Photochemical Generation of 16-Electron $[Rh(\eta^5-C_5H_5)(PMe_3)]$ and $[Ir(\eta^5-C_5H_5)(PMe_3)]$ in Low-temperature Matrices: Evidence for Methane Activation

Martin G. Partridge, Andrew McCamley and Robin N. Perutz*
Department of Chemistry, University of York, York YO1 5DD, UK

The photochemical reactions of $[Rh(\eta^5-C_5H_5)(PMe_3)(H)_2]$ and $[Ir(\eta^5-C_5H_5)(PMe_3)(H)_2]$ have been studied in Ar, CH_4, N_2 and CO-doped argon matrices by IR and UV/VIS spectroscopy. The UV photolysis in argon matrices results in the formation of the 16-electron complexes $[M(\eta^5-C_5H_5)(PMe_3)]$ with characteristic visible absorption maxima (M = Rh, λ_{max} 399 and 488 nm; M = Ir, λ_{max} 436 and 526 nm). The reaction is partially reversed by long-wavelength photolysis. The conversion of $[Rh(\eta^5-C_5H_5)(PMe_3)(H)_2]$ to $[Rh(\eta^5-C_5H_5)(PMe_3)(Me)H]$ on photolysis in methane matrices is confirmed by extensive isotopic labelling studies and by the use of alternative precursors for the methyl hydride, *viz.* $[Rh(\eta^5-C_5H_5)(PMe_3)(\eta^2-C_6F_6)]$ and $[Rh(\eta^5-C_5H_5)(PMe_3)(C_2H_4)]$. Evidence has also been obtained to show that irradiation of $[Ir(\eta^5-C_5H_5)(PMe_3)(H)_2]$ in methane yields $[Ir(\eta^5-C_5H_5)(PMe_3)(Me)H]$. Photolysis of $[M(\eta^5-C_5H_5)(PMe_3)(H)_2]$in N_2 and CO-doped Ar matrices generates $[M(\eta^5-C_5H_5)(PMe_3)L]$ (M = Rh or Ir, L = N_2 or CO).

Matrix isolation has proved to be a highly successful method of characterising co-ordinatively unsaturated 16-electron reaction intermediates.[1] If the usual inert matrices such as argon are replaced by methane, reaction with the matrix may ensue. When compared to studies of reactivity towards methane in solution, matrix isolation has advantages in spite of the low temperatures since methane is the only substrate present. Such matrix studies rely on photodissociation of CO, C_2H_4 or H_2 from 18-electron precursors. Many have been linked to investigations of the same reaction intermediates by time-resolved spectroscopy in solution.[2]

The investigations of d^8 half-sandwich intermediates and their reactions with methane have relied on metal carbonyl groups as reporters. The 16-electron $[M(\eta^5-C_5H_5)(CO)]$ complexes are observed on photolysis of suitable precursors in argon matrices; their formation is reversed on long-wavelength photolysis. For $[Rh(\eta^5-C_5H_5)(CO)]$, the most effective source is $[Rh(\eta^5-C_5H_5)(CO)(C_2H_4)]$;[3] for $[Ir(\eta^5-C_5H_5)(CO)]$, the dihydride $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ is best.[4]

The photolysis of $[M(\eta^5-C_5R_5)(CO)_2]$ (R = H or Me, M = Rh or Ir) and $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ in methane matrices at *ca.* 12 K leads to the formation of the C–H activation products $[M(\eta^5-C_5R_5)(CO)(Me)H]$.[4] These complexes exhibit a ν(CO) band *ca.* 55 cm^{-1} to high frequency of $[M(\eta^5-C_5H_5)(CO)]$. Although the ν(MH) bands of the methyl hydride complexes are weak compared to the ν(CO) bands, a ν(IrH) band is observed on photolysis of $[Ir(\eta^5-C_5H_5)(CO)_2]$. The ν(RhH) band for $[Rh(\eta^5-C_5H_5)(^{13}CO)(Me)H]$ has been detected only by using $[Rh(\eta^5-C_5H_5)(^{13}CO)(C_2H_4)]$ as the precursor.[3] These experiments indicate that initial CO or H_2 loss is followed by insertion of the remaining $[M(\eta^5-C_5R_5)(CO)]$ fragment into a C–H bond of the methane.

In related experiments the co-ordinatively unsaturated $[Os(\eta^6-C_6H_3Me_3-1,3,5)(CO)]$ fragment was generated by photolysis of $[Os](H)_2$ or [Os](Me)H $\{[Os] = Os(\eta^6-C_6H_3Me_3-1,3,5)(CO)\}$ in argon matrices.[5] The photolysis of [Os](CO) or $[Os](H)_2$ in methane matrices yields [Os](Me)H. Since the identity of [Os](Me)H may be confirmed by comparison with the spectrum of an authentic sample, these experiments offer more complete evidence for the dissociative pathway to methane activation than those on $[Ir(\eta^5-C_5H_5)(CO)]$ systems.

There is one case of a reaction with methane which has been followed by matrix photolysis of an 18-electron complex without a carbonyl group, *viz.* the $Fe(dmpe)_2$ system (dmpe = $Me_2PCH_2CH_2PMe_2$).[6] In addition, the insertion reactions of photoexcited metal atoms into C–H bonds of methane have been well studied.[7–9]

Many of the most successful C–H activators *in solution* have contained no metal carbonyl groups. For instance, Bergman and co-workers[10] discovered that the irradiation of $[Ir(\eta^5-C_5Me_5)(PMe_3)(H)_2]$ in several alkanes generated $[Ir(\eta^5-C_5Me_5)(PMe_3)(alkyl)H]$ complexes. The activation of methane was also achieved by the thermolysis of $[Ir(\eta^5-C_5Me_5)(PMe_3)(C_6H_{11})H]$ in cyclooctane under 20 atm of CH_4.[11] The analogous rhodium alkyl hydride complexes are stable only below −20 °C. The propyl hydride complex has been formed by irradiation of $[Rh(\eta^5-C_5Me_5)(PMe_3)(H)_2]$ in liquid propane, while the methyl hydride has been synthesised indirectly.[12]

Theoretical studies indicate that the fragments $[M(\eta^5-C_5H_5)L]$ (M = Rh or Ir, L = CO or PH_3) adopt the bent $^1A_1$ singlet state with a ring centre–M–P angle of *ca.* 140° (137° when L = CO).[13] The oxidative addition of CH_4 to $[Rh(\eta^5-C_5H_5)(CO)]$ is predicted to proceed *via* an $[M(\eta^5-C_5H_5)(CO)(CH_4)]$ intermediate.[14] The calculations match the experimental finding that the barrier to methane insertion is very low.[15]

Although the co-ordinatively unsaturated 16-electron species $[M(\eta^5-C_5Me_5)(PMe_3)]$ (M = Rh or Ir) have been postulated to be intermediates in the C–H activation process, these species have never been observed directly.[12,16] This paper reports on the matrix photochemistry of a group of $M(\eta^5-C_5H_5)(PMe_3)$ compounds $[Rh](H)_2$, $[Rh](\eta^2-C_6F_6)$, $[Rh](C_2H_4)$ and $[Ir](H)_2$ in inert and reactive matrices $\{[Rh] = Rh(\eta^5-C_5H_5)(PMe_3), [Ir] = Ir(\eta^5-C_5H_5)(PMe_3)\}$. We chose cyclopentadienyl complexes rather than their pentamethylcyclopentadienyl analogues, because they can be obtained in high purity and sublime readily without decomposition.† Although the bands associated with the $\eta^5-C_5H_5$ and PMe_3 ligands are very insensitive to change of other ligands and metals and relatively weak, the experiments provide evidence for the formation of the 16-electron intermediates $[M(\eta^5-C_5H_5)(PMe_3)]$ (M = Rh or

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† [Rh]CO is not a suitable precursor since it is photostable in matrices.

Table 1 IR data ($\tilde{\nu}$/cm^{-1}) for [Rh](H)$_2$ and [Ir](H)$_2$ in Ar matrices at 12 K

[Rh(η^5-C$_5$H$_5$)(PMe$_3$)(H)$_2$]	[Ir(η^5-C$_5$H$_5$)(PMe$_3$)(H)$_2$]	Assignment	
2987, 2979, 2973w	2986, 2970w	ν(CH$_3$)$_{sym}$	PMe$_3$
	2940, 2933w	ν(CH)	C$_5$H$_5$
2917, 2906w	2882, 2856w	ν(CH$_3$)$_{asym}$	PMe$_3$
2056–2021m	2174–2126m	ν(MH)	
1435w	1434w	δ(CH$_3$)$_{asym}$	PMe$_3$
1422w	1421w	δ(CH$_3$)$_{asym}$	PMe$_3$
1301w	1299w	δ(CH$_3$)$_{sym}$	PMe$_3$
1284, 1282w	1283, 1282w	δ(CH$_3$)$_{sym}$	PMe$_3$
1108w	1103, 1100w	δ(CH)	C$_5$H$_5$
1010w	1006w	δ(CH)	C$_5$H$_5$
994w	989w	δ(CH)	C$_5$H$_5$
953s	954, 952s	ρ(CH)	PMe$_3$
939m	935m	ρ(CH)	PMe$_3$
856w	867, 864w	δ(MH)	
849w	852w	—	
842w	847w	δ(CH)	C$_5$H$_5$
832w	835, 831w	—	
814w		—	
793w	803, 802w	δ(MH)	
772m	791, 785m	δ(CH)	C$_5$H$_5$
731, 727w	732, 728w	ν(PC)$_{asym}$	PMe$_3$
682m	683m	ν(PC)$_{sym}$	PMe$_3$
673w		δ(RhH)	
584w	591w	—	

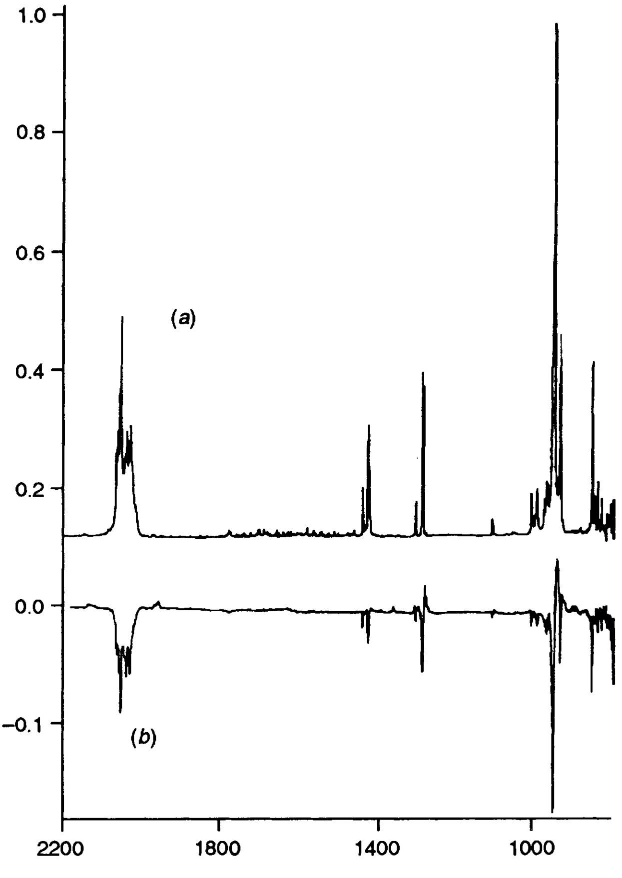


Fig. 1 IR spectrum of [Rh(η^5-C$_5$H$_5$)(PMe$_3$)(H)$_2$] isolated in an argon matrix at 12 K: (*a*) before photolysis and (*b*) after 60 min photolysis with λ > 210 nm presented as a difference relative to the deposition spectrum

Ir) and the corresponding methyl hydride complexes. The reactions of [M](H)$_2$ (M = Rh or Ir) with alkanes in solution are reported briefly.

Two of our precursor complexes have been investigated in matrices previously. The photolysis of [Rh](C$_2$H$_4$) in an argon matrix yields the vinyl hydride complex, [Rh](CH=CH$_2$)H.[17] The irradiation of [Rh](η^2-C$_6$F$_6$) in an argon matrix generates [Rh](C$_6$F$_5$)F and unco-ordinated C$_6$F$_6$.[18] The dinitrogen complex, [Rh](N$_2$), is formed by photolysis of [Rh](C$_2$H$_4$) or [Rh](η^2-C$_6$F$_6$) in a nitrogen matrix.[17,18] The irradiation of [Rh](C$_2$H$_4$) or [Rh](η^2-C$_6$F$_6$) in an argon matrix doped with 2% CO yields [Rh](CO).

Results

Photochemistry of [Rh](H)$_2$ *and* [Rh](D)$_2$.—(*a*) *In argon matrices*. The IR spectrum of [Rh](H)$_2$ isolated at high dilution in an argon matrix at 12 K [Fig. 1(*a*)] shows prominent bands at 1284/1282 and 953 cm^{-1} characteristic of the PMe$_3$ ligand, and at 2056–2021 cm^{-1} typical of the hydride ligands (Table 1). The presence of many bands for the rhodium–hydride stretching mode is very characteristic[19] and is caused by multiple conformations and trapping sites in the matrix. The assignment of the remaining bands was aided by studies carried out on [Rh](C$_2$H$_4$), and its various isotopomers.[17] The UV/VIS spectrum of [Rh](H)$_2$, a white compound, shows a band at 268 nm which tails off towards the visible.

Irradiation for 30 min with λ > 295 nm reduces the intensity of the ν(RhH) band by 31%. All the starting material bands are depleted and weak bands at 1277 and 946 cm^{-1} begin to appear, overlapping with precursor bands (Table 2). The UV/VIS spectrum recorded at this stage shows bands at *ca.* 340, 400 and 490 nm. Further photolysis (85 min) with λ > 295 nm plus 60 min with λ > 210 nm depletes more of the starting material [67% in total, Fig. 1(*b*)] and increases the intensity of the product bands. Long-wavelength photolysis with λ > 400 nm for 9 h brings about some reversal to [Rh](H)$_2$ and bleaches the bands in the UV/VIS spectrum. A UV/VIS spectrum of the product (λ_{max}/nm 399, 488) is obtained by spectral subtraction of the spectrum measured after long-wavelength photolysis from the spectrum measured beforehand (Fig. 2). This method ensures that any contribution from dinuclear species is eliminated.

(*b*) [Rh](H)$_2$ *in* 2% CO-*doped argon and nitrogen matrices*. Irradiation of [Rh](H)$_2$ in an argon matrix doped with 2% CO (1 min with λ > 285 nm) results in the depletion of 23% of the

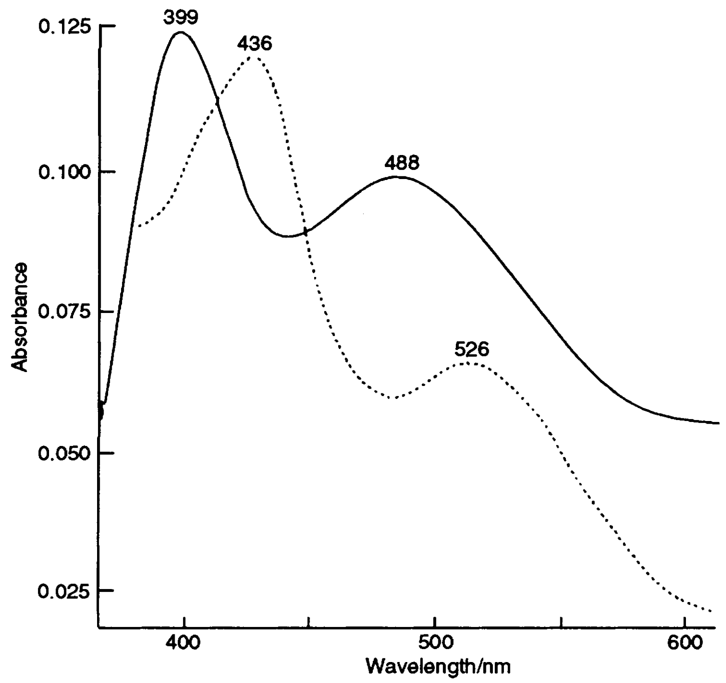


Fig. 2 UV/VIS spectra of the products of photolysis of $[M(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$ (M = Rh or Ir) isolated in argon matrices. The spectra are obtained by subtraction of spectra after short-wavelength photolysis from those obtained after long-wavelength photolysis [(——) M = Rh, (------) M = Ir]

Table 2 IR data ($\tilde{\nu}$/cm^{-1}) for the photoproducts generated on photolysis of $[Rh](H)_2$ and $[Ir](H)_2$ in argon matrices at 12 K

$[Rh(\eta^5\text{-}C_5H_5)(PMe_3)]$	$[Ir(\eta^5\text{-}C_5H_5)(PMe_3)]$	Assignment
1424	1423	$\delta(CH_3)_{asym}$ PMe_3
1414	1409	$\delta(CH_3)_{asym}$ PMe_3
1304	1303	$\delta(CH_3)_{sym}$ PMe_3
1277, 1275	1275	$\delta(CH_3)_{sym}$ PMe_3
1103	1098	$\delta(CH)$ C_5H_5
946	960	$\rho(CH)$ PMe_3
—	911	$\rho(CH)$ PMe_3

ν(RhH) band of the starting material and the appearance of a single intense band at 1946 cm^{-1}, assigned to the ν(CO) band of [Rh](CO).[17]

Photolysis of $[Rh](H)_2$ in a nitrogen matrix (2 min with λ > 285 nm) produces a single new intense band at 2118 cm^{-1} assigned to the ν(NN) band of $[Rh](N_2)$. There are also several weaker bands between 1400 and 700 cm^{-1}. After a total of 7 min photolysis with λ > 285 nm the starting material had been depleted by 32% (Fig. 3).

(*c*) $[Rh](H)_2$ *in methane matrices.* Irradiation of $[Rh](H)_2$ in a methane matrix (λ > 285 nm) depletes the starting material and generates a product with principal bands at 1186 and 951 cm^{-1}. In contrast with the experiment in an argon matrix, there were no new bands present in the UV/VIS spectrum even after 21 min photolysis.

If this reaction has effected insertion of rhodium into a methane C–H bond, a new rhodium–hydride stretching vibration should be present. In order to avoid any spectral interference from the ν(RhH) bands of the precursor, the experiment was repeated with $[Rh](D)_2$ in a CH_4 matrix and with $[Rh](H)_2$ in a CD_4 matrix. The spectrum of $[Rh](D)_2$ isolated in a CH_4 matrix is very similar to that of $[Rh](H)_2$ except that the ν(RhD) band is now observed at 1464 cm^{-1} and δ(RhH) bands are replaced by δ(RhD) bands at 567 and 476 cm^{-1}. Irradiation for 1 min with λ > 285 nm consumes some of the starting material, observed by loss of the ν(RhD) band. New bands are observed at 2020, 1185 and 950 cm^{-1} together with several weaker bands [Fig. 4(*a*), Table 3]. Further periods of photolysis with λ > 285 nm (5 min) and λ > 275 nm (31 min) consume more of the starting material and bring about an increase in the band at 2020 cm^{-1}, suspected to be a rhodium–hydride mode.

The irradiation of $[Rh](H)_2$ in a 20% CD_4-doped argon matrix (1 min, λ > 285 nm) consumes 10% of the starting material. A new broad band is observed at *ca.* 1458 cm^{-1} along with several others between 1400 and 550 cm^{-1} (Table 3). Further photolysis with λ > 285 nm (16 min) consumes a total of 55% of the starting material [Fig. 4(*b*)] and increases the intensity of the product bands. The absence of the bands at 1185 and 754 cm^{-1} in this experiment {compared with $[Rh](H)_2$ or $[Rh](\eta^2\text{-}C_6F_6)$ in CH_4} suggests that these bands are due to $\delta(CH_3)$ or δ(RhH) modes. A ν(RhD) band is predicted at 1435 cm^{-1} [by treating the Rh–H unit as a diatomic oscillator, ν(RhH) 2020 cm^{-1}] in satisfactory agreement with the calculated value.

In order to investigate the origin of the band at 1185 cm^{-1} a sample of $[Rh](H)_2$ isolated in a $^{13}CH_4$ matrix was irradiated for 10 min (λ > 295 nm) which consumed 14% of the starting material. After a total of 162 min irradiation (λ > 295 nm), 40% of the starting material had been consumed; the principal new product bands were observed at 1181, 952 and 785 cm^{-1}. The small shift to lower wavenumber from 1185 to 1181 cm^{-1} is consistent with the effect of substitution of $^{12}CH_3$ for $^{13}CH_3$ on a $\delta(CH_3)_{sym}$ vibration [see inset Fig. 4(*b*) and Discussion].

Photochemistry of $[Rh](C_2H_4)$ *and* $[Rh](\eta^2\text{-}C_6F_6)$ *in Methane.*—Irradiation of $[Rh](C_2H_4)$ isolated in a methane matrix (15 min with λ > 315 nm) results in 25% loss of starting

Table 3 IR data ($\tilde{\nu}$/cm^{-1}) for [Rh](Me)H at 12 K formed by photolysis of [Rh]L {L = C_2H_4, η^2-C_6F_6, $(H)_2$ or $(D)_2$, [Rh] = Rh(η^5-C_5H_5)(PMe_3)}

Precursor/matrix

[Rh]$(H)_2$/CH_4	[Rh](η^2-C_6F_6)/CH_4	[Rh](C_2H_4)/CH_4	[Rh]$(D)_2$/CH_4	[Rh]$(H)_2$/$^{13}CH_4$	[Rh]$(H)_2$/CD_4–Ar	Assignment
—	2038	2030	2020	—	—	ν(RhH)
—	—	—	—	—	1458	ν(RhD)
1186	1185	1185	1185	1181	—	$\delta(CH_3)_{sym}$
951	951	*a*	950	952	952	ρ(CH) PMe_3
942	938	938	937	936	936	ρ(CH) PMe_3
934		*a*				ρ(CH) PMe_3
b	853	*a*	852	855	852	δ(CH) C_5H_5
b	846	*a*	845	848	845	δ(CH) C_5H_5
b	838	838		838	835	
b	785	788	782	785	783	δ(CH) C_5H_5
b	750	754	754	750	—	δ(RhH)
b	678	680	676	680	678	$\nu(PC)_{sym}$
					545	δ(RhD)

[a] The bands of [Rh](CH=CH_2)H mask this region. [b] Not recorded.

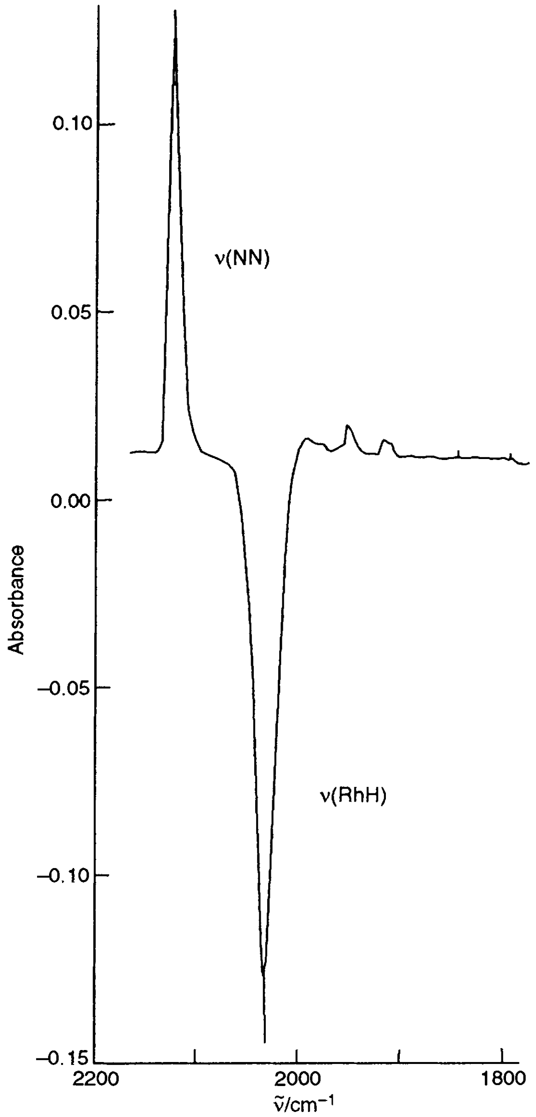


Fig. 3 IR spectrum recorded after 7 min photolysis (λ > 285 nm) of [Rh(η^5-C_5H_5)(PMe_3)$(H)_2$] isolated in a nitrogen matrix at 12 K presented as a difference relative to the deposition spectrum

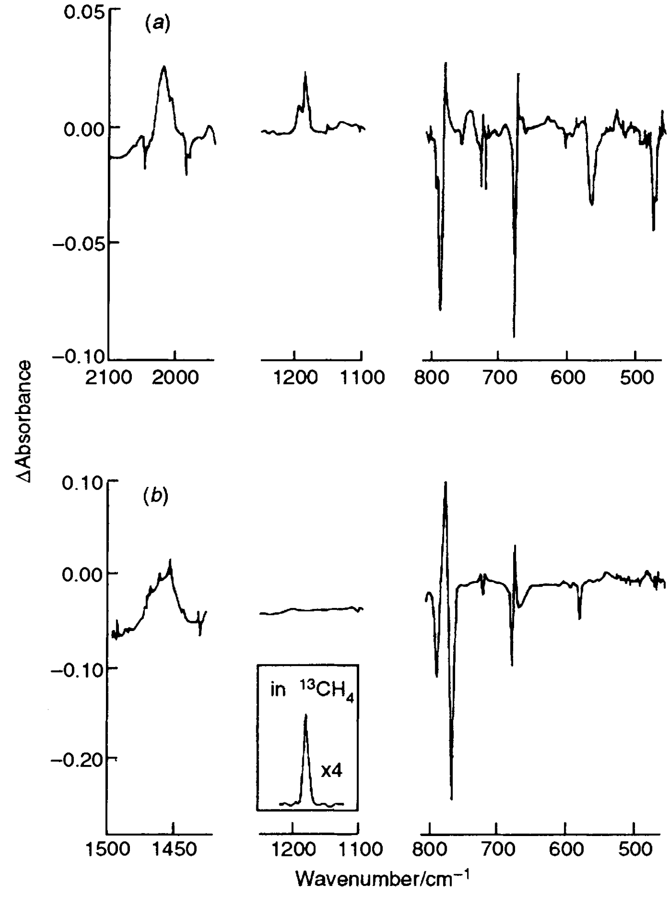


Fig. 4 Difference spectra for (*a*) [Rh(η^5-C_5H_5)(PMe_3)$(D)_2$] isolated in a CH_4 matrix, recorded after 31 min photolysis with λ > 285 nm; (*b*) [Rh(η^5-C_5H_5)(PMe_3)$(H)_2$] isolated in a 20% CD_4-doped argon matrix recorded after 16 min photolysis with λ > 285 nm. The inset shows the product band at 1181 cm^{-1} obtained on photolysis of [Rh(η^5-C_5H_5)(PMe_3)$(H)_2$] in $^{13}CH_4$

material and the appearance of [Rh](CH=CH_2)H,[17] with a very broad (full width at half maximum 40 cm^{-1}) ν(RhH) band at 2030 cm^{-1}, and with other bands between 1250 and 500 cm^{-1}. Further irradiation (+75 min λ > 315 nm) consumes more of the starting material, but does not generate more [Rh](CH=CH_2)H. Instead, a second product grows in with principal bands at 1185 and 754 cm^{-1}. The ν(RhH) band is also observed to grow.

Irradiation of [Rh](η^2-C_6F_6) isolated in a methane matrix (5 min with λ > 285 nm) releases C_6F_6 into the matrix (bands at 1533, 1018 and 998 cm^{-1}). There are other product bands

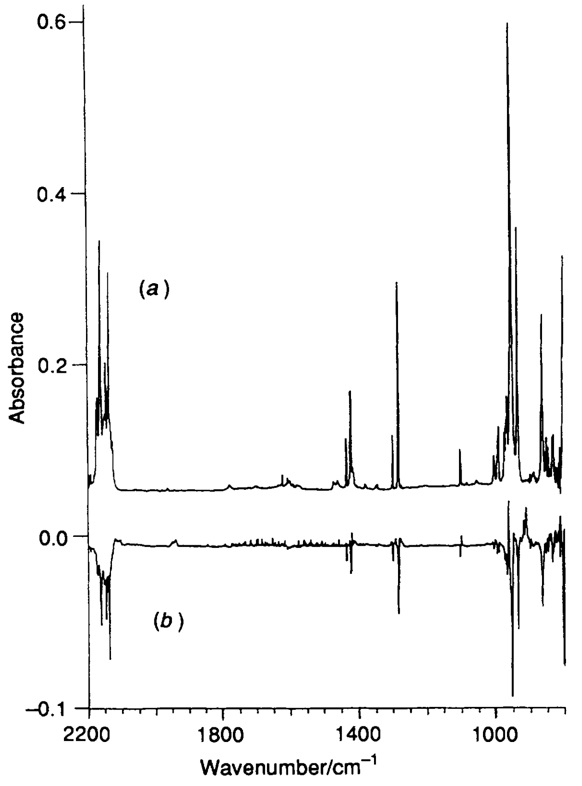


Fig. 5 IR spectrum of [Ir(η^5-C_5H_5)(PMe_3)$(H)_2$] isolated in an argon matrix at 12 K: (*a*) before photolysis and (*b*) after 60 min photolysis with λ > 210 nm presented as a difference relative to the deposition spectrum

observed at 2038, 1185 and 785 cm^{-1} (Table 3) but none characteristic of [Rh](C_6F_5)F.[18] Further photolysis (70 min) with λ > 285 nm increases the intensity of these bands and depletes those of [Rh](η^2-C_6F_6) by 56%. The broad feature centred at 2038 cm^{-1} is assigned as a ν(RhH) band.

Photochemistry of [Ir]$(H)_2$ *and* [Ir]$(D)_2$.—(*a*) *In argon and xenon matrices.* The IR spectrum of [Ir]$(H)_2$ isolated at high dilution in an argon matrix is shown in Fig. 5(*a*) and Table 1. The UV/VIS spectrum of the white compound shows bands at 224 nm and a shoulder at 266 nm. The starting material is depleted by 25% after 10 min irradiation with λ > 210 nm increasing to 50% after 65 min and 68% after 180 min. The IR spectrum shows product bands at 1098, 960 and 911 cm^{-1} [Fig. 5(*b*), Table 2]. The UV/VIS spectrum shows the formation of three bands at *ca.* 290, 430 and 520 nm. The use of long-wavelength photolysis with λ > 420 nm for 11 h causes the bleaching of the bands in the UV/VIS spectrum and partial reformation of [Ir]$(H)_2$ as observed by growth of the ν(IrH) band for this compound. The UV/VIS spectrum of the product is obtainable by subtracting the spectrum after long-wavelength photolysis from the spectrum recorded after short-wavelength photolysis (Fig. 2).

The experiment was repeated in xenon to examine whether the matrix host influences the position of the bands of the photoproduct in the UV/VIS spectrum. Such effects have been observed for $Cr(CO)_5$ in various matrices.[20] The photolysis of [Ir]$(H)_2$ in a xenon matrix for 30 min with λ > 210 nm depletes the bands of the starting material by 65%. The UV/VIS spectrum recorded at this time shows the presence of three bands at *ca.* 298, 436 and 526 nm. Irradiation of the sample with λ > 420 nm for 12 h bleaches the product bands in the UV/VIS spectrum. The IR spectrum shows 10% reversal to [Ir]$(H)_2$. The bands in the UV/VIS spectrum after the photolysis of [Ir]$(H)_2$ in xenon are in identical positions to those observed in an argon matrix.

Table 4 IR data ($\tilde{\nu}$/cm^{-1}) for [Ir](Me)H at 12 K formed by photolysis of [Ir]$(X)_2$ (X = H, D), [Ir] = Ir(η^5-C_5H_5)(PMe_3)

Precursor/matrix				
[Ir]$(H)_2$/CH_4	[Ir]$(D)_2$/CH_4	[Ir]$(H)_2$/CD_4	Assignment	
—	—	1539	ν(IrD)	
1226	1226	—	δ$(CH_3)_{sym}$	IrMe
1098	1098		δ(CH)	C_5H_5
951	950	943	ρ(CH)	PMe_3
932	931		ρ(CH)	PMe_3
899		898		
856		855		
848	848	848	δ(CH)	C_5H_5
840	841			
798	796	798	δ(CH)	C_5H_5
729		730	ν$(PC)_{asym}$	PMe_3
679	679	678	ν$(PC)_{sym}$	PMe_3
588	588			

(*b*) [Ir]$(H)_2$ *in* 1% CO-*doped argon matrices.* Irradiation of a mixture of isotopomers, [Ir]$D_{2-x}H_x$(x = 0, 1 or 2, %D = 70), in an argon matrix doped with 1% CO for 1 min with λ > 295 nm generates an intense band at 1935 cm^{-1} which is assigned to the ν(CO) band of [Ir](CO), and several much weaker bands in this region at 2079, 2027 and 1978 cm^{-1}.

(*c*) [Ir]$(H)_2$ *in methane matrices.* Irradiation of [Ir]$(H)_2$ in a methane matrix (5 min, λ > 210 nm) depletes all the bands of the starting material and results in the formation of weak bands at 1226, 951, 848, 798 and 679 cm^{-1} (Table 4). Any growth of a new ν(IrH) band in this experiment would be masked by the bands of the starting material.

The irradiation of [Ir]$(H)_2$ in a 100% CD_4 matrix (5 min, λ > 210 nm) reduces the intensity of all the bands of the starting material. Product bands are observed at 1539 (broad), 943, 848, 798 and 678 cm^{-1} (Table 4). There is no band observed at 1226 cm^{-1}, indicating that this is probably a δ(CH_3) band which has been shifted on isotopic substitution. The band at 1539 cm^{-1} is assigned to a ν(IrD) mode by comparison with [Ir]$(D)_2$ which has a ν(IrD) band centred at 1548 cm^{-1}.

The IR spectrum of [Ir]$D_{2-x}H_x$(x = 0, 1 or 2, %D = 70) isolated in a methane matrix is very similar to that of [Ir]$(H)_2$ with the ν(IrH) band supplemented by an ν(IrD) band at 1548 cm^{-1}. Irradiation (5 min, λ > 210 nm) depletes all of the bands of the precursor and yields new bands at 1226, 950, 848, 796 and 679 cm^{-1}. Further photolysis increases the yield of the product bands. The extent of deuteriation of the precursor was insufficient to observe growth of a new ν(IrH) band.

Photochemistry of [Rh]$(H)_2$ *and* [Ir]$(H)_2$ *in Alkane Solvents.*—(*a*) [Rh]$(H)_2$ *in methylcyclohexane.* Irradiation of [Rh]$(H)_2$ in [$^2H_{14}$]methylcyclohexane at −60 °C for 1.5 h with λ > 285 nm generates no stable alkyl hydride products.[10b] After photolysis the ^{31}P-{^{1}H} NMR spectrum shows a doublet at δ 14.26 [*J*(RhP) 157 Hz] for [Rh]$(H)_2$ and a doublet of 1 : 1 : 1 triplets [*J*(RhP) 157, *J*(DP) 6 Hz, 40% conversion] to slightly lower field, assigned to [Rh](H)D. This observation of an (H)D complex indicates that the solvent has been activated as it is the only source of deuterium in the reaction. The solvent activation product is probably similar to that found for the iridium analogue (see below), but thermally very unstable.

(*b*) [Ir]$(H)_2$ *in cyclohexane.* The photolysis of [Ir]$(H)_2$ in cyclohexane (4 h with λ > 285 nm) yields a single product with 30% conversion. The ^{1}H, ^{31}P-{^{1}H}, and ^{13}C NMR spectra measured after redissolving in C_6D_6 (see Experimental section) demonstrate conclusively that the product is [Ir](C_6H_{11})H. The spectra resemble those for the η^5-C_5Me_5 analogue.[16b] The photolysis of [Ir]$(H)_2$ in [$^2H_{12}$]cyclohexane for 2 h with λ > 285 nm brings about 40% conversion to product. The ^{1}H NMR spectrum of the reaction shows a new η^5-C_5H_5 resonance at δ 4.92, a new PMe_3 resonance at δ 1.53, and a new hydride resonance at δ −18.61. The $^{31}P-\{^{1}H\}$ NMR spectrum shows a 1:1:1 triplet at δ −39.36 and a singlet at δ −39.50 for the products. The products are assigned as $[Ir](C_6D_{11})D$ and its hydride analogue. The resonance for $[Ir](H)_2$ appears at δ −42.32 and there is also a 1:1:1 triplet at δ −42.21 assigned to [Ir](H)D. The presence of a hydride ligand on the product and a deuteride ligand on the starting material suggests that some reaction may occur by a ring-slip mechanism.[4a,21]

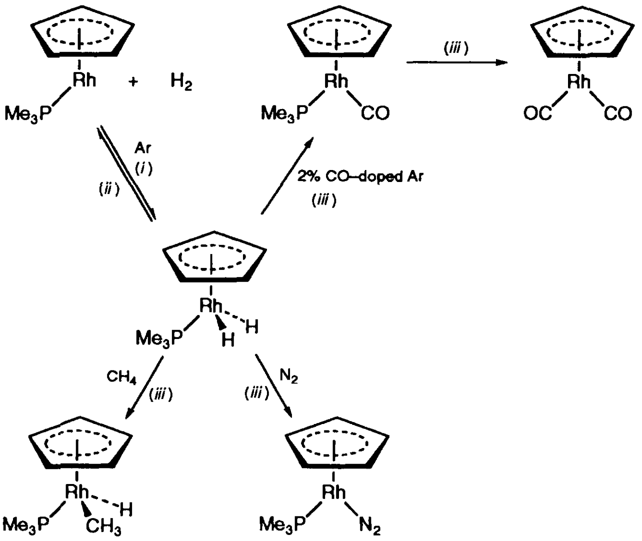
Discussion

Evidence for 16-*electron* $[Rh(\eta^5-C_5H_5)(PMe_3)]$.—The photolysis of $[Rh](H)_2$ or $[Rh](\eta^2-C_6F_6)$ in an argon matrix doped with 2% CO generates [Rh](CO), and in a nitrogen matrix $[Rh](N_2)$. The $[Rh](\eta^2-C_6F_6)$ complex also yields the C–F activation product, $[Rh](C_6F_5)F$.[18] These reactions point to a mechanism involving the photodissociation of H_2 or C_6F_6 from the precursor and substitution by another ligand, presumably *via* the co-ordinatively unsaturated $[Rh(\eta^5-C_5H_5)(PMe_3)]$ fragment. Unlike the photochemistry[22] of $[Co(\eta^5-C_5H_5)(CO)_2]$, there is no evidence for ring-slip products in the matrix photochemistry of any of the above rhodium complexes.

The main product bands from irradiation of $[Rh](H)_2$ isolated in an argon matrix (1277 and 946 cm^{-1}) are assigned to modes of the PMe_3 ligand (Table 2). The expulsion of C_6F_6 from $[Rh](\eta^2-C_6F_6)$ can be detected directly but the identification of other product IR bands formed from this precursor is hampered by the presence of $[Rh](C_6F_5)F$. Since the irradiation of $[Rh](\eta^2-C_6F_6)$ does not generate any bands assignable to ν(RhH) bands, the formation of photoproducts by cyclometallation of the PMe_3 ligand or metallation of the $\eta^5-C_5H_5$ ring is most unlikely. The UV/VIS spectrum after photolysis of $[Rh](H)_2$ in argon shows the formation of three bands at *ca.* 340, 399 and 488 nm. These bands are bleached with $\lambda > 400$ nm leading to partial reformation of the starting material. This behaviour implies that the photoproduct is the co-ordinatively unsaturated 16-electron fragment $[Rh(\eta^5-C_5H_5)(PMe_3)]$. The band at *ca.* 490 nm is also observed on photolysis of $[Rh](\eta^2-C_6F_6)$ in an argon matrix. (The higher energy bands are probably masked by those of the starting material and the other photoproduct $[Rh](C_6F_5)F$, both of which are orange.) In contrast, the photolysis of $[Rh](H)_2$ in a methane matrix does not generate any bands in the UV/VIS spectrum between 300 and 700 nm.

Rest *et al.*[4] reported that the photolysis of $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ in an argon matrix yields $[Ir(\eta^5-C_5H_5)(CO)]$ which regenerated some of the precursor when photolysed with $\lambda > 375$ nm.[3] A similar phenomenon of photoreversal has been observed for other dihydride systems: $Fe(CO)_4 + H_2$,[23] $Os(\eta^6-C_6H_3Me_3-1,3,5)(CO) + H_2$,[5] $Ru(dmpe)_2 + H_2$,[24] $Fe + H_2$[25] and $Mn + H_2$.[26] The observation of only partial reversal suggests that some of the dissociated H_2 has escaped from the matrix cage, and so cannot be reco-ordinated.

Evidence for Methane Activation by $[Rh(\eta^5-C_5H_5)(PMe_3)]$ *at* 12 K.—The first line of evidence for methane activation by $[Rh(\eta^5-C_5H_5)(PMe_3)]$ arises from metal–hydride stretching vibrations which are formed on irradiation of $[Rh](\eta^2-C_6F_6)$, $[Rh](C_2H_4)$ and $[Rh](D)_2$ in CH_4 matrices. There is some variation in the frequency of the product bands (Table 3), but this may be attributed to the extreme sensitivity of metal–hydride vibrations to their environment. Hence, the different expelled ligands may perturb these high-amplitude vibrations appreciably.[19] The observation of a new ν(RhD) or ν(RhH) band in the IR spectrum on photolysis of $[Rh](H)_2$ in CD_4 or $[Rh](D)_2$ in CH_4 is necessary, but not conclusive evidence for formation of a methyl hydride/deuteride complex. In the solution photochemistry of $[Rh](H)_2$, photolysis in deuteriated alkanes results in H/D exchange. The exchange would give rise to new ν(RhD) bands without the formation of an activation product. However, this possibility can be ruled out because the photolysis of $[Rh](\eta^2-C_6F_6)$ in a methane matrix produces a ν(RhH) band and the precursor has no exchangeable hydride ligands.



Scheme 1 Matrix photochemistry of $[Rh(\eta^5-C_5H_5)(PMe_3)(H)_2]$ at 12 K: $\lambda > 400$ (*i*), > 295 (*ii*) or > 285 nm (*iii*)

Evidence for methane activation is also obtained from lower frequency vibrations where we find common product vibrations (Table 3) from $[Rh](C_2H_4)$, $[Rh](\eta^2-C_6F_6)$, $[Rh](H)_2$ and $[Rh](D)_2$. The characteristic bands are now considered in turn. The band at 1185 cm^{-1} appears on photolysis of either $[Rh](\eta^2-C_6F_6)$ and $[Rh](C_2H_4)$. It is also formed from $[Rh](H)_2$ and $[Rh](D)_2$ in CH_4, but not on photolysis of $[Rh](H)_2$ in an Ar–CD_4 matrix,* while it is shifted to 1181 cm^{-1} with $[Rh](H)_2$ in $^{13}CH_4$. The band is therefore assigned as the $\delta(CH_3)_{sym}$ mode of a co-ordinated methyl group (*cf.* 1148 cm^{-1} for CH_3FeH and 1208, 1233 cm^{-1} for CH_3NiH, the bands of the latter shifting 7 cm^{-1} on ^{13}C labelling).[8,9] The band at *ca.* 950 cm^{-1} is observed in all the methane matrix experiments regardless of precursor or isotope and is assigned as a $\rho(CH_3)$ vibration of the PMe_3 ligand (Table 3). A further product band appears at 754 cm^{-1} in CH_4 matrix experiments, at 750 cm^{-1} in $^{13}CH_4$, but is shifted to 545 cm^{-1} in Ar–CD_4 (frequency ratio 754:545 = 1.39). It is assigned as a δ(RhD) mode by comparison with the bands of $[Rh](D)_2$ which appear at 567 and 476 cm^{-1} (methane matrix). In conclusion, the evidence for the formation of [Rh](Me)H is extremely powerful.

The photochemistry of $[Rh](H)_2$ in various matrices is summarised in Scheme 1, while the methods of generating [Rh](Me)H are shown in Scheme 2.

Evidence for $[Ir(\eta^5-C_5H_5)(PMe_3)]$ *and* $[Ir(\eta^5-C_5H_5)(PMe_3)(Me)H]$.—There is substantial evidence for $[Rh(\eta^5-C_5H_5)(PMe_3)]$ and for $[Rh(\eta^5-C_5H_5)(PMe_3)(Me)H]$. The evidence for the $[Ir(\eta^5-C_5H_5)(PMe_3)]$ analogue is not as decisive because we are confined to the hydride and deuteride precursors. Other suitable precursors are ruled out because $[Ir](C_2H_4)$ only undergoes intramolecular isomerisation[17] and $[Ir](\eta^2-C_6F_6)$ has been characterised in solution but not isolated.[18]

The photolysis in an argon matrix doped with 1% CO yields [Ir](CO) and other carbonyl containing products showing that H_2 is eliminated on photolysis in matrices at 12 K. The argon matrix experiments show the depletion of starting material and formation of a product with a comparable UV/VIS spectrum to

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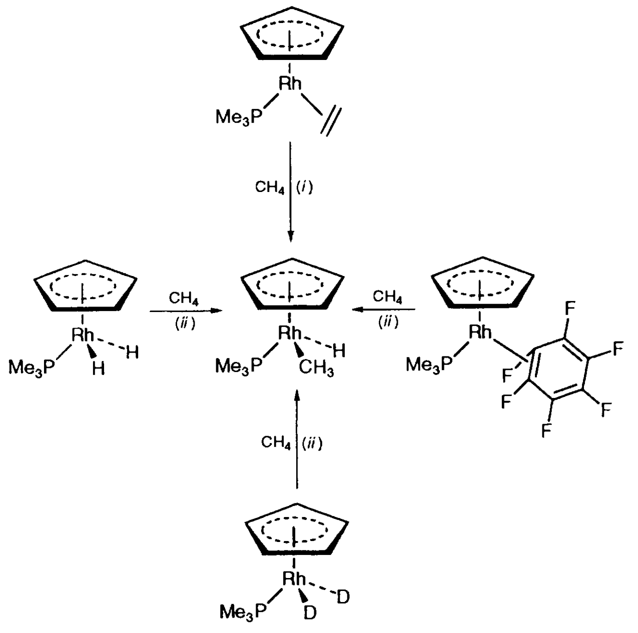
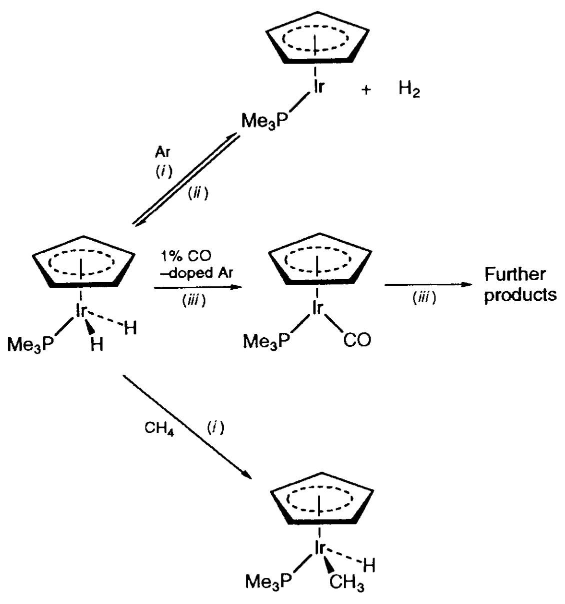
* The $\delta(CD_3)$ vibration is expected in a congested region of the spectrum around 850 cm^{-1} and is probably masked by other bands.



Scheme 2 Formation of $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(Me)H]$ at 12 K: $\lambda > 315$ (*i*) or > 285 nm (*ii*)



Scheme 3 Matrix photochemistry of $[Ir(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$ at 12 K: $\lambda > 210$ (*i*), > 420 (*ii*) or > 295 nm (*iii*)

that of $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)]$. The reaction is again partially reversible. The processes of H/D exchange and ring slip can also be envisaged for this system as they were for the rhodium system, and they are less easily ruled out.

The photolysis of $[Ir](H)_2$ in a CH_4 matrix depletes all the bands of the starting material and generates a band at 1226 cm^{-1} and several others at lower frequency (Table 4). The ν(IrH) region is masked by bands of the precursor. The photolysis of $[Ir](D)_2$ in a CH_4 matrix generates bands within 2 cm^{-1} of those observed in the first experiment. A new ν(IrH) band is not identifiable because of incomplete deuteriation of the precursor.

The photolysis of $[Ir](H)_2$ in a CD_4 matrix yields several new bands similar to those observed in the two previous experiments and also a band at 1539 cm^{-1} which is assigned to a ν(IrD) band by comparison with the ν(IrD) band of $[Ir](D)_2$ at 1548 cm^{-1}. In this experiment there is no product band observable at 1226 cm^{-1}. Since the latter band is observed only in the experiments with CH_4 as the matrix gas, it is assigned to a $\delta(CH_3)_{sym}$ band for a co-ordinated methyl group. The $\delta(CD_3)$ band is probably masked by other bands in the spectrum. The growth of new δ(IrH) or δ(IrD) bands in the region 900 to 500 cm^{-1} is hard to detect due to overlap with other bands.

The observation of essentially identical product bands from photolysis of $[Ir](H)_2$ and $[Ir](D)_2$ in CH_4 suggests the formation of a common product and rules out a simple H/D exchange process. The product bands show the presence of η^5-C_5H_5, PMe_3 and hydride/deuteride ligands on the iridium (Table 4) leading to an assignment as [Ir](Me)H (Scheme 3). The ability of $[Ir](H)_2$ to act as an alkane C–H activator is confirmed by the solution experiments showing reaction with cyclohexane to form $[Ir](C_6H_{11})H$. However, complications arise from H/D exchange (*cf.* $[Ir(\eta^5\text{-}C_5H_5)(CO)(H)_2]$).[4a]

Conclusion

(1) The co-ordinatively unsaturated species $[M(\eta^5\text{-}C_5H_5)(PMe_3)]$ (M = Rh or Ir) are formed by photolysis of $[M(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$ isolated in argon matrices and identified through IR and UV/VIS spectra. The photodissociation is partially reversed by long-wavelength irradiation. The $[M(\eta^5\text{-}C_5H_5)(PMe_3)]$ species and their η^5-C_5Me_5 analogues have been postulated as the reactive intermediates in the activation of alkane, arene and alkene C–H bonds but have never been observed directly before.[10,12,16]

(2) Three different precursors, $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$, $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2H_4)]$ and $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}C_6F_6)]$, have been shown to yield $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(Me)H]$ on photolysis in methane matrices. A similar reaction occurs with $[Ir(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$. These represent the first examples of methane activation by the $[M(\eta^5\text{-}C_5H_5)(PMe_3)]$ fragments.

(3) Photolysis of $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(H)_2]$ in CO and N_2 matrices generates $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(CO)]$ and $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(N_2)]$ respectively.

Experimental

Syntheses and manipulations were carried out under argon using standard Schlenk-line techniques. Solvents were dried by refluxing over sodium–benzophenone and distilled under argon prior to use. Deuteriated solvents were obtained from Aldrich and dried under argon prior to use. Gases for matrix isolation experiments were B.O.C. research grade except for CD_4 (99 atom% D) and $^{13}CH_4$ (99.1 atom% ^{13}C) which were obtained from MSD Isotopes Ltd.

The irradiation source for the matrix and solution reactions was a Philips HPK 125 W medium-pressure Hg lamp with a quartz focussing lens and a water filter to remove excess heat. The NMR spectra were recorded on a Bruker MSL300 spectrometer. Proton and ^{13}C NMR chemical shifts are referenced to solvent resonances and ^{31}P NMR shifts are quoted relative to H_3PO_4.

Matrix Isolation Methods.—The matrix isolation apparatus has been described previously.[2] In brief, the matrices were deposited on a CsI window (experiments with IR detection only) or a BaF_2 window (experiments with combined IR and UV/VIS detection) cooled by a closed-cycle cooler. Matrices were deposited continuously at 20 (argon), 25 (CH_4) or 30 K (xenon) at 1.8–3.5 mmol h^{-1}. The samples were deposited concurrently with the matrix gas by sublimation from a heated glass side-arm. Sublimation temperatures were as follows: $[Rh](H)_2$ 294, $[Ir](H)_2$ 300, $[Rh](C_2H_4)$ 290 and $[Rh](\eta^2\text{-}C_6F_6)$ 358 K. After deposition the matrices were cooled to 12 K. The IR spectra were recorded on a Mattson Sirius or Mattson RS FTIR spectrometer at 1 cm^{-1} resolution and UV/VIS spectra measured with a Perkin-Elmer Lambda 7G spectrometer at 2 nm resolution.

Syntheses.—The following compounds were synthesised by literature procedures: $[Rh](C_2H_4)$,[27] $[Rh](\eta^2\text{-}C_6F_6)$,[28] $[Ir](H)_2$[29] and $[Ir](D)_2$.[30]

$[Rh](H)_2$. The synthesis was adapted from ref. 10(*b*). To a suspension of $[Rh]I_2$[10b] (0.29 g, 0.58 mmol) in toluene (10 cm^3) was added 3.2 mol dm^{-3} Red-Al $\{Na[AlH_2(OCH_2CH_2OMe)_2]\}$ (0.8 cm^3). On stirring the mixture for 1.5 h at room temperature the solution changed from a dark to a milky white. The toluene was removed under vacuum leaving a pale yellow gum which was dissolved in the minimum amount of tetrahydrofuran (thf); hexane was then added to precipitate the salts. The solution was purified by flash chromatography on a short silica column with 5:1 hexane–thf. The removal of the solvent afforded pale yellow crystals which were purified by sublimation at 44 °C, 3×10^{-4} mbar onto a liquid-nitrogen cooled finger.

$[Rh](D)_2$. A few drops of degassed D_2O were added to a sample of $[Rh](H)_2$ in CD_3CN which was sealed under vacuum in an NMR tube. The sample was left at 5 °C for 16 d, after which the ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded. The spectra indicated the complex to be >90% deuteriated. $^{31}P\text{-}\{^1H\}$ NMR: δ 12.81 (doublet of 1:2:3:2:1 quintets) *J*(RhP) 145, *J*(DP) 5.5 Hz.

$[Ir](C_6H_{11})H$. The photolysis of $[Ir](H)_2$ in cyclohexane (4 h with $\lambda > 285$ nm) yielded a single product with 30% conversion. The solvent was removed under vacuum and the sample dissolved in C_6D_6 for NMR analysis. NMR data for $[Ir](C_6H_{11})H$ (in C_6D_6): ^1H δ 4.90 [d, *J*(PH) 1, 5 H, C_5H_5], 2.2–1.5 (m, 11 H, C_6H_{11}), 1.20 [d, *J*(PH) 10, 9 H, PMe_3], −18.30 [d, *J*(PH) 36 Hz, 1 H, IrH]; $^{13}C\text{-}\{^1H\}$ δ 82.1 [d, *J*(PC) 3, C_5H_5], 50.5 [d, *J*(PC) 3, C_β], 48.2 [d, *J*(PC) 3, $C_{\beta'}$], 33.0 (s, C_γ), 32.8 (s, $C_{\gamma'}$), 28.3 (s, C_δ), 22.3 [d, *J*(PC) 38, PMe_3], 4.7 [d, *J*(PC) 6 Hz, C_α]; $^{31}P\text{-}\{^1H\}$ δ −39.49 (s).

Acknowledgements

We are pleased to acknowledge the support of The Royal Society, SERC, British Gas, NATO and the European Commission.

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Received 18*th July* 1994; *Paper* 4/04366I