binding of the matrix host in the vacant fifth coordination site of the complex was shown by the large perturbation in the UV–visible spectrum of the complex upon changing from argon (423 nm) through methane (385 nm) to xenon (352 nm), such that the molecule was better represented as the specifically solvated species Ru(CO)₂(PMe₃)₂·S. This behavior is similar to that originally reported for M(CO)₅·S (M = Cr, Mo, W), although the shifts in the energy of the absorption band for the d⁸ ruthenium complex are much larger than those observed for d⁶ Cr(CO)₅·S (S = Ar to Xe: 4770 cm⁻¹ for Ru(CO)₂(PMe₃)₂·S, 1560 cm⁻¹ for Cr(CO)₅·S).[4a]

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Whereas $Ru(CO)_2(PMe_3)_2$ is only stable in a matrix at 12 K, Caulton, Eisenstein and co-workers have reported that the related 16-electron complex $Ru(CO)_2$-$(P^tBu_2Me)_2$ can be isolated and characterized by X-ray crystallography at room temperature.[9] The structure shows *trans* axial phosphine ligands and a bond angle of 133° between the CO groups, very similar to the structure which we proposed for **I**. Although the stability of $Ru(CO)_2(P^tBu_2Me)_2$ is clearly due to the bulk of the phosphine ligands protecting the metal center, the nonplanar geometry arises from a stabilization of the high-energy d orbitals associated with Ru(0) by strong $\pi^*(CO)$ interactions. The importance of π-acceptor ligands in influencing the geometry of RuL_4 complexes is shown by the nonplanar structures adopted by $Ru(CO)_4$[10] and $Ru(CO)_2L_2$ (L = phosphine), in contrast to square-planar $Ru(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2$-PMe_2).[11]

We now report our studies on the matrix and solution photochemistry of $Ru(CO)_3(dmpe)$ (**II**), and the detection of the 16-electron complex $Ru(CO)_2(dmpe)\cdot S$ (S = solvent). The constrained bidentate ligand forces the phosphines to adopt *cis* positions such that the geometry of the intermediate solvent complex has to be different from that of **I**. Indeed, the shifts in the UV−visible absorption bands upon changing the matrix are even larger than those observed for **I**.

Results

1. Preparation and Characterization of Ru-(CO)₃(dmpe) (II). The starting complex was prepared in a manner similar to that for $Ru(CO)_3(dppe)$,[12] by heating $Ru_3(CO)_{12}$ with a 3-fold quantity of the phosphine at 65 °C for 1 week under 8 bar of CO. Complex **II** was readily purified to give a pale yellow solid by crystallization from hexane at −20 °C or sublimation onto an ice-cooled finger at 60 °C. The compound was characterized using standard spectroscopic and analytical techniques. The IR spectrum in hexane solution showed three strong bands in the carbonyl region at 2005, 1934, and 1915 cm⁻¹, at lower frequency than those of either $Ru(CO)_3(dppe)$[12] or $Ru(CO)_3(dfepe)$[13] (dppe = $Ph_2PCH_2CH_2PPh_2$, dfepe = $(C_2F_5)_2PCH_2CH_2P$-$(C_2F_5)_2$), reflecting the more potent σ-donating dmpe ligand. Although none of these complexes have been characterized crystallographically, an axial−equatorial coordination of the bidentate phosphine has been established in $Fe(CO)_3(dppe)$.[14] This geometry is also likely for $Ru(CO)_3(dmpe)$ and is consistent with the appearance of three carbonyl bands of similar intensity in the IR spectrum. The axial−equatorial arrangement of the phosphines appears to be favored over equatorial−equatorial substitution on the basis of reduced strain in the PCH_2CH_2P backbone. The $^{31}P\{^1H\}$ NMR
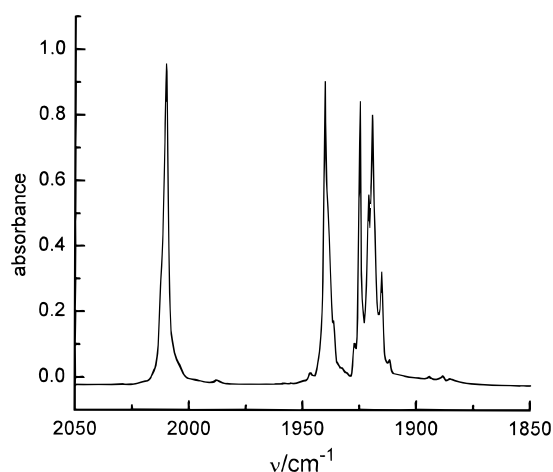
Figure 1. IR spectrum of $Ru(CO)_3(dmpe)$ (**II**) isolated in an argon matrix at 12 K.

spectrum of **II** exhibits a singlet at δ 40, and the ^{13}C-$\{^1H\}$ NMR spectrum shows a single carbonyl resonance at δ 213, split into a triplet by ^{31}P coupling. Similar NMR spectra indicating a fluxional molecule undergoing rapid rearrangement have been found for related $Fe(CO)_3(P-P)$ (P-P = dmpe, dfepe) complexes.[15]

2. Photochemistry of II in Low-Temperature Argon Matrices. The IR spectrum of **II** in an argon matrix at 12 K exhibited three bands in the carbonyl stretching region at 2010, 1943, and a split feature with components at 1925 and 1918 cm⁻¹ (Figure 1, Table 1) and bands at lower frequency assigned to the dmpe ligand.[16] The UV−visible absorption spectrum of the pale yellow complex in the same matrix was broad and featureless.

Filtered UV photolysis (λ = 234−376 nm, 45 min) resulted in a 40% depletion of all three carbonyl bands and formation of two new bands at 1966 and 1904 cm⁻¹ (integrated intensity ratio 1.0:0.82) (Table 1). A band for free CO (2138 cm⁻¹) was also observed. No new bands were observed in the low-frequency region of the spectrum. The UV−visible spectrum showed the appearance of two new strong bands in the visible region at 410 and 600 nm in an approximate ratio of 2:1 (Figure 2).

Long-wavelength photolysis (λ = 420−450 nm, 80 min), designed to select the red side of the higher energy visible band, resulted in the depletion of both visible bands. The IR spectrum showed a decrease in the bands at 1966 and 1904 cm⁻¹ and growth of the starting material bands. In a separate experiment, initial UV photolysis was followed by irradiation into the long-wavelength visible band (λ > 580 nm, 900 min) and resulted in similar observations in both the IR and UV−visible spectra. The reversibility of the photochemistry upon long-wavelength photolysis and the positions of the product bands are consistent with the formation of a coordinatively unsaturated 16-electron complex.[17]

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(16) IR bands for Ru(CO)₃(dmpe) in an argon matrix at 12 K (cm⁻¹): 2980 w, 2910 w, 2010 vs, 1940 vs, (1925, 1921, 1918, 1915) vs, 1420 m, (1302, 1298) w, (1288, 1284) m, (948, 942, 934) s, 911 w, 894 m, 834 m. Values in parentheses denote components of a band that is matrix-split.
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Table 1. Wavenumbers of Carbonyl Bands Recorded in IR Spectra in Matrices and Solution (ν/cm^{-1})

species	Ar matrix, 12 K	CH$_4$ matrix, 12 K	Xe matrix, 35 K	alkane solution, 293 K
Ru(CO)$_3$(dmpe)	2010, 1940, 1925,[a] 1918[a]	2007, 1933, 1913	2005, 1932, 1909	2005, 1934, 1915[b] 2009, 1933, 1912[c]
Ru(CO)$_2$(dmpe)·S	1966, 1904	1963, 1898	1960, 1896	1962, 1898[c]
Ru(CO)$_2$(dmpe)H$_2$	2022, 1973[d]			2017, 1968[b]
Ru(CO)$_2$(dmpe)(SiEt$_3$)H				2006, 1961[b]

[a] Principal components of a band which is matrix-split. [b] Hexane. [c] TRIR experiments in heptane. [d] H$_2$-doped Ar matrix.
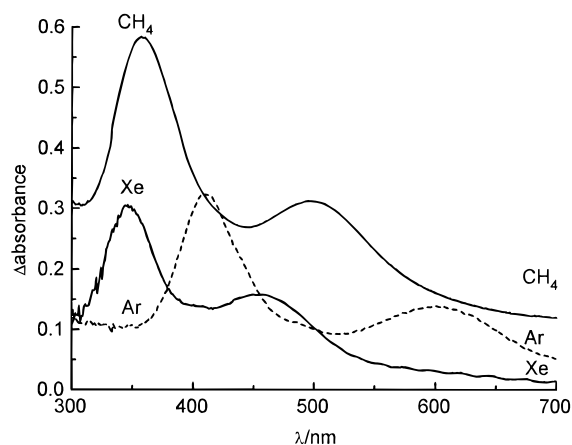
Figure 2. UV−visible spectra of Ru(CO)$_2$(dmpe)·S for S = Ar, CH$_4$, and Xe. The spectra were obtained by subtraction of the deposition spectrum from that recorded after UV photolysis.

The IR data suggest that photolysis of Ru(CO)$_3$(dmpe) results in loss of CO and the formation of Ru(CO)$_2$-(dmpe), which displays two carbonyl bands of similar intensity, indicating a *cis* stereochemistry. A bond angle of 84° between the carbonyl ligands is calculated from the intensity ratio.[18] The assignment of both visible bands to Ru(CO)$_2$(dmpe) is clearly established from the selective photolysis experiments.

3. Photolysis of II in Low-Temperature Methane and Xenon Matrices. Complex **II** proved to be more photosensitive in a methane matrix than in argon. Filtered UV photolysis (λ = 234−376 nm, 10 min) resulted in a 50% loss of the carbonyl bands of the starting material at 2007, 1933 and 1913 cm^{-1} (Table 1) and the appearance of two new bands at 1963 and 1898 cm^{-1} (Figure 3a, Table 1). The UV−visible spectrum showed two bands at 357 and 500 nm (Figure 2). Selective photolysis (λ = 490−509 nm, 300 min) resulted in depletion of the photoproduct bands at 357 and 500 nm in the UV−visible spectrum, loss of the IR bands at 1963 and 1898 cm^{-1}, and growth of the IR bands of the starting material (Figure 3b).

The IR spectrum of **II** in a xenon matrix at 35 K showed three highly split carbonyl bands at 2005, 1932, and 1909 cm^{-1} (Table 1). Filtered photolysis (λ = 234−376 nm, 45 min) again resulted in the appearance of two new bands in the carbonyl region at 1960 and 1896 cm^{-1} (Table 1). The UV−visible difference spectrum showed two bands at 345 and 457 nm (Figure 2).

4. Photolysis of II in an H$_2$-Doped Argon Matrix. UV photolysis (λ = 234−376 nm) of **II** in a hydrogen-doped argon matrix (10% H$_2$:90% Ar) for 10 min resulted in the appearance of two bands of similar intensity at 1967 and 1904 cm^{-1} and two other weaker bands also of similar intensity at 2022 and 1973 cm^{-1} (Table 1).

(18) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.
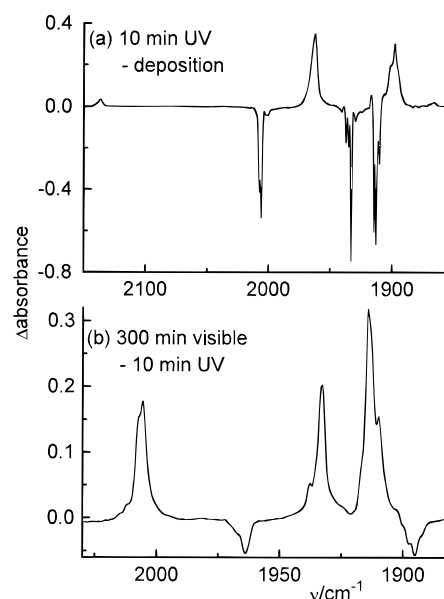
Figure 3. IR spectra of Ru(CO)$_3$(dmpe) isolated in a methane matrix at 12 K: (a) after 10 min of photolysis (λ = 234−376 nm), presented as a difference spectrum relative to the deposition spectrum; (b) after 300 min of photolysis (λ = 490−509 nm), shown as a difference spectrum relative to the spectrum recorded after UV photolysis (note the expanded scales relative to spectrum a).

The first two bands are assigned to Ru(CO)$_2$(dmpe) by comparison to those in section 2, while the shift to higher frequency for the last two carbonyl bands is consistent with the formation of the ruthenium(II) species Ru(CO)$_2$(dmpe)H$_2$. This was confirmed by the independent synthesis of this complex (see section 6).

5. Transient Photochemistry of II in Solution. The large shifts in the two UV−visible bands of Ru(CO)$_2$-(dmpe) observed in matrices upon changing the host from Ar to CH$_4$ to Xe are comparable to the observations on Ru(CO)$_2$(PMe$_3$)$_2$ and suggest that the intermediate is present as the solvent complex Ru(CO)$_2$(dmpe)·S (S = Ar, CH$_4$, Xe). We have probed the lifetime and reactivity of Ru(CO)$_2$(dmpe)·heptane in solution by nanosecond/microsecond time-resolved spectroscopy with both IR and UV−visible detection.

The TRIR spectrum recorded after flash photolysis (λ_{exc} = 266 nm) of **II** in heptane solution ([**II**] = 1.0 × 10^{-3} mol dm^{-3}) under 2 atm of argon at 293 K is shown in Figure 4. At short times after the laser flash (100 ns), there is clear depletion (negative bands) of the carbonyl bands of the starting material at 2009, 1933, and 1912 cm^{-1} and two new bands appear at 1962 and 1898 cm^{-1}, assigned to the alkane complex Ru(CO)$_2$-(dmpe)·heptane by comparison to Ru(CO)$_2$(dmpe)·CH$_4$. At a longer time after the flash (8 μs), product bands are seen at 1962, 1925, and 1898 cm^{-1} and there is a further depletion of the bands due to **II**.

The decay of Ru(CO)$_2$(dmpe)·heptane monitored at
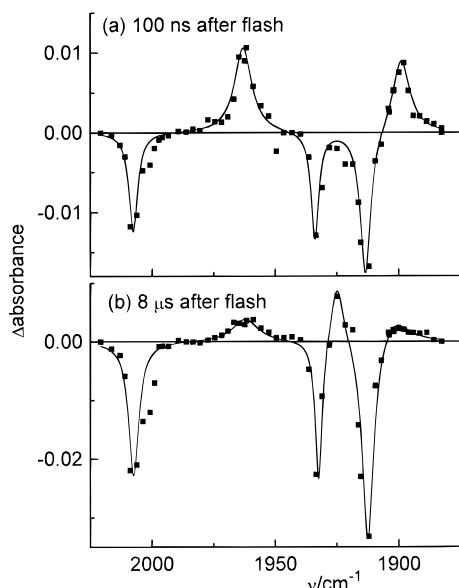
Figure 4. Transient IR difference spectra for Ru(CO)₃-(dmpe) in heptane under argon after 266 nm photolysis. Spectra were recorded (a) 100 ns and (b) 8 μs after the laser pulse. Negative absorbance peaks correspond to loss of starting material bands and positive peaks to product bands. The continuous line represents a Lorentzian fit through the data points.

1962 cm⁻¹ follows first-order kinetics ($k_{obs} = 1.9 \times 10^6$ s⁻¹), to yield a longer lived species; the growth of this long-lived complex monitored at 1925 cm⁻¹ shows the same kinetics ($k_{obs} = 2.2 \times 10^6$ s⁻¹). The parent band at 1912 cm⁻¹ shows an initial fast depletion due to the laser pulse followed by an additional slower decay ($k_{obs} = 1.9 \times 10^6$ s⁻¹). The TRIR data therefore suggest that decay of Ru(CO)₂(dmpe)·heptane occurs by reaction with the parent complex **II** with a second-order rate constant of 1.9×10^9 dm³ mol⁻¹ s⁻¹ to yield a species with three terminal CO bands at 1962, 1925 and 1898 cm⁻¹. When the experiment was repeated in the presence of 200 Torr of CO, the decay of the heptane complex became too fast to monitor accurately.

Upon flash photolysis ($\lambda_{exc} = 308$ nm) of **II** in heptane solution ([**II**] = 4.1×10^{-4} mol dm⁻³) under argon with UV−visible detection, we were unable to detect the short-lived heptane complex, which was expected to absorb in the regions 350−360 and 480−520 nm. However, in the short-wavelength region, we observed the growth of the long-lived photoproduct ($k_{obs} = 4.1 \times 10^5$ s⁻¹), which was stable for at least 100 ms. After the sample was subjected to 200 laser shots, a clear difference in the ground-state UV−visible spectrum was observed with the appearance of a strong new band at 320 nm. The IR spectrum of the same sample recorded after concentrating the solution showed the presence of a weak band at 1962 cm⁻¹ and a stronger band at 1925 cm⁻¹, confirming that the long-lived species is the same as that observed in the TRIR experiments and that it is a stable dimeric photoproduct.[19] The second-order rate constant for the reaction of Ru(CO)₂(dmpe)·heptane with Ru(CO)₃(dmpe) calculated from the UV−visible experiments is 1.0×10^9 dm³ mol⁻¹ s⁻¹, in good

agreement with the value from the TRIR experiments.

When the flash experiment was repeated under 180 Torr of CO (made up to a total pressure of 750 Torr with argon), no quenching of the long-lived species was observed, although the transient yield was reduced by a factor of 4. No transient signal at all was observed when the flash photolysis of **II** in heptane was conducted in the presence of 0.1 mol dm⁻³ Et₃SiH, implying a rapid quenching reaction of the alkane complex by the silane.

6. Steady-State Photochemistry of II in Solution. The short lifetime of Ru(CO)₂(dmpe)·heptane demonstrated by the flash photolysis experiments suggested a highly reactive species which should be readily trapped in the presence of added ligands.

Photolysis of **II** in hexane solution at 273 K under a dihydrogen purge yielded the dihydride complex Ru(CO)₂(dmpe)H₂ as a very volatile, pale yellow oil. The IR spectrum of the complex contained two ν(CO) modes of equal intensity at 2017 and 1968 cm⁻¹, consistent with a *cis* arrangement of the carbonyl ligands and very close to the positions of the carbonyl bands found for the ruthenium(II) product formed upon photolysis of **II** in an H₂-doped matrix at 12 K. The ¹H NMR spectrum of the dihydride complex in toluene-d_8 at 293 K exhibited two distinct hydride resonances at δ −6.9 and −8.5, each of which appeared as a doublet of doublets of doublets. The resonance at lowest field showed a large ³¹P coupling of 73 Hz, placing the corresponding hydride *trans* to a phosphorus atom (eq 1). The structure is consistent with the related iron complexes Fe(CO)₂-(dppe)H₂[20] and Fe(CO)₂(dfepe)H₂,[15b] although both of these species are fluxional at room temperature.
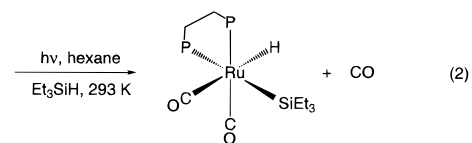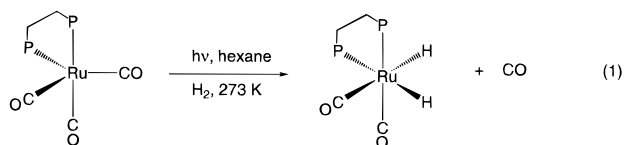
Photolysis of **II** in the presence of Et₃SiH generated a single product, resulting from the oxidative addition of the Si-H bond to give the ruthenium silyl hydride complex Ru(CO)₂(dmpe)(SiEt₃)H. The IR spectrum of the complex contained two carbonyl bands of very similar intensity at 2006 and 1961 cm⁻¹, again indicating a *cis* arrangement of the carbonyl groups (eq 2). The ¹H NMR spectrum showed a single hydride resonance split by two ³¹P nuclei, with the largest coupling of 27 Hz, placing it *cis* to the two phosphorus atoms.[21]

Discussion

Photolysis of Ru(CO)₃(dmpe) (**II**), in low-temperature matrices results in the loss of CO and the formation of the 16-electron complex Ru(CO)₂(dmpe). The IR spectrum of this species in an argon matrix shows two carbonyl bands at 1966 and 1904 cm⁻¹ of similar intensity, indicating a *cis* arrangement of the CO

(19) Ru(CO)₄·C₆D₆ similarly reacts rapidly with the parent Ru(CO)₅ to form Ru₂(CO)₉, which is stable for at least 1 s: Grevels, F.-W.; Klotzbücher, W. E.; Schrickel, J.; Schaffner, K. *J. Am. Chem. Soc.* **1994**, *116*, 6229.

(20) Schubert, U.; Knorr, M. *Inorg. Chem.* **1989**, *28*, 1765.
(21) The same arrangement of ligands has been found in the iron complex Fe(CO)₂(dppe)(SiR₃)H (R = Me, Cl): Knorr, M.; Müller, J.; Schubert, U. *Chem. Ber.* **1987**, *120*, 879.

Scheme 1. Matrix Photochemistry of Ru(CO)₃(dmpe) (II)
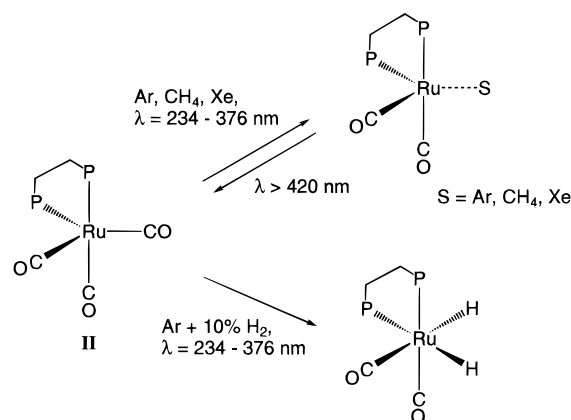
ligands with a bond angle of close to 90° between them. As **II** adopts structure A, we favor structure B for the
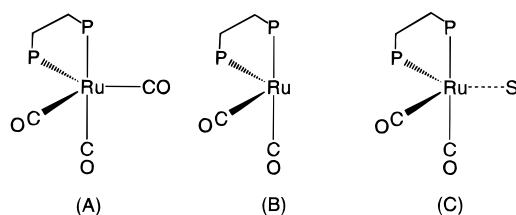
16-electron species resulting from the dissociation of an equatorial CO ligand followed by essentially zero reorganization of the remaining fragment. This structure is also consistent with the nonplanar geometries adopted by the related ruthenium(0) carbonyl phosphine fragments Ru(CO)₂(PMe₃)₂ and Ru(CO)₂(P'Bu₂Me)₂.[8,9] The IR spectrum of Ru(CO)₂(dmpe) shows the characteristic reduction in CO stretching frequencies compared to those of **II** and Ru(CO)₂(dmpe)H₂ (average reduction of 62 cm⁻¹).

As for many coordinatively unsaturated species, selective irradiation into the long-wavelength absorption bands of Ru(CO)₂(dmpe) in the visible region results in recombination with CO. The sensitivity of its two UV−visible bands to change in the matrix host indicates that Ru(CO)₂(dmpe) is better represented as the five-coordinate solvent complex Ru(CO)₂(dmpe)·S (S = Ar, CH₄, Xe), as shown by structure C and in the summary of the matrix photochemistry in Scheme 1. The evidence for methane complexes is now overwhelming (see Introduction), even though their molecular structures have not been determined by experiment.[1,4a] Xenon complexes are also well-documented, especially d⁶ M(CO)₅Xe (M = Cr, Mo, W) and d⁸ Rh(η^5-C₅Me₅)(CO)-Xe.[4a,7,22–24] The perturbation observed in the positions of the two bands of Ru(CO)₂(dmpe)·S (Table 2) upon changing S from Ar to CH₄ ($\Delta \nu$ = 3620, 3330 cm⁻¹) is the largest yet observed for any matrix-solvated fragment (Cr(CO)₅, $\Delta \nu$ = 1690 cm⁻¹;[4a] Mn(dmpe)₂H, $\Delta \nu$ = 2850, 2760 cm⁻¹;[25] Ru(CO)₂(PMe₃)₂, $\Delta \nu$ = 2330 cm⁻¹). The increased shifts from matrix coordination for Ru-

Table 2. Perturbation of UV−Visible Spectra for Matrix-Solvated Complexes in Methane and Xenon

	UV−vis band maxima, λ/nm		
	λ_{max} (Ar)	λ_{max} (Xe)	λ_{max} (CH₄)
Cr(CO)₅[a]	533	492	489
Ru(CO)₂(PMe₃)₂	423	352	385
Ru(CO)₂(dmpe)	410, 600	345, 457	357, 500

	shift in the UV−vis spectrum	
	δ(Xe-Ar)/cm⁻¹	δ(CH₄-Ar)/cm⁻¹
Cr(CO)₅[a]	1560	1690
Ru(CO)₂(PMe₃)₂	4770	2330
Ru(CO)₂(dmpe)	4600, 5220	3620, 3330

[a] From ref 4a.

(CO)₂(dmpe)·S compared to Ru(CO)₂(PMe₃)₂·S do not, however, provide evidence of a stronger metal−solvent interaction and a more stable alkane complex, since the spectra will be influenced by the change in coordination position of the ligands and the change in bond angles. Ru(CO)₂(dmpe)·S has *cis* phosphines and an OC−Ru−CO bond angle of 84° compared to the *trans* arrangement of PMe₃ ligands in Ru(CO)₂(PMe₃)₂·S, in which OC−Ru−CO is ca. 130°. The reduced steric congestion associated with dmpe relative to PMe₃ has been proposed by Nayak and Burkey[26] to explain the energetics of the photochemical substitution reactions of Fe(CO)₃-(PMe₃)₂ and Fe(CO)₃(dmpe).

The electronic structure of a d⁸ ML₄ species with C_{2v} symmetry forms one of the paradigms of the isolobal principle.[27] There are two frontier orbitals in this carbene-like fragment pointing into the equatorial plane away from the M−L bonds, which are occupied by two electrons.[27] Walsh diagrams demonstrate the sensitivity of these orbitals to L−M−L bond angles. Detailed calculations are available for two species closely related to Ru(CO)₂(dmpe), viz. Ru(CO)₄ and Ru(CO)₂(PH₃)₂.[9,10b] However, the latter calculations allow a very open P−Ru−P angle, rather than the small angle enforced by chelating dmpe. Assuming that the longest wavelength absorption band of Ru(CO)₂(dmpe) corresponds to the HOMO-LUMO transition, we associate the sensitivity of the transition energy to change in S with the perturbation of the orbitals by S-coordination in the ground state and a variation in the bond angles at ruthenium.[28] We anticipate a singlet ground state for Ru(CO)₂(dmpe), as observed by experiment for Ru(CO)₂-('Bu₂Me)₂ and predicted for Ru(CO)₄ and Ru(CO)₂-(PH₃)₂.[9,10b]

The IR spectrum of Ru(CO)₂(dmpe)·heptane, measured by TRIR methods at 300 K, proved almost identical with that of Ru(CO)₂(dmpe)·CH₄ measured at 12 K in the matrix. We conclude, therefore, that the alkane plays an equivalent role in the two situations. Solvent coordination can have a very marked influence on reaction kinetics, as in the case of Cr(CO)₅·S or Rh-(η^5-C₅Me₅)(CO)·S.[4e,7] To our surprise, we found that Ru-

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(28) A reviewer has suggested that cordination of S could be confined to the excited state; i.e., we are observing an exciplex. The coordination of alkane and of Xe is demonstrated to be a ground-state effect in M(CO)₅Xe (M = Cr, Mo, W) and Rh(η^5-C₅Me₅)(CO)Xe and other examples mentioned. That the same applies to Ru(CO)₂(dmpe)S is strongly suggested by the labilization of S on long-wavelength photolysis.

$(CO)_2(dmpe)\cdot$heptane decays very rapidly in solution (k_{obs} = ca. 1×10^6 s^{-1}) by reaction with the parent complex **II**, with a second-order rate constant of ca. 10^9 dm^3 mol^{-1} s^{-1}. This rate constant is almost as high as that of Co(η^5-C$_5$H$_5$)(CO), for which both the kinetic and spectroscopic evidence argue against solvent coordination.[29] Preliminary TRIR experiments indicate that the lifetime of Ru(CO)$_2$(PMe$_3$)$_2\cdot$heptane in solution is about 10 times longer than that of Ru(CO)$_2$(dmpe)$\cdot$heptane.[30] Thus the shifts in the UV–vis spectra do not provide guidance on the kinetic stability of the alkane complex, probably because ligand attack proceeds by an associative mechanism.[24]

Conclusions

The photochemistry of Ru(CO)$_3$(dmpe) has been studied by matrix isolation, by time-resolved spectroscopy with IR and UV detection, and by preparative methods. Loss of CO yields a reaction intermediate, Ru(CO)$_2$-(dmpe)$\cdot$S, in which the matrix host or solvent interacts specifically with the metal carbonyl fragment. The coordination of methane or xenon in the matrix is manifested by extraordinarily large shifts in the UV–visible spectrum. Nevertheless, solvent coordination provides negligible kinetic stabilization of the intermediate in solution. The photochemical reactivity of Ru-(CO)$_3$(dmpe) has been employed on a preparative scale to synthesize Ru(CO)$_2$(dmpe)H$_2$.

Experimental Section

General Methods and Materials. Ruthenium trichloride hydrate (Johnson Matthey) and dmpe (Strem) were used as received. All compounds were handled using standard Schlenk and high-vacuum techniques. Solvents for synthesis were dried by refluxing over sodium/benzophenone (benzene, hexane, thf) and then distilled under an argon atmosphere. Heptane (Aldrich HPLC Grade) for use in the flash photolysis experiments was refluxed and distilled from CaH$_2$ under argon. Et$_3$SiH was distilled from activated 3 Å molecular sieves. Deuterated solvents (Goss Scientific Instruments Ltd.) were dried by stirring over potassium/benzophenone and then distilled. Gases used for synthesis were BOC Research Grade (CO, 99.999% purity) or BOC Standard Grade (H$_2$, 99.9% purity). Gases used for matrix experiments and flash photolysis experiments (Ar, CH$_4$, Xe, H$_2$, CO) were BOC Research Grade (99.999% purity).

NMR spectra were recorded with either Bruker MSL300 or AMX500 spectrometers. ^{1}H spectra were referenced to residual protiated solvent (toluene-d_7, δ 2.10; thf-d_7, δ 3.70). ^{13}C-{^{1}H} spectra were referenced to toluene-d_8 (δ 21.5) and thf-d_8 (δ 20.4). ^{31}P{^{1}H} spectra were referenced externally to 85% H$_3$PO$_4$ at δ 0. Elemental analysis was performed by Elemental Microanalysis Limited, Okehampton, Devon, U.K.

Matrix Isolation Experiments. The matrix isolation apparatus has been described in detail elsewhere.[31] Samples for combined IR and UV–visible spectroscopy were deposited onto a BaF$_2$ window cooled by an Air Products CS202 closed-cycle refrigerator to 12–35 K. Complex **II** was sublimed from a right-angled glass tube at 321 K at the same time as a gas stream entered the vacuum shroud through a separate inlet. Typical deposition rates and temperatures were as follows: 20 K for argon (2 mmol h^{-1}), 25 K for CH$_4$ (2 mmol h^{-1}), 35 K for

Xe (1.7 mmol h^{-1}). The samples were then cooled to 12 K (the xenon matrix was maintained at 35 K for photolysis) before recording IR spectra (Mattson-Unicam Research Series FTIR spectrometer fitted with a TGS detector and CsI beam splitter and continuously purged with dry CO$_2$-free air; spectra recorded at 1 cm^{-1} resolution with 128 scans co-averaged, 25 K data points with two-times zero-filling) and UV–visible spectra (Perkin-Elmer Lambda 7G spectrometer). Matrices were photolyzed through a quartz window with a Philips HPK 125 W medium-pressure mercury arc fitted with a quartz focusing lens and water filter. Photolysis wavelengths were selected with cutoff or interference filters.

Laser Flash Photolysis. The apparatus for flash photolysis in York has been described previously.[11] Briefly, a XeCl excimer laser (308 nm) is used as the excitation source and a pulsed Xe arc lamp as the monitoring source. A digital oscilloscope connected to a PC is used for recording and processing data. Samples of **II** were sublimed prior to use and loaded into a 10 mm path length quartz cuvette fitted with Young's PTFE stopcock and degassing bulb. Heptane was added via cannula under argon using a Schlenk line backed by a diffusion pump. The samples were made up to an absorbance of 0.5–1.0 at 308 nm and then degassed by three freeze–pump–thaw cycles before being back-filled to 750–760 Torr with the appropriate gas or gas mixture. Rate constants derived from individual measurements usually carry a 10% uncertainty.

The Nottingham TRIR system has been described in detail elsewhere.[32] A pulsed Nd:YAG laser (Quanta Ray GCR-11, 266 nm, 7 ns) was used to initiate the photochemical reactions and combined with a continuously tunable IR diode laser (Mütek Model 1100S) to monitor the transient IR absorptions and build up the IR spectrum in a "point-by-point" method. Heptane solutions of **II** were flowed through the IR cell (1 mm path length) under 2 atm of argon such that a fresh solution was used for each laser shot. Rate constants derived from individual measurements carry an uncertainty of about 25%.

Synthesis of Ru(CO)$_3$(dmpe) (II). Ru$_3$(CO)$_{12}$ (380 mg, 0.85 mmol) was heated and stirred at 65°C with a 3-fold excess of dmpe (320 μL, 2.5 mmol) in benzene (50 mL) in a Fisher-Porter bottle pressurized with 8 bar of CO for 1 week. After release of the pressure, the orange-red solution was transferred to a Schlenk tube and the solvent removed under vacuum. Extraction of the residue with hexane gave an orange-yellow solution. Complex **II** was obtained as a pale yellow solid (yield 200 mg, 23%) upon crystallization from hexane at −20°C or sublimation at 60 °C. IR (hexane): ν(CO) 2005, 1934, 1915 cm^{-1}. Anal. Calcd for RuC$_9$H$_{16}$P$_2$O$_3$: C, 32.24; H, 4.81. Found: C, 32.33; H, 4.81. ^{1}H NMR (toluene-d_8, 293 K): δ 1.03 (d, $^2J_{PH}$ = 19.5 Hz, 4H, 2 × CH_2), 1.12 (t, |$^2J_{PH}$ + $^4J_{PH}$| = 9.2 Hz, 12H, 4 × CH_3). ^{31}P{^{1}H} NMR: δ 40.0 (s). ^{13}C{^{1}H} NMR: δ 21.1 (t, |$^1J_{PC}$ + $^4J_{PC}$| = 25.4 Hz, CH$_3$), 31.6 (t, |$^1J_{PC}$ + $^4J_{PC}$| = 50.3 Hz, CH$_2$), 212.7 (t, $^2J_{PC}$ = 10.2 Hz, CO). MS (m/z): 336, M$^+$; 308, (M − CO)$^+$; 280, (M − 2CO)$^+$.

Synthesis of Ru(CO)$_2$(dmpe)H$_2$. A solution of **II** (50 mg, 0.15 mmol) dissolved in 30 mL of hexane was photolyzed at 0 °C, during which a hydrogen purge was maintained through the solution. The reaction was monitored by IR spectroscopy and stopped after the disappearance of the bands at 2005, 1934, and 1915 cm^{-1} and the growth of the bands at 2017 and 1968 cm^{-1}. The solvent was evaporated at 0 °C to leave a volatile, yellow-orange oil. IR (hexane): ν(CO) 2017, 1968 cm^{-1}. ^{1}H NMR (toluene-d_8, 293 K): δ −8.55 (ddd, $^2J_{PH}$ = 27.9 Hz, $^2J_{PH}$ = 22.3 Hz, $^2J_{HH}$ = 3.9 Hz, 1H, Ru−H), −6.95 (ddd, $^2J_{PH}$ = 73.2 Hz, $^2J_{PH}$ = 26.2 Hz, $^2J_{HH}$ = 3.9 Hz, 1H, Ru−H), 1.00 (d, $^2J_{PH}$ = 8.6 Hz, 3H, CH_3), 1.06 (d, $^2J_{PH}$ = 7.6 Hz, 3H, CH_3), 1.14 (d, $^2J_{PH}$ = 8.4 Hz, 3H, CH_3), 1.19 (d, $^2J_{PH}$ = 10.0 Hz, 3H, CH_3), 1.90–1.93 (br m, 4H, 2 × CH_2). ^{31}P{^{1}H} NMR: δ 35.5 (d, $^2J_{PP}$ = 17.2 Hz), 41.6 ($^2J_{PP}$ = 17.2 Hz). ^{13}C{^{1}H}

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NMR: δ 19.2 (d, $^1J_{PC}$ = 25.1 Hz, CH_3), 20.7 (d, $^1J_{PC}$ = 19.1 Hz, CH_3), 22.2 (d, $^1J_{PC}$ = 24.5 Hz, CH_3), 24.3 (d, $^1J_{PC}$ = 36.5 Hz, CH_3), 31.9 (dd, $^1J_{PC}$ = 25.3 Hz, $^2J_{PC}$ = 13.0 Hz, CH_2), 32.2 (dd, $^1J_{PC}$ = 28.9 Hz, $^2J_{PC}$ = 8.0 Hz, CH_2), 202.4 (dd, $^2J_{PC}$ = 10.5 Hz, $^2J_{PC}$ = 6.4 Hz, CO), 204.2 (dd, $^2J_{PC}$ = 79.5 Hz, $^2J_{PC}$ = 7.4 Hz, CO). MS (m/z): 308, (M − 2H)$^+$.

Synthesis of Ru(CO)₂(dmpe)(SiEt₃)H. Complex **II** (34 mg, 0.10 mmol) was photolyzed in a mixture of hexane (3.5 mL) and Et₃SiH (0.5 mL) in an ampule under an argon atmosphere at 293 K. After 1.5 h, IR spectroscopy showed the loss of the bands at 2005, 1934, and 1915 cm^{-1} and new bands at 2006 and 1962 cm^{-1}. Removal of the solvent yielded an orange oil. IR (hexane): ν(CO) 2006, 1961 cm^{-1}. ^{1}H NMR (thf-d_8, 293 K): δ −8.76 (dd, $^2J_{PH}$ = 27.2 Hz, $^2J_{PH}$ = 22.8 Hz, 1H, Ru−H), 0.85 (m, 6H, 3 × CH_2CH₃), 1.10 (t, $^3J_{HH}$ = 7.7 Hz, 9H, 3 × CH₂CH_3), 1.55 (d, $^2J_{PH}$ = 7.7 Hz, 3H, CH_3), 1.61 (d,

$^2J_{PH}$ = 9.1 Hz, 3H, CH_3), 1.66 (d, $^2J_{PH}$ = 8.6 Hz, 3H, CH_3), 1.70 (d, $^2J_{PH}$ = 8.3 Hz, 3H, CH_3), 1.8−2.0 (br). ^{31}P{^{1}H} NMR: AB system, δ 33.3 (J_{AB} = 18.5 Hz), 34.2 (J_{AB} = 18.5 Hz). ^{13}C{^{1}H} NMR: δ 11.0 (s, CH₂CH₃), 14.6 (t, $^3J_{PC}$ = 3.3 Hz, CH₂-CH₃), 19.6 (d, $^1J_{PC}$ = 22.9 Hz, CH₃), 21.4 (d, $^1J_{PC}$ = 19.6 Hz, CH₃), 22.5 (d, $^1J_{PC}$ = 24.5 Hz, CH₃), 23.1 (d, $^1J_{PC}$ = 31.6 Hz, CH₃)**,** 31.2 (dd, $^1J_{PC}$ = 25.6 Hz, $^2J_{PC}$ = 13.1 Hz, CH₂), 33.7 (dd, $^1J_{PC}$ = 31.1 Hz, $^2J_{PC}$ = 25.1 Hz, CH₂), 206.0 (dd, $^2J_{PC}$ = 10.4 Hz, $^2J_{PC}$ = 5.4 Hz, CO), 207.2 (dd, $^2J_{PC}$ = 75.8 Hz, $^2J_{PC}$ = 8.7 Hz, CO).