

sorption correction based upon a series of ψ scans, were applied. Intensities of equivalent reflections were averaged, and 12 reflections were rejected because their intensities differed significantly from the average. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.⁶⁴ All non-hydrogens were refined with anisotropic thermal parameters. Hydrogen positions were calculated except for H1,

which was located from a difference map. Additional details are given elsewhere.³⁵

Acknowledgment. We thank the NIH for support of this research, Mr. N. Quirós Méndez for UV/visible spectra, and Dr. C. M. Garner for assistance with entries 5 and 6 of Scheme III.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for $3a.e^+PF_6^-$ and $(RS,SR)-5e$ (6 pages); tables of calculated and observed structure factors for $3a.e^+PF_6^-$ and $(RS,SR)-5e$ (71 pages). Ordering information is given on any current masthead page.

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Photochemical Isomerization of Metal Ethene to Metal Vinyl Hydride Complexes: A Matrix-Isolation and Solution NMR Study

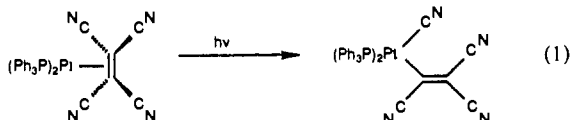
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Abstract: CpRh(PMe₃)(C₂H₄) (**1**), CpIr(PMe₃)(C₂H₄) (**6**), and CpIr(C₂H₄)₂ (**8**) (Cp = η^5 -C₅H₅) are isomerized on photolysis in argon matrices at 12–20 K to metal vinyl hydride complexes CpM(L)(C₂H₃)H (L = PMe₃, C₂H₄). The products are identified by their characteristic metal hydride and vinyl group vibrations in the IR spectra and by the effect of ²H-labeling experiments. The same products may be generated by photolysis of a frozen toluene solution at 77 K (**1** and **8**) or a cold toluene solution (**6**) and characterized by ¹H, ¹³C, and ³¹P NMR. The vinyl hydride complexes exhibit a wide range of thermal stabilities isomerizing to their precursors at the following temperatures: CpRh(PMe₃)(C₂H₃)H at ~253 K, CpIr(PMe₃)(C₂H₃)H at ~393 K, CpIr(C₂H₄)(C₂H₃)H at ~273 K. Photolysis of **1** in toluene solution at 188 K generates a mixture of CpRh(PMe₃)(C₂H₃)H and isomers of CpRh(PMe₃)(tolyl)H; at higher temperatures only insertion into toluene C–H bonds is observed. These and other studies lead to the proposal of an intermediate cage complex, [CpM(L)···C₂H₄], in the isomerization pathway. The reaction mechanism tends toward the intramolecular limit in the order **1** < **8** < **6**. Secondary photolysis of CpIr(C₂H₄)(C₂H₃)H in Ar matrices causes ethene loss and formation of a product identified as the vinylidene complex CpIr(C=CH₂)H₂. Photolysis of **8** in CO and N₂ matrices leads to substitution products CpIr(C₂H₄)L (L = CO, N₂), CpIr(CO)(C₂H₃)H, and CpIr(C₂H₄)(C₂H₃)H. Photolysis of **1** in CO matrices generates CpRh(PMe₃)CO only; use of N₂ matrices results in formation of CpRh(PMe₃)N₂ and CpRh(PMe₃)(C₂H₃)H. The photoproducts of **6** in CO matrices include CpIr(PMe₃)(C₂H₃)H and CpIr(PMe₃)CO.

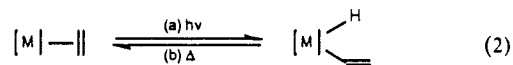
Introduction

It was first reported in 1971 that a metal alkene complex could be isomerized on photolysis (eq 1).³



Evidence that a similar process could occur for an ethene complex came from the measurements of Kafafi et al. on Fe(C₂H₄) isolated in low-temperature matrices.⁴ Yet this appeared to be

a special case, since Fe(C₂H₄) is hydrogen bonded not π -bound. Nevertheless, this observation was followed in 1986 by Baker and Field's discovery⁵ of the photoisomerization of Fe(dmpe)₂(C₂H₄), our own⁶ for CpIr(C₂H₄)₂ and Wenzel and Bergman's⁷ for CpRe(PMe₃)₂(C₂H₄), all conventionally π -bound ethene complexes (dmpe = Me₂PCH₂CH₂PMe₂, Cp = η^5 -C₅H₅). The discovery of further examples of metal ethene to metal vinyl hydride isomerization (eq 2a and Scheme 1) made it clear that this was far from an isolated phenomenon.⁸⁻¹⁰ Although reaction 2a



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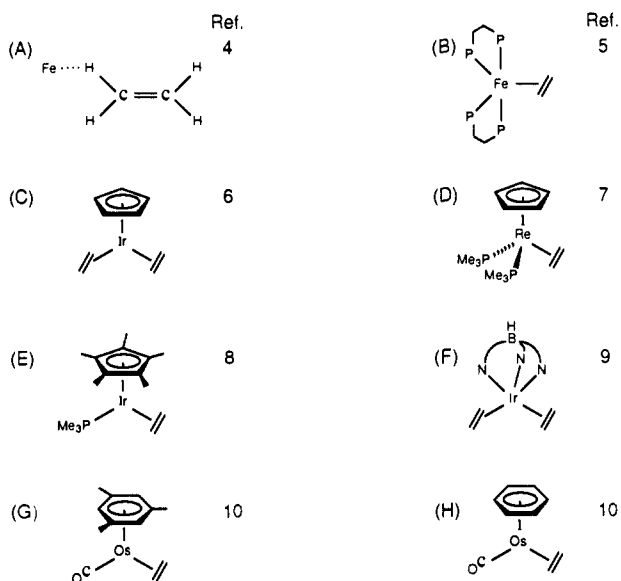
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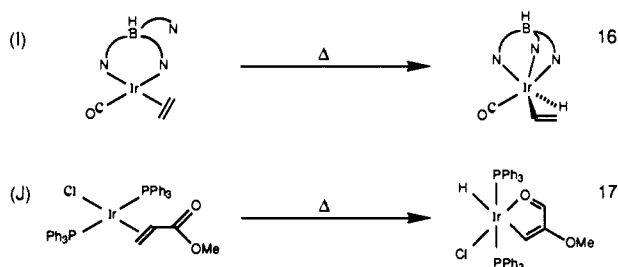
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Scheme I

Photochemical Isomerization of Metal(ethene) Complexes



Thermal Isomerization of Metal(alkene) Complexes



represents a distinct alternative to the more conventional photoejection of ethene,¹¹⁻¹³ it is not yet clear by what mechanism it proceeds. Meanwhile, Stoutland and Bergman had demonstrated that $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_6\text{H}_{11})\text{H}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) reacts with *incoming ethene* to form both the ethene complex $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ and the corresponding vinyl hydride by independent pathways.^{8,14} Their evidence pointed to formation of a σ (or agostic) complex, $\text{Cp}^*\text{Ir}(\text{PMe}_3)\cdots\text{C}_2\text{H}_4$, prior to insertion. This intermolecular insertion pathway has been examined theoretically.¹⁵ Similar intermolecular reactions with ethene have been observed for mononuclear iron and rhenium complexes.^{5,7}

The majority of metal vinyl hydride complexes are thermodynamically unstable with respect to the corresponding ethene complexes (eq 2b), isomerizing at temperatures ranging from 0 °C ($\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$) to 180 °C ($\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$).

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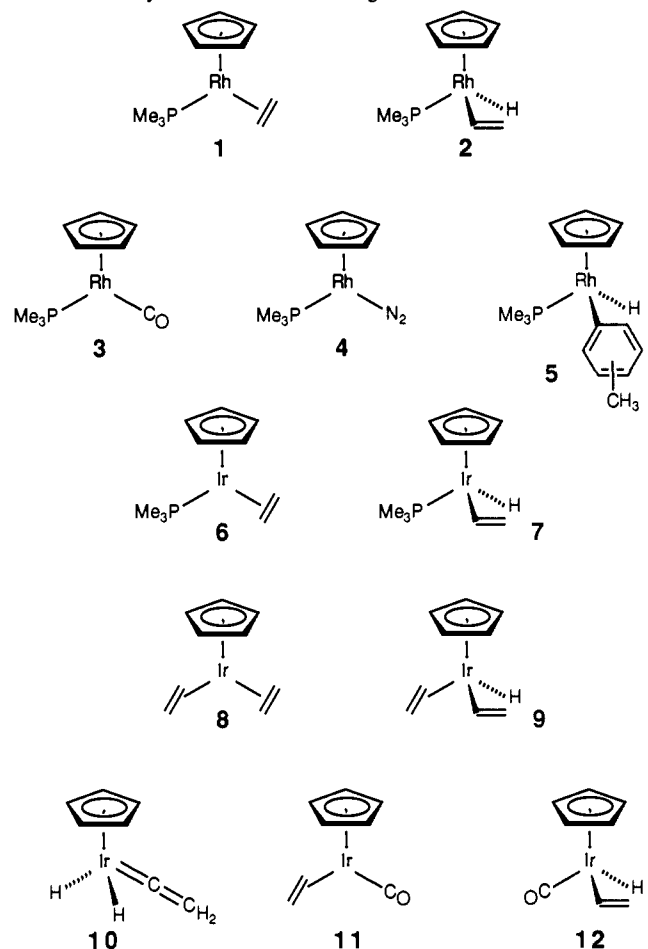
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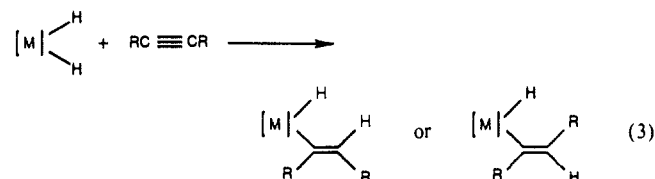
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Scheme II. Key to Formula Numbering



However, there are a few notable exceptions in which the relative stabilities are reversed (Scheme I).^{16,17} In the case of reaction I, the isomerization of the ethene complex to the vinyl hydride is accompanied by coordination of the third nitrogen of the pyrazolylborate ligand, while in Werner's example, J, stabilization is achieved by coordination of the carbonyl group of the alkenyl ligand.¹⁷

The photoisomerization of ethene complexes represents an important new route to vinyl hydride complexes. It is complementary to the reaction of metal dihydrides with alkynes (eq 3), which is a well-documented method of forming alkenyl hydride complexes, but is usually confined to alkynes with electron-withdrawing substituents.¹⁸



Vinyl C-H activation has also proved significant in H/D exchange experiments. For instance, Fallor and associates have examined the H/D exchange between C_6D_6 and *tert*-butylethene catalyzed by $\text{H}_3\text{Ir}(\text{PPr}_3)_2$,¹⁹ while we have found that photoin-

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Table I. IR Data for CpRh(PMe₃)(C₂H₃)H (**2**) and Its Isotopomers, Formed by Photolysis of CpRh(PMe₃)(C₂H₄) (**1**) in Argon Matrices (ν/cm⁻¹)

2, CpRh(PMe ₃)(C ₂ H ₃)H ^a				
d ₀	d ₉ -PMe ₃	d ₅ -Cp	d ₄ -ethene	assignment
2039		2039	1462 ^b	ν(RhH)
2027	2027	2027		
2013				
1955				
1952				
1948	1948		1948	ν(CO), 3 ^d
1562	1562	1562	1498	ν(CC), vinyl
1554	1556	1555		
1422		1419	1419	δ(CH ₃), PMe ₃
1370	1370	1369	1038	δ(CH ₂), vinyl
1365		1365		
1300	1046	1300	1300	δ(CH ₃), PMe ₃
1283	1022	1284	1283	δ(CH ₃), PMe ₃
	1011			
1243	1244	1242	995 ^c	δ(CH), vinyl
1239				
998	998	988 ^c		ρ(CH), vinyl
996				
954	792	954	953	ρ(CH), PMe ₃
940	771	940	940	ρ(CH), PMe ₃
878	878	877		δ(RhH)
875	874	875		
871	871			
855		855	855	
854				
786				
785	771 ^c	587	783	δ(CH) (⊥), Cp
751		750	698	δ(RhH)
683	684	680	679	ν(PC)
680				
640	640			
585	585	c	550	

^a d₀, d₉, d₅, d₄, refer to the undeuterated, the P(CD₃)₃, the C₅D₅, and the C₂D₄ isotopomers, respectively. ^b A very weak band is observed at 2027 cm⁻¹, corresponding to ν(RhH) formed from the C₂D₃H isotopomer. ^c Partially obscured. ^d ν(CO) of **3** formed through trace CO impurity.

duced exchange of C₂D₄ with CpRh(C₂H₄)₂ leads to H/D scrambling.^{11d}

Vinyl activation of alkenes occurs in a slightly different guise for dinuclear complexes in which the vinyl group can act as a bridging 3-electron donor.²⁰

The isomerization of CpIr(C₂H₄)₂ was discovered as part of our examination of the photochemistry of complexes containing inert ethene ligands using matrix isolation. We have continued to find that matrix isolation is a good test of such isomerization, because the vibrations of the vinyl group are very characteristic. We have followed up positive matrix experiments by photolysis of frozen or cold solutions and subsequent observation of the products by solution NMR, as in the case of (η⁶-arene)Os(CO)(C₂H₄)₁₀. We now demonstrate that CpM(PMe₃)(C₂H₄) (M = Rh, Ir) undergo similar isomerizations and provide a full account of the low-temperature photochemistry of CpIr(C₂H₄)₂. The requirement for a rigid host for the isomerization of CpRh(PMe₃)(C₂H₄) and CpIr(C₂H₄)₂ is interpreted as evidence for an intermediate cage or σ-complex. The metal vinyl hydride complexes are found to vary enormously in thermal stability with respect to the corresponding ethene complexes.

A key to the numbering of the compounds is given in Scheme II.

Results

1. CpRh(PMe₃)(C₂H₄) (1**).** The photolysis of **1** in solution at room temperature generates products consistent with C₂H₄ loss

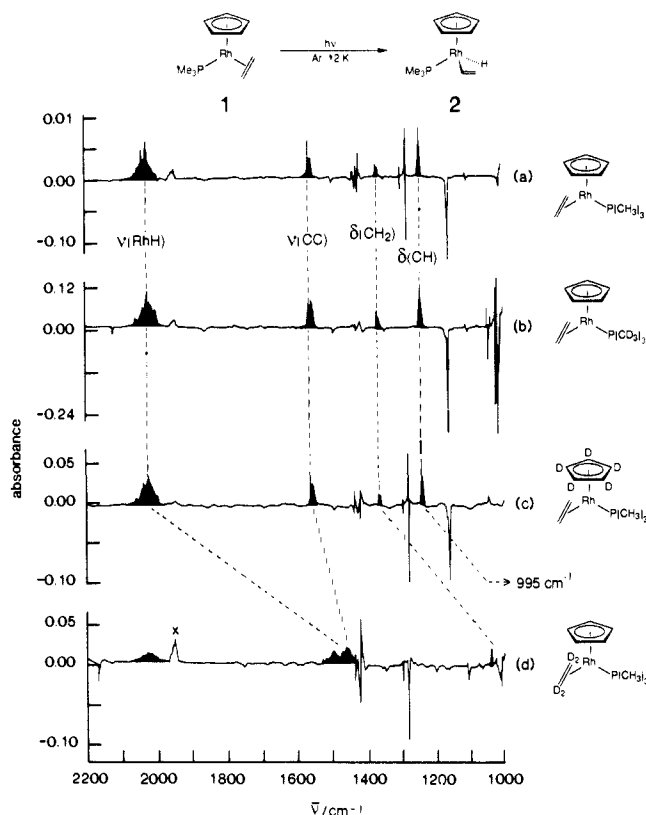


Figure 1. IR difference spectra showing the formation of CpRh(PMe₃)(C₂H₃)H (**2**) on photolysis of CpRh(PMe₃)(C₂H₄) (**1**) isolated in argon matrices at 20 K. Positive-going bands show product, and negative-going bands show loss of precursor **1**. The four bands shown in black represent the signature of the rhodium vinyl hydride unit. Spectra (a) with unlabeled **1** as the precursor, (b) with P(CD₃)₃-labeled **1** as the precursor, (c) with C₅D₅-labeled **1** as the precursor, and (d) with C₂D_xH_{4-x}-labeled **1** as the precursor. Note that only labeling of the ethene has a significant effect on the product spectrum in this region. The ν(RhH) band at 2030 cm⁻¹ retains some intensity in the final spectrum because of the incomplete deuteration of the ethene ligand. X = CpRh(PMe₃)CO generated from CO impurity. Photolysis times are given in the text; spectra were recorded on a Mattson Sirius FTIR spectrometer at 1-cm⁻¹ resolution.

as the only primary photoprocess (the UV/vis spectral data for **1** are given in footnote 21). For instance, photolysis in benzene yields CpRh(PMe₃)(Ph)H and photolysis in C₆F₆ gives CpRh(PMe₃)(η²-C₆F₆).^{11f} In the light of these results, it seemed plausible that photolysis in a matrix would yield CpRh(PMe₃) or its cyclometalated isomer, CpRh(η²-PMe₂CH₂)H.

1.a. CpRh(PMe₃)(C₂H₄) in Argon Matrices. The IR spectrum of **1** isolated at high dilution in an argon matrix at 20 K (7.7 mmol of Ar, 210 min of deposition) shows intense bands at 1282 and 951 cm⁻¹ characteristic of the PMe₃ ligand, at 1162 cm⁻¹ (coordinated ethene), and at 774 cm⁻¹ (cyclopentadienyl).²² The UV/vis spectrum of **1**, also in solid argon, shows bands at 232, 276, and 329 nm. Irradiation for 15 min (λ > 315 nm) reduces the intensity of IR bands of coordinated ethene to 30% of their original intensity and generates a broad product band at 2027 cm⁻¹. Other product bands in the IR are observed at 1562, 1370, 1243, 954, and 785 cm⁻¹ (Figure 1a; Table I). The intense product band at 954 cm⁻¹ lies close both to the positions of matrix-isolated ethene and to the most intense bands of coordinated PMe₃. No other fundamentals of ethene are detected. The band at 785 cm⁻¹ is readily assigned as a new δ(Cp) mode. There is no evidence

(21) The UV spectrum of **1** and **8** in cyclohexane solution has the following maxima (nm), extinction coefficients in parentheses (dm³ mol⁻¹ cm⁻¹): **1**—211 (2.0 × 10⁴), 240 (shoulder 1.1 × 10⁴), 285 (4.9 × 10³), 337 (shoulder 1.2 × 10³), 416 (shoulder 140); **8**—203 (1.7 × 10⁴), 233 (shoulder 4.7 × 10³), 264 (shoulder 2.4 × 10³).

(22) The IR spectra of the precursors will be discussed fully in a separate publication.

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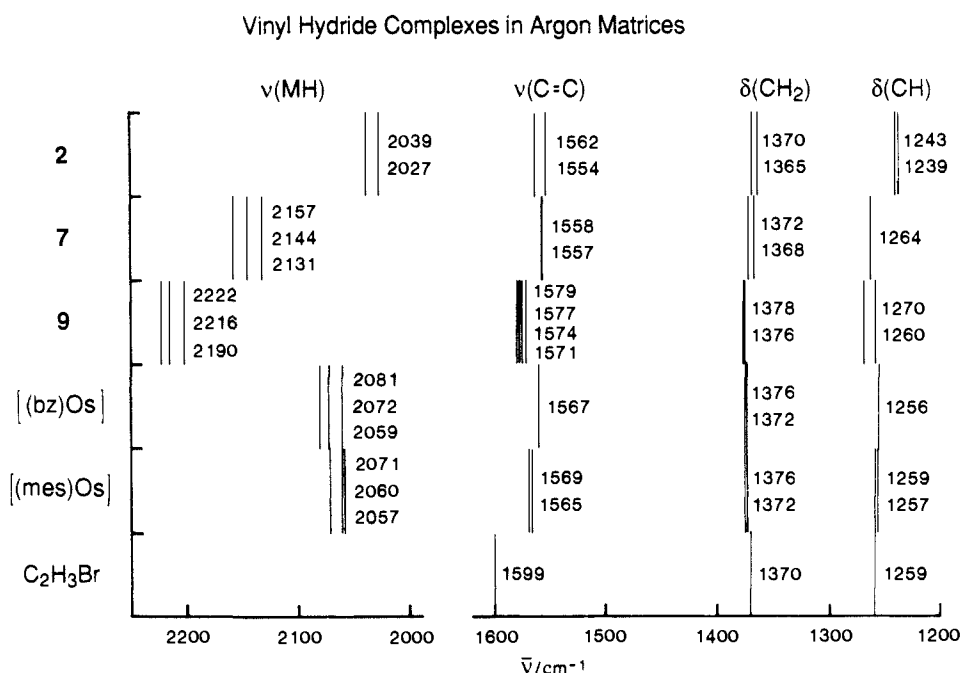


Figure 2. Schematic diagram showing metal-hydride stretching bands and the principal IR bands of the vinyl group in argon matrices for all the metal vinyl hydride complexes discussed: CpRh(PMe₃)(C₂H₃)H (**2**); CpIr(PMe₃)(C₂H₃)H (**7**); CpIr(C₂H₄)(C₂H₃)H (**9**). Also shown for comparison are bands of ($\eta^6\text{-C}_6\text{H}_6$)Os(CO)(C₂H₃)H and ($\eta^6\text{-C}_6\text{H}_3\text{Me}_3$)Os(CO)(C₂H₃)H (labeled [(bz)Os] and [(mes)Os], respectively) and of bromoethene. The bands are split into several components in most cases, because of the multiple site and/or conformational effects.

for the production of CpRh(C₂H₄).^{11c} A second period of 75 min of photolysis increases the yield of this product to ~50%. Further irradiation at a variety of wavelengths ($\lambda > 280$, $\lambda > 365$, $\lambda > 416$, $\lambda = 436$ nm) has no effect upon the spectrum. A UV difference spectrum shows the formation of product bands at 255, 305, and 351 nm, decreasing in intensity in the same order. (The UV measurements are made on the same sample as IR measurements, so ensuring the validity of the comparison.)

1.b. ($\eta^5\text{-C}_5\text{H}_5$)Rh(P(CD₃)₃)(C₂H₄) in Argon Matrices. The most intense band in the IR spectrum of **1** is shifted from 951 to 788 cm⁻¹ upon deuteration of the PMe₃ ligand. Irradiation ($\lambda > 315$ nm) for 110 min consumes 55% of the starting material (Figure 1b). Product bands are again observed at 2027, 1562, 1370, and 1244 cm⁻¹. The regions around 1440 and 950 cm⁻¹, where ethene has its most intense fundamentals (ν_{12} and ν_7), remain completely clear throughout the experiment: there is definitely no release of ethene. The positions and intensities of the phosphine IR bands of the precursor and its photoproduct are very similar in both the P(CH₃)₃ and P(CD₃)₃ complexes, indicating that the phosphine ligand is retained in the product (Table I).

1.c. ($\eta^5\text{-C}_5\text{D}_5$)Rh(P(CH₃)₃)(C₂H₄) in Argon Matrices. Deuteration of the cyclopentadienyl ligand of **1** causes shifts in several bands in the matrix IR spectrum (e.g. the most intense Cp mode at 774 cm⁻¹ is shifted to 582 cm⁻¹) but has negligible effect upon the IR spectrum in the region 2200–1150 cm⁻¹. Irradiation ($\lambda > 315$ nm) for 25 min reduces the intensities of the bands of the starting material by 50%. New *d*₅-Cp product bands are observed close to the positions of the *d*₅-Cp precursor bands (Figure 1c). The similarity in number of observed bands and their wavenumbers indicates that the integrity of the Cp ligand is maintained in the product. Product bands are again observed at 2027, 1562, 1369, and 1242 cm⁻¹ (Table I).

1.d. ($\eta^5\text{-C}_5\text{H}_5$)Rh(P(CH₃)₃)(C₂D_{4-x}H_x) in Argon Matrices. A sample of (C₅H₅)Rh(C₂D_{4-x}H_x)P(CH₃)₃, 83% deuterated at the ethene (corresponding to a distribution of 50% *d*₄, 35% *d*₃, and 15% *d*₂ isotopomers), was deposited into an argon matrix. The most intense band of the coordinated C₂H₄ ligand of **1** is shifted from 1162 to 932 cm⁻¹ upon deuteration. Irradiation ($\lambda > 315$ nm) for 15 min consumes 40% of the starting material (Figure 1d); new phosphine and Cp modes appear as described for the undeuterated molecule. There is no evidence for the production

of either C₂D₄ or C₂D₃H (their most intense bands are expected at 721 and 919 cm⁻¹). The product band at 2027 cm⁻¹ is greatly reduced in intensity compared to the spectra obtained by photolysis of the other isotopomers. The bands at 1562, 1369, and 1243 cm⁻¹, common to the *d*₀, *d*₅-Cp, and *d*₉-PMe₃ isotopomers, are all shifted to lower frequency upon deuteration of the ethene ligand (Table I).

1.e. Identification of the Photoproduct of 1. We have considered several possible assignments for the photoproduct of **1**. Production of CpRh(C₂H₄)/CpRh(C₂D₄) can be discounted since its spectrum is known.^{11c} There is no release of C₂H₄ from CpRh(PMe₃)(C₂H₄), nor of C₂D₄ from CpRh(PMe₃)(C₂D₄), so eliminating the possibilities of unsaturated CpRh(PMe₃), and its phosphine-cyclometalated or ring-metalated isomers. The product band at 2027 cm⁻¹ is plausible as a $\nu(\text{RhH})$ stretch, by comparison with CpRh(CO)(CH₃)H ($\nu(\text{RhH}) = 2056$ cm⁻¹) and with known compounds.^{11b,23a} The group of three bands at 1562, 1370, and 1244 cm⁻¹ may then be assigned to the $\nu(\text{CC})$, $\delta(\text{CH}_2)$, and $\delta(\text{CH})$ vibrations of a coordinated vinyl group with the implication that **2** is CpRh(PMe₃)(C₂H₃)H.

This assignment is supported by the deuteration experiments: deuteration of the Cp and PMe₃ groups shows that these ligands are retained in the product. Deuteration of the ethene almost completely eliminates the rhodium-hydride stretch at 2027 cm⁻¹, replacing it with a new band at 1462 cm⁻¹. The CC stretching mode is shifted down from 1562 to 1498 cm⁻¹, so it is possible that these two modes are strongly mixed in the deuterated molecule.^{23b} Substantial shifts are also observed in the $\delta(\text{CH}_2)$ (1370–1038 cm⁻¹) and $\delta(\text{CH})$ modes (1243–995 cm⁻¹), whereas these bands are completely unaffected by deuteration of either the cyclopentadienyl ligand or the phosphine ligand (Table I). The

(23) (a) Rh–H stretching vibrations: CpRh(PMe₃)₂ at 2050 cm⁻¹, Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. CpRh(C₂H₄)₂ at 2062 cm⁻¹, ref 11b. CpRh(C₂H₄)(SiEt₃)H at 2060 cm⁻¹, ref 11b. (b) The feasibility of mechanical mixing of $\nu(\text{RhD})$ and $\nu(\text{CC})$ depends on the angle between the corresponding vectors. In the crystal structure of Cp*Ir(PMe₃)(C₂H₃)H, the H–Ir–C–C unit is close to planar and the angle between the relevant vectors is ca. 39°, consistent with mixing.⁸ In the calculations of Silvestre et al.,¹⁵ there are two conformers, one with a similar geometry to the experimental one and one that brings the vectors closer to the orthogonal position that would preclude mixing. Deuteration also alters the mixing of $\nu(\text{CC})$ with $\delta(\text{CH}_2)$ and $\delta(\text{CH})$, affecting both the frequency and intensity distribution.

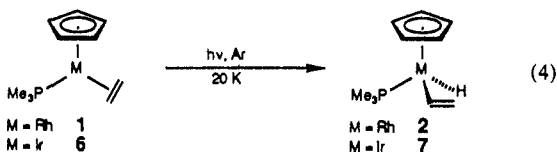
Table II. IR Data for the Photoproducts of CpRh(PMe₃)(C₂H₄) (**1**) in CO and N₂ Matrices and for CpRh(PMe₃)CO (**3**) in Argon Deposited Directly (ν/cm^{-1})^a

photolysis products of CpRh(PMe ₃)(C ₂ H ₄) (1)		direct deposition of CpRh(PMe ₃)CO (3)	assignment
CO	N ₂	Ar	
	2118		$\nu(\text{NN})$, 4
2049	2048 } 2022 }		$\nu(\text{CO})$, CpRh(CO) ₂ $\nu(\text{RhH})$, 2
1987			$\nu(\text{CO})$, CpRh(CO) ₂
1945		1958 } 1954 }	$\nu(\text{CO})$, 3
	1558		$\nu(\text{CC})$, vinyl 2
	1555		
	1370	1422	$\delta(\text{CH}_3)_a$ $\delta(\text{CH}_2)$, vinyl 2
1288	1285	1304 } 1286 } 1283 }	$\delta(\text{CH}_3)$, PMe ₃ 2/3
	1244		
1016	995 } 990 }	1013	
		985 } 953 } 939 }	$\delta(\text{CH})$, () Cp 3 $\rho(\text{CH}_3)$ 3
	875 } 873 } 871 }		
854 } 846 }	839 } 793 }	851 } 846 }	
			2
735 } 682 } 680 } 676 }	681	774 } 735 }	$\delta(\text{CH})$, (⊥) Cp 2/3 $\nu(\text{PC})_a$, 3
558 } 530 }		678	$\nu(\text{PC})_a$, 3/4
526 }		557 } 530 } 524 }	$\delta(\text{RhCO})$, 3 $\delta(\text{RhCO})$, 3

^a (**2**) = CpRh(PMe₃)(C₂H₃)H, (**4**) = CpRh(PMe₃)(N₂).

deuteration will also alter the degree of mixing between these deformation modes and $\nu(\text{CC})$.

We have compared the IR spectrum of the photoproduct to that of bromoethene, CH₂CHBr, isolated in an argon matrix. The similarity is quite striking, as is demonstrated in Figure 2. We conclude that the rhodium ethene complex, **1**, isomerizes photochemically to the corresponding rhodium vinyl hydride, **2** (eq 4).



1.f. Photochemistry of CpRh(PMe₃)(C₂H₄) in CO and N₂ Matrices. Irradiation of **1** isolated in a CO matrix for 5 min ($\lambda > 315$ nm) results in the loss of 55% of the starting material and the appearance of a single, intense, terminal $\nu(\text{CO})$ mode at 1945 cm⁻¹, assigned to CpRh(PMe₃)CO (**3**). The position of this band and the positions of seven other weaker bands in the region 1300–500 cm⁻¹ agree very well with the IR spectrum of an authentic sample of CpRh(PMe₃)CO isolated in an argon matrix (Table II). There is no trace of the vinyl hydride product in the matrix. Further irradiation increases the conversion, and a small amount of CpRh(CO)₂ is formed.

Irradiation of **1** isolated in a nitrogen matrix for 15 min with $\lambda > 315$ nm results in the consumption of 25% of the precursor and the appearance of bands characteristic of **2** (Table II). A weak band, of intensity comparable with that of the $\nu(\text{RhH})$ band of **2**, is observed at 2118 cm⁻¹. A further 60 min of irradiation does not produce any more **2**, but the feature at 2118 cm⁻¹, assigned to the $\nu(\text{NN})$ stretch of CpRh(PMe₃)N₂ (**4**) increases in intensity. The major photochemical reaction in nitrogen matrices is ethene C–H activation to form **2**. Photosubstitution is

a comparatively minor reaction, in contrast to the reaction in a CO matrix.

1.g. Photochemistry of CpRh(PMe₃)(C₂H₄) in Toluene Glasses.

The vinyl hydride photoproduct of **1** is an 18-electron, coordinatively saturated complex, potentially stable in solution at low temperature. Accordingly, a dilute solution of **1** in *d*₈-toluene in an NMR tube with attached short path length cuvette was frozen in liquid nitrogen, forming an optically clear glass, and photolyzed at 77 K for 8 h ($\lambda > 290$ nm, see Experimental Section). The sample was melted and ¹H and ³¹P NMR spectra were recorded at 203 K.

The ¹H NMR spectrum (Table III) shows that the PMe₃ resonance of **1** has decreased in intensity by ~26% on photolysis. New Cp, PMe₃, and hydride resonances appear, the last two as doublets of doublets due to coupling to ¹⁰³Rh and ³¹P nuclei. An expansion of the low-field part of the spectrum shows three complex multiplets at $\delta = 7.88$, 6.58, and 5.82 ppm, each of area equivalent to one proton. The assignment to the vinyl ligand signals in **2** is confirmed by selective decoupling experiments. A small amount of free ethene is also detected in the solution (5.29 s). A very weak, broad doublet at $\delta = 0.87$ ppm ($J(\text{PH}) \sim 11$ Hz) is assigned as CpRh(PMe₃)(C₆D₄CD₃)D (see below).

The ³¹P{¹H} NMR spectrum reveals one major product downfield of **1**, with a reduced rhodium–phosphorus coupling (**1**, $J(\text{RhP}) = 197$ Hz; product, $J = 156$ Hz; both doublets). It has been demonstrated that $J(\text{RhP})$ is sensitive to the rhodium oxidation state in (C₅R₅)Rh(PMe₃) complexes, with a smaller coupling constant of ~150 Hz indicative of a Rh(III) species and a larger ~200 Hz coupling constant characteristic of a Rh(I) species.²⁴ The coupling of phosphorus to the hydridic proton has been measured in the ¹H spectrum (41.6 Hz) and, by selective decoupling, in the ³¹P spectrum. The values agree within 0.2 Hz. These NMR experiments leave no doubt that the product of photolysis of **1** in a toluene glass is vinyl hydride **2**.

When the solution is warmed to 253 K for approximately 1 min all signals due to **2** disappear, with complete regeneration of **1**.

Thus, the combination of matrix-isolation (20 K) experiments with IR detection and low-temperature (77 K) hydrocarbon glass experiments with NMR detection provides unequivocal evidence for the vinylic C–H activation of the ethene ligand of CpRh(PMe₃)(C₂H₄) and consequent formation of CpRh(PMe₃)(C₂H₃)H.

1.h. Photochemistry of CpRh(PMe₃)(C₂H₄) in Toluene Solution. Complex **1** was photolyzed ($\lambda > 375$ nm) in *h*₈-toluene solution for 22 h at room temperature. After removal of the solvent, ¹H NMR spectra recorded in *d*₆-benzene show 85% loss of **1**. Formation of two hydridic products accounts for 72% of the starting material, while the remainder reacts to form CpRh(PMe₃)₂. The hydride resonances of the major products appear as closely spaced doublets of doublets. These products also show overlapping peaks for the methyl group of a tolyl moiety and peaks in the aromatic region. They overlap again in the ³¹P{¹H} spectrum and show RhP coupling constants of 158 Hz characteristic of Rh(III).²⁴ We conclude that photolysis of **1** generates isomers of CpRh(PMe₃)(C₆H₄CH₃)H (**5**) (cf. the Cp* analogue).²⁴

Since **2** is unstable at room temperature it is understandable that it is not observed under these conditions. Accordingly, a solution of **1** in *d*₈-toluene was photolyzed ($\lambda > 290$ nm) at 213 K and NMR spectra were recorded at the same temperature. The major product was the tolyl deuteride, **5-d**₈; no **2** was formed even though it is stable at this temperature. An additional minor product, with a PMe₃ resonance at significantly lower field, disappears on warming to room temperature. Its thermal instability and different chemical shift suggest that it is the benzylic insertion product, CpRh(PMe₃)(CD₂C₆D₅)D, rather than an aryl complex. The photolysis was repeated at 188 K, only 8 deg above

(24) (a) Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (c) Jones, W. D.; Dong, L. *Organometallics* **1989**, *111*, 8722. (d) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

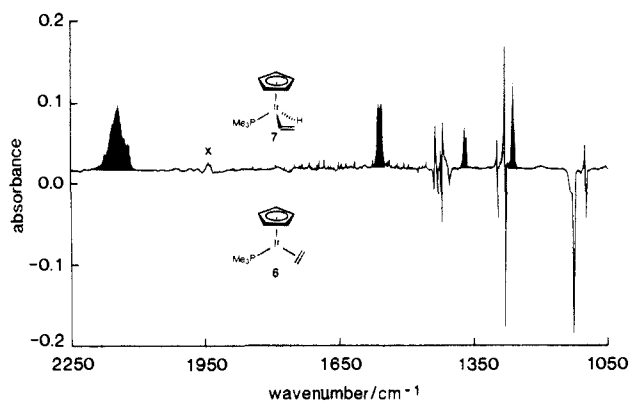


Figure 3. IR difference spectrum obtained following 20 min of photolysis ($\lambda > 290$ nm) of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ (**6**) isolated in an argon matrix at 20 K. Positive-going bands show growth of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (**7**), and negative-going bands show loss of **6**. The bands shown in black correspond to the $\nu(\text{IrH})$ and vinyl modes. X = $\text{CpIr}(\text{PMe}_3)\text{CO}$ generated from CO impurity. The spectrum was measured at 1-cm^{-1} resolution on a Mattson Sirius FTIR spectrometer.

the melting point of the solvent, and NMR spectra were recorded again at 213 K. Complexes **2** and **5** were formed in almost equal proportions together with a small amount of the benzylic insertion product (5 h, $\lambda > 290$ nm, 52% conversion).

2.a. Photochemistry of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ in Argon and Carbon Monoxide Matrices. The iridium analogue of **1** has not been reported previously, although $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ has been generated in mixtures with $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ or $\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}_2$.⁸ Complex **6**, $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$, was synthesized following Werner's method²⁵ by reaction of $\text{CpIr}(\text{PMe}_3)(\text{CH}_3)_2$ with $[\text{Ph}_3\text{C}][\text{PF}_6]$ in dichloromethane. The resulting $[\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)\text{H}][\text{PF}_6]$ was deprotonated with NaH in THF yielding the desired product, **6**.

The IR spectrum of **6** in an argon matrix (10.9 mmol of Ar, 270 min of deposition) is very similar to the IR spectrum of the Rh congener, **1**. The most intense bands in the spectrum are observed at 1282 and 948 cm^{-1} (PMe_3 ligand), at 788 cm^{-1} (Cp), and at 1126 cm^{-1} (coordinated ethene).

After 20 min of irradiation ($\lambda > 285$ nm), the bands of the starting material are reduced by 70%. New bands are observed at 2144, 1564, 1372, and 1264 cm^{-1} (Figure 3; Table IV). The striking similarity to the spectrum of **2** in Figure 1 allows us to assign the product as the corresponding iridium vinyl hydride, $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (**7**) (eq 4). After an additional 75 min of irradiation with $\lambda > 285$ nm, the conversion of **6** to **7** exceeds 95%.

When **6** is photolyzed in solid CO ($\lambda > 315$ nm, 26 min), **7** is again generated as is evident from the vinyl modes (Table IV). In addition, several new carbonyl products are formed with similar intensities (2046 , 2042 , 1990 , 1980 , 1929 cm^{-1}) and ethene is released. Of these, the band at 1929 cm^{-1} may be identified as $\text{CpIr}(\text{PMe}_3)\text{CO}$ (compare the rhodium analogue). On repeating the experiment in a CO/Ar (2:98) matrix, **7**, ethene, and $\text{CpIr}(\text{PMe}_3)\text{CO}$ (1936 cm^{-1}) are generated once again; the remaining unidentified carbonyl products are reduced in intensity relative to $\text{CpIr}(\text{PMe}_3)\text{CO}$. The absorbance ratio of **6**:**7** in subtraction spectra measured at 1130 and 1264 cm^{-1} respectively increases

from 1.9 (Ar) to 2.2 (Ar/CO) and 2.3 (CO). Hence, the ratio of isomerization/carbonyl products may be estimated as ca. 6 in CO/Ar and ca. 5 in pure CO.

2.b. Photochemistry of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ in Toluene Solution. Following the characterization of **2** in low-temperature toluene solution, a similar synthesis of **7** was attempted, but without freezing the solution. A colorless solution of **6** in d_8 -toluene was cooled to 188 K and irradiated for 5 h ($\lambda > 285$ nm). ^1H , ^{31}P , and ^{13}C NMR spectra were subsequently recorded at 253 K.

The ^1H NMR spectrum of the resultant solution showed that conversion of **6** to **7** exceeds 90%. The Cp and PMe_3 resonances exhibit large ^{31}P couplings. The lower field portion of the spectrum reveals the α -vinyl proton as a 16-line multiplet (Figure 4a), with couplings to the two inequivalent β -vinyl hydrogens, the iridium hydride, and the ^{31}P of the phosphine. The β -vinyl hydrogens show similar multiplicities. Decoupling at the hydride (Figure 4b) results in the removal of one small coupling in each of the vinyl hydrogens.

The $^{31}\text{P}\{^1\text{H}\}$ spectrum shows an intense singlet at $\delta = -38.9$ ppm, which splits into a doublet with selective irradiation targeted to retain hydride coupling. The value of $J(\text{PH})$ (34.4 Hz) agrees well with the phosphorus-hydride coupling of 34.5 Hz measured in the ^1H NMR spectrum confirming the assignment of this resonance to **7**. There is no evidence for insertion into the toluene.

The ^{13}C spectrum, measured with use of a DEPT pulse sequence, allows unambiguous assignment of all carbon resonances. The ^1H , ^{31}P , and ^{13}C NMR data for **7** in d_8 -toluene solution are summarized in Table IV.

Complex **7** isomerizes slowly to **6** on heating to 393 K, a temperature 140 deg higher than that required for the Rh analogue, **2**. Since it is so stable, it should be possible to generate it by photolysis at room temperature. Indeed, after 1 h of irradiation of **6** at 300 K, complex **7** is the major species present ($[\text{7}]:[\text{6}] = 3.4$), but several other products are formed in much smaller amounts and a little ethene is released. In short, photolysis at room temperature is effective but not so specific as at low temperature.

3.a. Photochemistry of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ in Argon and Neon Matrices. The IR spectrum of matrix-isolated $\text{CpIr}(\text{C}_2\text{H}_4)_2$ (**8**) is dominated by the characteristic doublet of the two $\nu(\text{CC})-\delta(\text{CH}_2)$ modes of coordinated ethene and by the ring deformations at 1006 and 808 cm^{-1} .²² The UV spectrum of this white complex, also recorded in solid argon, shows a maximum at 202 nm with shoulders at 234 and 261 nm.²¹ Irradiation of **8** in an argon matrix at 16 K for 60 min with $\lambda > 360$ nm results in $\sim 20\%$ loss of starting material. Only a very small amount of ethene is released into the matrix. The major product, **9**, exhibits a band at 2193 cm^{-1} in the Ir-H stretching region, bands at 1579, 1369, and 1265 cm^{-1} which we now recognize as $\nu(\text{CC})$, $\delta(\text{CH}_2)$, and $\delta(\text{CH})$ vibrations of a coordinated vinyl ligand, a band at 1189 cm^{-1} in the region of coordinated ethene, and further product bands to lower frequency (Figure 5a; Table V). Most of the product bands exhibit several components, especially the Ir-H stretching (center 2193 cm^{-1}), C=C stretching mode (center 1579 cm^{-1}), and $\delta(\text{CH})$ mode (center 1265 cm^{-1}). Table V lists the full set of bands. An additional product band at 1681 cm^{-1} is shown unequivocally to belong to a different species, **10**, by a period of shorter wavelength photolysis (65 min, $\lambda > 280$ nm). Following this second photolysis, the loss of **8** increases to 50%, **9** is formed in improved yield, large amounts of free ethene (951 cm^{-1}) are released, and the band at 1681 cm^{-1} becomes more intense than the band of **9** at 1579 cm^{-1} (Figure 5b). It is now evident that **10** exhibits a band at 2184 cm^{-1} in the $\nu(\text{IrH})$ region overlapping with that of **9** and several lower frequency modes in addition to the prominent band at 1681 cm^{-1} .

The photochemistry of **8** in neon matrices at 4.5 K (Table V) proceeds similarly to that in argon matrices at 16 K. However, there is a considerable reduction in the splitting of the product bands in the C=C stretching region. Nevertheless, the Ir-H stretching region still contains several overlapping bands, and the $\delta(\text{CH})$ mode of the vinyl group is still split into two components 14-cm^{-1} apart (Figure 6).

(25) Roder, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686.
 (26) C=C stretching vibrations of vinylidene complexes: (a) $\text{tr-Rh}(\text{PPR}_3)_2(\text{Cl})(\text{CCH}_2)$ at 1620 cm^{-1} , Alonso, F. J. D.; Hoehn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406. (b) $\text{tr-Ir}(\text{PPR}_3)_2(\text{Cl})(\text{CCH}_2)$ at 1640 cm^{-1} , Hoehn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255. (c) $\text{Ir}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2](\text{CCH}_2)$ at 1648 cm^{-1} , Fryzuk, M. D.; McManus, N. T.; Rettig, S. J.; White, G. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 73. (d) $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{CCH}_2)]^+$ at 1630 cm^{-1} , Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (e) $[\text{CpFe}(\text{dppe})(\text{CCH}_2)]^+$ at 1625 cm^{-1} , Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. (f) $[\text{CpRu}(\text{PMe}_3)_2](\text{CCH}_2)^+$ at 1632 cm^{-1} , Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203. (g) $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{CCH}_2)]^+$ at 1641 cm^{-1} , Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

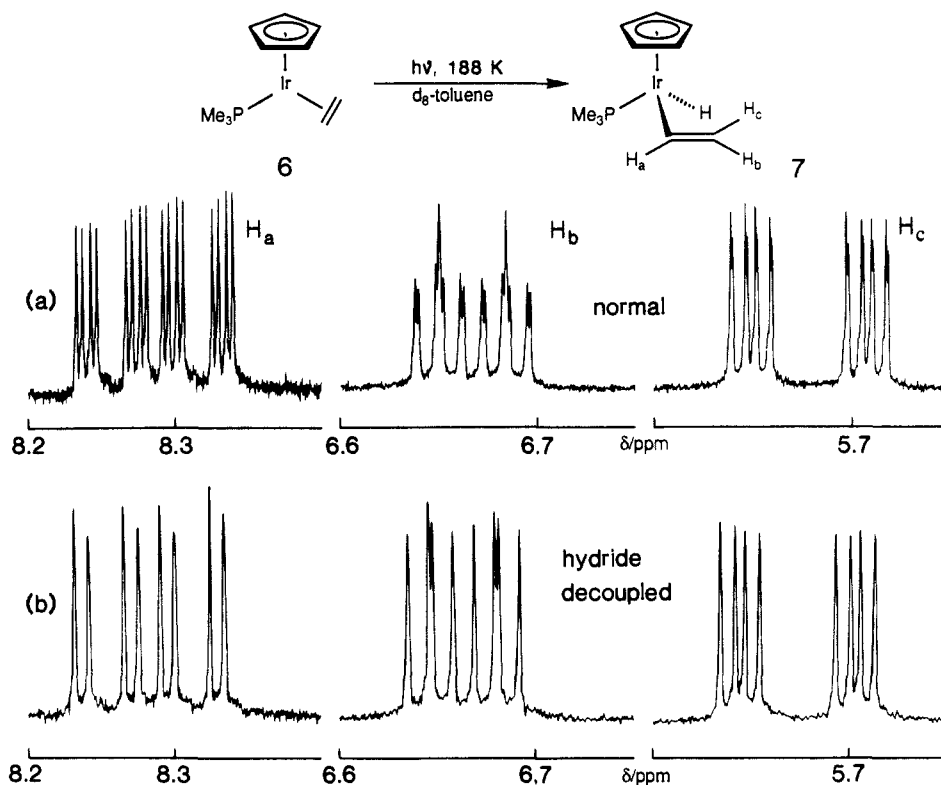


Figure 4. ^1H NMR spectra (300 MHz, recorded on Bruker MSL300) of vinyl protons of $\text{Cplr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (7) recorded at 253 K following 5 h of photolysis ($\lambda > 290$ nm) of $\text{Cplr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ (6) in d_8 -toluene at 188 K: (a) normal spectrum; (b) spectrum recorded with decoupling at -17 ppm corresponding to the hydride resonance. The labeling of the protons (a–c) is shown in the figure. All the protons are coupled to ^{31}P , the other vinyl protons, and the hydride.

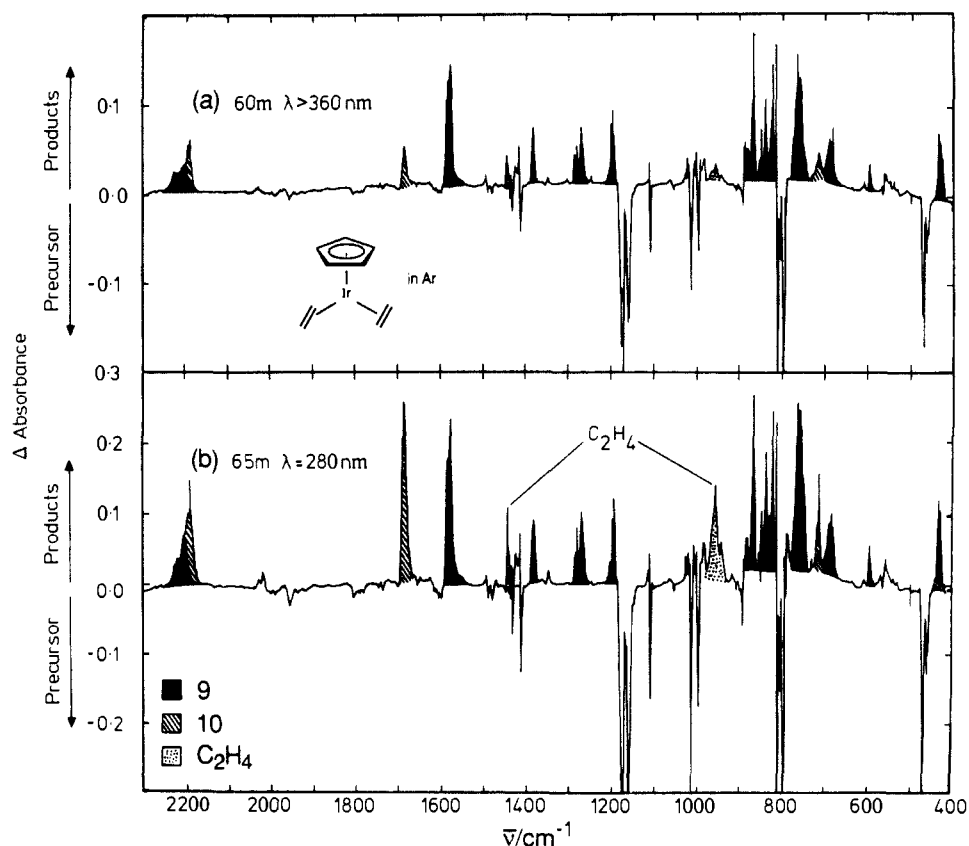


Figure 5. IR difference spectra relative to the deposition spectrum obtained following photolysis of $\text{Cplr}(\text{C}_2\text{H}_4)_2$ (8) in an argon matrix at 16 K. Positive-going bands show growth of product, and negative-going bands loss of precursor. (a) Spectrum after 60 min of photolysis with $\lambda > 360$ nm, generating principally $\text{Cplr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (9) (shown black) with a small amount of 10 (shaded); (b) spectrum after 65 min of additional photolysis with a $\lambda = 280$ nm interference filter. This last stage of photolysis causes a major increase in secondary product, $\text{Cplr}(\text{C}_2\text{H}_3)_2$ (10), and releases ethene (stippled). Spectra were recorded at 0.5-cm^{-1} resolution on a Bruker IFS 113v FTIR spectrometer.

Table III. ^1H , ^{31}P , and ^{13}C NMR Data for $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (**2**), $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (**7**), and $\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (**9**) in d_8 -Toluene^a

	δ/ppm multiplicity	J/Hz	integration	assignment
CpRh(PMe₃)(C₂H₃)H (2)				
^1H , 300 MHz, 203 K	7.88 (dddd)	$J(\text{H}_a\text{H}_c) = 17.3$ $J(\text{H}_a\text{H}_b) = 9.6$ $J(\text{H}_a\text{P}) = 2.8$ $J(\text{H}_a\text{Rh}) = 1.0$	1 H	H _a (CHCH ₂)
	6.58 (ddd)	$J(\text{H}_b\text{H}_a) = 9.6$ $J(\text{H}_b\text{H}_c) = 2.2$ $J(\text{H}_b\text{Rh}) < 0.5$	1 H	H _b (CHCH ₂)
	5.82 (ddd)	$J(\text{H}_c\text{H}_a) = 17.3$ $J(\text{H}_c\text{H}_b) = 2.2$ $J(\text{H}_c\text{Rh}) < 0.5$	1 H	H _c (CHCH ₂)
	5.16 (dt)	$J(\text{H}_d\text{P}) = 1.2$ $J(\text{H}_d\text{H}_f) = 0.5$ $J(\text{H}_d\text{Rh}) = 0.5$	5 H	H _d (C ₅ H ₅)
	0.95 (dd)	$J(\text{H}_e\text{P}) = 10.6$ $J(\text{H}_e\text{Rh}) = 1.1$	9 H	H _e (PMe ₃)
	-13.52 (dd)	$J(\text{H}_f\text{P}) = 41.6$ $J(\text{H}_f\text{Rh}) = 31.5$	1 H	H _f (RhH)
^{31}P , 121 MHz	13.9 (dd)	$J(\text{RhP}) = 156.1$ $J(\text{H}_f\text{P}) = 41.8$		PMe ₃
CpIr(PMe₃)(C₂H₃)H (7)				
^1H , 300 MHz, 253 K	8.31 (dddd)	$J(\text{H}_a\text{H}_c) = 17.6$ $J(\text{H}_a\text{H}_b) = 10.1$ $J(\text{H}_a\text{P}) = 2.9$ $J(\text{H}_a\text{H}_f) = 1.2$	1 H	H _a (CHCH ₂)
	6.73 (dddd)	$J(\text{H}_b\text{H}_a) = 10.1$ $J(\text{H}_b\text{H}_c) = 3.7$ $J(\text{H}_b\text{P}) = 3.2$ $J(\text{H}_b\text{H}_f) = 0.5$	1 H	H _b (CHCH ₂)
	5.72 (dddd)	$J(\text{H}_c\text{H}_a) = 17.6$ $J(\text{H}_c\text{H}_b) = 3.7$ $J(\text{H}_c\text{P}) = 2.3$ $J(\text{H}_c\text{H}_f) = 0.3$	1 H	H _c (CHCH ₂)
^{13}C , 75 MHz	4.93 (d) ^b	$J(\text{H}_d\text{P}) = 1.0$	5 H	H _d (C ₅ H ₅)
	1.28 (d)	$J(\text{H}_e\text{P}) = 10.6$	9 H	H _e (PMe ₃)
	-17.05 (d)	$J(\text{H}_f\text{P}) = 34.5$	1 H	H _f (IrH)
	126.7 (d)	$J(\text{C}_a\text{P}) = 3.3$		C _a (CHCH ₂)
	117.1 (d)	$J(\text{C}_b\text{P}) = 13.3$		C _b (CHCH ₂)
^{31}P , 121 MHz	83.2 (d)	$J(\text{C}_c\text{P}) = 2.9$		C _c (C ₅ H ₅)
	22.9 (d)	$J(\text{C}_d\text{P}) = 40.1$		C _d (PMe ₃)
	-38.9 (d)	$J(\text{PH}_f) = 34.4$		PMe ₃
CpIr(C₂H₄)(C₂H₃)H (9)				
^1H , 360 MHz, 253 K	7.26 (dd)	$J(\text{H}_a\text{H}_c) = 17.4$ $J(\text{H}_a\text{H}_b) = 9.8$	1 H	H _a (CHCH ₂)
	6.33 (dd)	$J(\text{H}_b\text{H}_a) = 9.8$ $J(\text{H}_b\text{H}_c) = 2.3$	1 H	H _b (CHCH ₂)
	5.35 (dd)	$J(\text{H}_c\text{H}_a) = 17.4$ $J(\text{H}_c\text{H}_b) = 2.5$	1 H	H _c (CHCH ₂)
	4.61 (s)		5 H	H _h (C ₅ H ₅)
	3.10 (dd)	$J(\text{HH}_{\text{trans}}) = 11.5$ $J(\text{HH}_{\text{cis}}) = 8.8$	1 H	H _d (C ₂ H ₄)
	~2.7	overlaps with 8		H _e , H _f (C ₂ H ₄)
^{13}C , 90 MHz	1.41 (dd)	$J(\text{HH}_{\text{trans}}) = 11.0$ $J(\text{HH}_{\text{cis}}) = 8.5$	1 H	H _g (C ₂ H ₄)
	-16.03 (s)		1 H	H _j (IrH)
	122.1 (s)			C _a (CHCH ₂)
	118.5 (s)			C _b (CHCH ₂)
	86.5 (s)			C _c (C ₅ H ₅)
	27.7 (s)			C _d (C ₂ H ₄)
	19.7 (s)			C _e (C ₂ H ₄)

^a ^{13}C assignments secured by DEPT. ^bAt 293 K, the Cp resonance shows an additional coupling of 0.4 Hz to the hydride proton.

3.b. Photolysis of CpIr(C₂D₄)₂ in Argon Matrices. The synthesis of CpIr(C₂D₄)₂ proceeds without exchange problems leading to >96% deuteration at ethene. The photolysis of **8** in solid argon proceeds as for the d_0 isotopomer. The presence of $\nu(\text{CD})$ modes between 2150 and 2320 cm^{-1} in precursor and products makes it impossible to determine from the $\nu(\text{IrH})$ region whether any hydride has been formed. Moreover, the $\nu(\text{IrD})$ bands of the photoproduct appear at 1578 cm^{-1} , almost coincident with one of the bands of protiophotoproduct **9**. Nevertheless, we could establish that the pattern of deuterium shifts in the vinyl bands

of **9** follows that established for **2** (Table V). This time there are two further bands that exhibit substantial shifts, consistent with the presence of coordinated ethene.

The formation of the secondary product is easier to follow: free C₂D₄ is conspicuous (723 cm^{-1}), and the prominent band of **10** at 1681 is replaced by one at 1658 cm^{-1} . The isotopic selectivity can be gauged from the absence of any product bands between 1660 and 1700 cm^{-1} .

3.c. Photolysis of CpIr(C₂H₄)₂ in Ethene-Doped Argon Matrices. We also investigated the effect on the product distribution

Table IV. IR Data for $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (**7**) Formed by Photolysis of $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ (**6**) in Argon and Carbon Monoxide Matrices (ν/cm^{-1})

$\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ (7)		assignment	
Ar	CO		
2157	a	$\nu(\text{IrH})$	
2144			
2131			
1565	1558	$\nu(\text{CC})$, vinyl	
1563			1553
1558			
1557			
1420	1416	$\delta(\text{CH}_2)$, vinyl	
1372	1369		
1368			
1300		$\delta(\text{CH}_3)$, PMe_3	
1283	1285	$\delta(\text{CH}_3)$, PMe_3	
1264	1264	$\delta(\text{CH})$, vinyl	
1103	1102	$\nu(\text{CC})$, Cp	
994	997	$\rho(\text{CH})$, vinyl	
956	b	$\rho(\text{CH})$, PMe_3	
940	b	$\rho(\text{CH})$, PMe_3	
873			
869	c	$\delta(\text{IrH})$	
837	c		
835			
797	c	$\delta(\text{CH})$, (\perp) Cp	
732	c	$\nu(\text{PC})_3$	
727			
684	c	$\nu(\text{PC})_2$	
590	c		

^aObscured by CO. ^bObscured by ethene released on photolysis.
^cNot recorded.

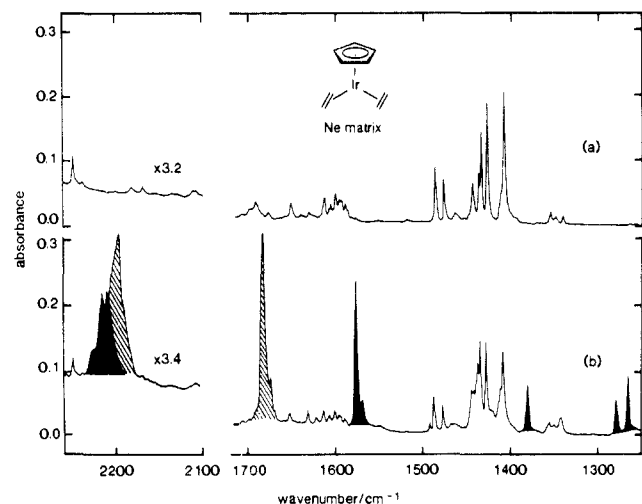


Figure 6. (a) IR spectrum of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ (**8**) in a neon matrix at 4 K; (b) spectrum obtained after 30 min of photolysis at $\lambda = 280$ nm (interference filter). The bands shown in black correspond to the $\nu(\text{IrH})$ and vinyl modes of $\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (**9**). The $\nu(\text{IrH})$ and $\nu(\text{C}=\text{C})$ modes of **10** are shown shaded. Notice the reduction in matrix splittings of most of the bands compared to those in Figure 5. Spectra were recorded at 0.5-cm^{-1} resolution on a Bruker IFS 113v FTIR spectrometer.

of doping the matrix with either C_2H_4 or C_2D_4 . Photolysis of **8** in a matrix of $\text{C}_2\text{H}_4/\text{Ar}$ (1:9) generated products **9** and **10** as previously shown, except for slight shifts ($<7\text{ cm}^{-1}$) in the bands and alterations in the splitting patterns. The course of reaction in a $\text{C}_2\text{D}_4/\text{Ar}$ (1:9) matrix was harder to follow because of a band of C_2D_4 at 1570 cm^{-1} which overlaps with the deuterated analogue of **9**. Nevertheless, we could establish that both **9** and **10** were formed in undeuterated form. There was no formation of deuterated **10**, and deuterated **9**, if it was formed at all, was far exceeded by undeuterated product.

3.d. Identity of 9. The generation of **9** proceeds without release of ethene, suggesting that we are forming an isomer of **8**. Since

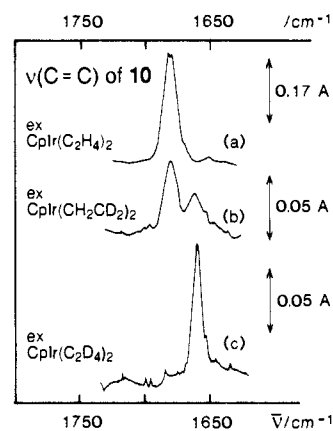
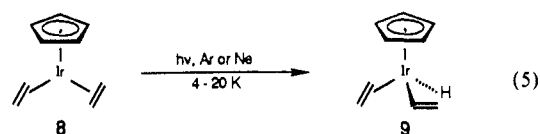


Figure 7. IR spectra showing the $\nu(\text{C}=\text{C})$ mode of product **10** generated on photolysis of matrices containing (a) $\text{CpIr}(\text{C}_2\text{H}_4)_2$, (b) $\text{CpIr}(\text{CH}_2=\text{CD}_2)_2$, and (c) $\text{CpIr}(\text{C}_2\text{D}_4)_2$. Notice the presence of two bands in spectrum b with wavenumbers close to those recorded in a and c—strong evidence that **10** is $\text{CpIr}(\text{CCH}_2)\text{H}_2$.

9 is generated in the presence of excess ethene, it is likely that it is an 18-electron complex. The presence of bands in the $\nu(\text{IrH})$ region and the complete set of bands of a coordinated vinyl group $\nu(\text{CC})$, $\delta(\text{CH}_2)$, and $\delta(\text{CH})$ demonstrates that **9** must be a metal vinyl hydride. Three further bands between 900 and 1200 cm^{-1} characteristic of coordinated ethene and a cyclopentadienyl ligand (see Table V) lead us to assign **9** as $\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$. The isomerization shown in eq 5 is, therefore, the first observed photochemical reaction of **8**.



3.e. Photolysis of $\text{CpIr}(\text{CH}_2=\text{CD}_2)_2$ in Argon Matrices and the Identity of 10. The formation of **10**, the secondary photolysis product of **8**, requires shorter wavelength irradiation than for **9** and releases ethene. The position of its fundamentals, and the isotopic shift observed in the 1681-cm^{-1} band with C_2D_4 substitution, makes it clear that this species contains a CC multiple bond and an iridium-hydride bond. The lack of effect of excess ethene or N_2 (see below) on its formation suggests that **10** is also an 18-electron complex. The CC stretching mode has a frequency too high for a vinyl complex (see above), but two other assignments are possible: either a vinylidene complex, $\text{CpIr}(\text{C}=\text{CH}_2)(\text{H})_2$, or an ethyne complex, $\text{CpIr}(\eta^2\text{-C}_2\text{H}_2)(\text{H})_2$. The CC stretch of **10** is a little higher than $\nu(\text{CC})$ of more stable vinylidene complexes which fall in the range $1620\text{--}1641\text{ cm}^{-1}$.²⁶ Ethyne complexes exhibit a wider range of $\nu(\text{CC})$ frequencies, varying from 1613 to 1712 cm^{-1} .²⁷

However, the two possible assignments should be distinguishable conclusively by use of a precursor labeled with $\text{CH}_2=\text{CD}_2$. The vinylidene product would be formed as a mixture of two isotopomers, A and B. The $\text{Ir}(\text{CCH}_2)(\text{D}_2)$ isotopomer should have a $\nu(\text{CC})$ mode close to 1681 cm^{-1} , and the $\text{Ir}(\text{CCD}_2)(\text{H}_2)$ isotopomer should absorb close to 1658 cm^{-1} . In contrast, there should be one isotopomer C for the ethyne complex (discounting the effect

(27) CC stretching vibrations of some ethyne complexes: (a) $\text{Ir}(\text{PPr}_3)_2(\text{Cl})(\text{CHCH})$ 1700 cm^{-1} , Hoehn, A. Dissertation, University of Würzburg, 1986 (the original value in the literature is incorrect). (b) $\text{Rh}(\text{PPr}_3)_2(\text{Cl})(\text{CHCH})$ at 1712 cm^{-1} , Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327. (c) $\text{Cp}_2\text{Mo}(\text{HCCH})$ at 1613 cm^{-1} , Wong, K. L. T.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. (d) $\text{CpCr}(\text{NO})(\text{CO})(\text{CHCH})$ at 1720 cm^{-1} , Herberhold, M.; Alt, H.; Kreiter, C. G. *J. Organomet. Chem.* **1972**, *42*, 413. (e) $\text{Ir}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2(\text{CHCH})$ at 1678 cm^{-1} , Camia, M.; Lachi, M. P.; Ben-zoni, L.; Zanzoterra, C.; Tacchi Venturi, M. *Inorg. Chem.* **1970**, *9*, 251. (f) $\text{Ir}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2](\text{CHCH})$ at 1958 cm^{-1} , ref 26d; this complex appears out of line with the others and must be regarded as a tentative identification at this stage.

Table V. IR Data for the Photoproducts of $\text{Cplr}(\text{C}_2\text{H}_4)_2$ (**8**) and $\text{Cplr}(\text{C}_2\text{D}_4)_2$ (**8-d₄**) in Ar and Ne Matrices (ν/cm^{-1})

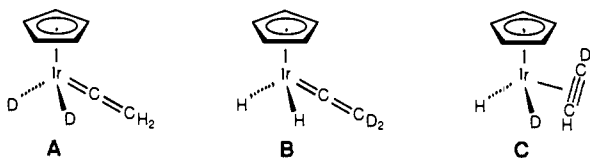
$\text{Cplr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (9)				$\text{Cplr}(\text{CCH}_2)\text{H}_2$ (10) + free ethene								
<i>ex 8</i> Ne	<i>ex 8</i> Ar	<i>ex 8-d₄</i> Ar	assignment	<i>ex 8</i> Ne	<i>ex 8</i> Ar	<i>ex 8-d₄</i> Ar	assignment					
2215 } 2209 } 2202 }	2222 } 2216 } 2190 }	1578	$\nu(\text{IrH}/\text{IrD})$	2197	2198 } 2194 } 2184 }	1578	$\nu(\text{IrH}/\text{IrD})$					
1576 } 1568 }	1579 } 1577 } 1574 }				1501			$\nu(\text{CC})$ vinyl	1682 } 1673 }	1681 } 1679 }	1658	$\nu(\text{CC})$ vinylidene
	1571 } 1419 } 1410 }								<i>b</i>	$\delta(\text{CH})$ Cp		
<i>b</i> <i>b</i>	<i>a</i> <i>a</i>	1301	$\nu(\text{CC}) + \delta(\text{CH}_2)$ coord ethene	953	951	723	ν_7 ethene					
1380 } 1279 } 1265 }	1378 } 1376 } 1280 }	1048	$\delta(\text{CH}_2/\text{CD}_2)$ vinyl	<i>b</i> <i>b</i>	<i>b</i> <i>b</i>	832	$\delta(\text{CH})$ Cp					
	1276 } 1265 } 1194 }					995	$\delta(\text{CH}/\text{CD})$ vinyl	716	711 } 708 }	688	$\delta(\text{IrH}/\text{IrD})$	
1193 } <i>b</i>	1190 } 1188 }	947	$\nu(\text{CC})-\delta(\text{CH}_2)$ coord ethene	1106 } 912 }	<i>b</i>	549	$\delta(\text{IrH}/\text{IrD})$					
864 } 846 } 835 } 829 }	864 } 861 } 834 }							1106 } 912 }	$\nu(\text{CC})$ Cp	818 } 770 } 761 } 756 } 747 }	818 } <i>b</i>	$\delta(\text{CH})$ (\perp) Cp
684 } 592 } 560 } 427 }	685 } 681 } 677 }	549	$\delta(\text{IrH}/\text{IrD})$	592 } 560 }	<i>b</i> <i>b</i>	431 } 426 }	$\delta(\text{IrH}/\text{IrD})$					
	427 }							<i>b</i>	$\delta(\text{IrH}/\text{IrD})$			

^aAdditional weak bands are observed at 2015 cm^{-1} (Ne matrices) and 2015, 2012 cm^{-1} (Ar matrices), which are assigned to an unidentified product. ^bObscured or not observed.

Table VI. IR Spectra (ν/cm^{-1}) of Photolysis Products of $\text{Cplr}(\text{C}_2\text{H}_4)_2$ (**8**) in CO, CO/Ar (1:10), and N_2 Matrices above 900 cm^{-1}

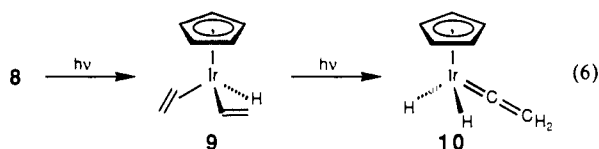
C_2H_4		$\text{Cplr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (9)		$\text{Cplr}(\text{CCH}_2)\text{H}_2$ (10)		$\text{Cplr}(\text{CO})(\text{C}_2\text{H}_4)$ (11)		
CO	N_2	CO	N_2	CO	N_2	CO	$^{12}\text{CO}/\text{Ar}$	$^{12}\text{CO}/^{13}\text{CO}/\text{Ar}$
1435	1435	1571	1572	1677	1681	1974	1979	1979 $\nu(^{12}\text{CO})$
935	951	1376	1380					1931 $\nu(^{13}\text{CO})$
		1263	1264					
		1196	1195					
$\text{Cplr}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$ (12)			$\text{Cplr}(\text{CO})_2$		$\text{Cplr}(\text{N}_2)(\text{C}_2\text{H}_4)$ (13)			
CO	$^{12}\text{CO}/\text{Ar}$	$^{12}\text{CO}/^{13}\text{CO}/\text{Ar}$	CO		$^{14}\text{N}_2$	$^{14}\text{N}_2/^{15}\text{N}_2$		
2021	2019	2020 $\nu(^{12}\text{CO})$	2040 $\nu(\text{CO})_s$		2135	2133.7 $\nu(^{14}\text{N}_2)$		
1571		1974 $\nu(^{13}\text{CO})$	1974 $\nu(\text{CO})_a$			2062.5 $\nu(^{15}\text{N}_2)$		
		$\nu(\text{CC})$						

of diastereomers) with an intermediate $\nu(\text{CC})$ band at $\sim 1670 \text{ cm}^{-1}$.



Accordingly, $\text{Cplr}(\text{CH}_2\text{CD}_2)_2$ was synthesized and its photochemistry examined in argon matrices. The IR spectrum showed that *two* product bands were formed in this region, at 1679 and 1660 cm^{-1} (Figure 7). We associate the former with isotopomer A and the latter with isotopomer B. The lower frequency band was considerably weaker than the higher frequency one, but we cannot be certain whether this was the result of a kinetic isotope effect or differences in intrinsic intensity. (Amplitudes and in-

tensities are usually smaller in deuterated compounds.) However, this experiment rules decisively in favor of the vinylidene complex, $\text{Cplr}(\text{CCH}_2)(\text{H}_2)$. The secondary reaction of **8** in argon matrices is shown in eq 6.²⁸



(28) In our communication (ref 6) we argued that there was a third photoproduct, $\text{Cplr}(\text{C}_2\text{H}_4)$, which we identified tentatively by comparison of the spectra with and without excess ethene. However, following remeasurement of several spectra using FTIR spectrometers, we have concluded that there is no sustainable evidence for the formation of $\text{Cplr}(\text{C}_2\text{H}_4)$. The changes observed on ethene doping can be explained by solvation, band broadening, and alteration of site effects.

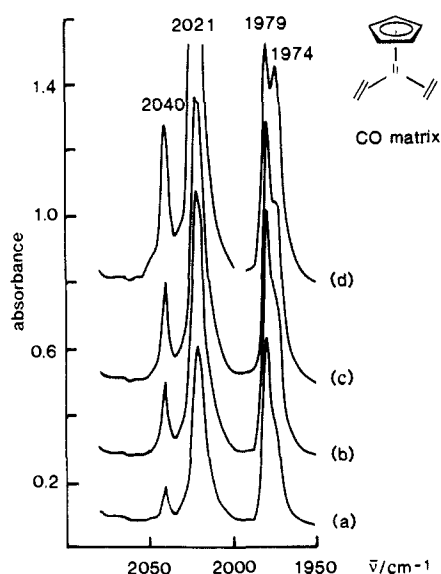


Figure 8. IR spectra in the $\nu(\text{CO})$ region showing the effect of photolysis of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ (**8**) in a CO matrix at 20 K. Before photolysis there are no bands in this region. Spectra (a) after 32 min of irradiation of $\lambda > 290$ nm, (b) after 105 min of additional photolysis at $\lambda > 315$ nm, (c) after 110 min of additional photolysis with Cd arc ($\lambda = 229$ and 326 nm), and (d) after 670 min of additional photolysis with the Cd arc. The band at 1979 cm^{-1} corresponds to $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_4)$ (**11**) and that at 2021 cm^{-1} to $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$ (**12**), and those bands at 2040 and 1974 cm^{-1} correspond to $\text{CpIr}(\text{CO})_2$. Spectra were recorded on a Perkin-Elmer 580 spectrometer.

3.f. Photochemistry of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ in CO, CO/Ar, and N_2 Matrices. Irradiation of **8** in a CO matrix (32 min, $\lambda > 290$ nm) results in the formation of both **9** and **10**, as indicated by the $\text{C}=\text{C}$ stretching bands at 1571 and 1677 cm^{-1} . Although the yield of **10** is considerably reduced compared to that of Ar and Ne matrices, more ethene is released in CO matrices. Three intense $\nu(\text{CO})$ bands are observed at 1979 (with a shoulder at 1974), 2021, and 2040 cm^{-1} (Figure 8a,b). Subsequent photolysis with a Cd arc ($\lambda = 229$ and 326 nm, 780 min) causes increases in the bands at 1974, 2021, and 2040 cm^{-1} (Figure 8c,d; Table VI). The band at 2021 cm^{-1} increases faster than the others, making it clear that it belongs to a different product. At the same time, the bands of **9** increase in intensity, but the $\nu(\text{CC})$ mode of **10** remains weak. The bands at 2040 and 1974 cm^{-1} are readily assigned as $\text{CpIr}(\text{CO})_2$ by comparison with previous matrix experiments.²⁹ Of the initial photoproducts, the band at 1979 cm^{-1} may be assigned to the substitution product, $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_4)$ **11**, by comparison with its CpRh and Cp*Ir analogues.^{11c,30} The other $\nu(\text{CO})$ band at 2021 cm^{-1} lies 42 cm^{-1} to high frequency, implying that metal oxidation has occurred. It continues to grow when **11** is decreasing and contributes to the intensity of the 1570 cm^{-1} band. It is notable that the intensity ratio of the 2021 and 1570 cm^{-1} bands changes from ~ 5 after initial photolysis to ~ 8 after final photolysis. We assign this product as $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$ (**12**), the CO substituted analogue of **9**.

Photolysis of **8** in CO/Ar (1:9) matrices proceeds similarly. Initial photolysis with the Cd arc generates both **11** and **12** with the anticipated reduction in yield of $\text{CpIr}(\text{CO})_2$. Subsequent photolysis ($\lambda > 315$ nm) increases the yield of **12**. A final period of shorter wavelength photolysis ($220 < \lambda < 340$ nm) causes a large increase in **12** and $\text{CpIr}(\text{CO})_2$.

The stoichiometry of the metal carbonyl products was checked with ^{13}CO substitution. Photolysis of **8** in a $^{13}\text{CO}/^{12}\text{CO}/\text{Ar}$ (5:5:90) matrix generated both **11** and **12** and their ^{13}CO -substituted analogues (see Table VI). Notably, production of $\text{CpIr}(\text{CO})_2$ and its ^{13}CO -substituted analogues was avoided by shorter photolysis times, and no bands were observed in positions

in which any mixed $\text{Ir}(^{12}\text{CO})(^{13}\text{CO})$ carbonyls would be expected.

The photochemistry of **8** was also investigated in N_2 matrices. Irradiation (70 min, $\lambda > 290$ nm) causes formation of **9** and **10** as for Ar matrices, but an additional band is detected at 2135 cm^{-1} . When the experiment was repeated with a $^{14}\text{N}_2/^{15}\text{N}_2$ (1:1) matrix, two bands appeared in this region with equal intensities, one at 2133.7 and one at 2062.5 cm^{-1} . The shift caused by isotopic labeling is only 0.9 cm^{-1} less than that expected for a diatomic oscillator. The absence of intermediate bands shows that the product must be a mono(dinitrogen) complex. These bands are shifted as much as 44 cm^{-1} to low frequency of the $\nu(\text{NN})$ bands of $\text{CpRh}(\text{N}_2)(\text{C}_2\text{H}_4)$, compared with a shift of 10 cm^{-1} in the $\nu(\text{CO})$ bands of $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_4)$ relative to its rhodium analogue.^{11b} Nevertheless, the evidence strongly suggests that this extra product is $\text{CpIr}(\text{N}_2)(\text{C}_2\text{H}_4)$ (**13**). (This molecule has also been observed by photolysis of **8** in liquid xenon.)³¹

3.g. Photochemistry of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ in Toluene Glasses and Solution. The products of photolysis of **8** in matrices are 18-electron complexes, which may well have considerable stability at higher temperatures. However, photolysis of **8** in a variety of low-temperature solutions gives mixtures of products in low yields. Instead, we investigated the photolysis of a frozen solution of **8** in *d*₈-toluene at 77 K. Following 7 h of photolysis ($\lambda > 285$ nm), the glass was thawed and NMR spectra recorded at 198 K. The spectra revealed 30% conversion to a single product, with no release of ethene. A new Cp resonance, a characteristic hydride resonance together with doublets of doublets for each of the protons of a vinyl group, strongly suggested formation of **9** (Table III). The protons of the coordinated ethene of **9** should all be inequivalent. Two sets of doublets of doublets are detected clearly at δ 3.09 and 1.40. Decoupling experiments establish the connectivity of the protons of the coordinated vinyl and ethene and show that the remaining ethene protons overlap with the lower field signal of **8**. Further decisive evidence for **9** is obtained from the $^{13}\text{C}\{^1\text{H}\}$ spectrum recorded with the DEPT pulse sequence, which showed each of the carbons of the product with the appropriate phase, including the inequivalent ethene carbons (Figure 9). After the solution was warmed to 273 K for several hours the resonances of **9** disappear, regenerating **8**. However, the solution acquires a pale yellow tinge, showing that some decomposition has also occurred. There is no evidence for formation of **10** or any other products than **9** in these experiments.

When **8** is photolyzed in toluene solution at 188 K, the solution rapidly darkens (contrast photolysis at 77 K). After 7 h of photolysis ($\lambda > 290$ nm), the hydride region of the ^1H NMR spectrum, measured at 213 K, shows the formation of **9** and another hydride at -15.9 ppm in 3:1 proportions. Unlike the photolysis at 77 K, a substantial amount of ethene is generated. A similar experiment conducted with photolysis at 213 K generated **9** and the new hydride in the ratio 2:1. The new product also exhibits resonances in the region of coordinated ethene, showing that it is not **10**. It has not been positively identified, but these experiments show that the reaction does not lead to isomerization alone but results in ethene loss and further oxidative addition.

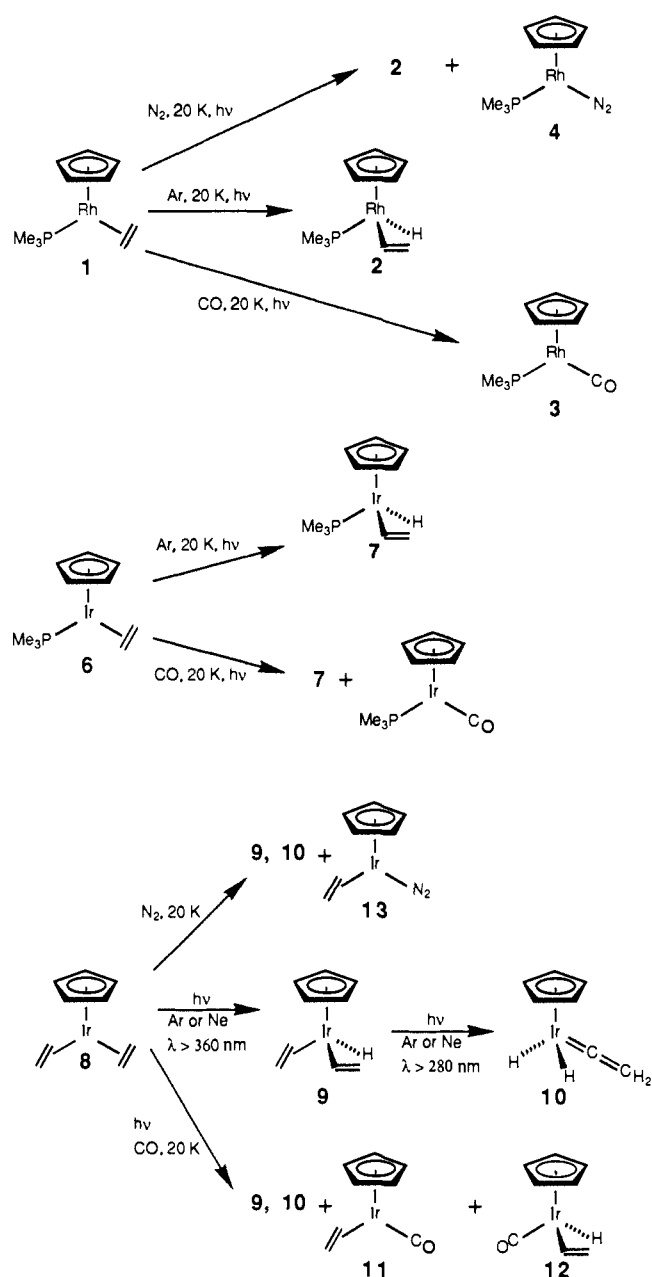
Discussion

The matrix experiments described here establish that the ethene complexes **1**, **6**, and **8** undergo photoinduced isomerization to vinyl hydride complexes (Scheme III). Each of the product complexes exhibits a characteristic $\nu(\text{M}-\text{H})$ vibration, and three vibrations of the vinyl group ($\nu(\text{CC})$, $\delta(\text{CH}_2)$, and $\delta(\text{CH})$). The vinyl vibrations vary remarkably little from one complex to another (Figure 2) and are also close in frequency to $\text{C}_2\text{H}_3\text{Br}$ and $\text{Fe}(\text{C}_2\text{H}_3)\text{H}$.⁴ Invariably, however, complications arise on deuteration because of changes in the vibrational mixing of $\nu(\text{MH})$, $\nu(\text{CC})$, and $\delta(\text{CH}_2)$ vibrations.^{23b} Vinyl hydrides **2** and **9** may be generated in solution by photolysis of the precursors in frozen toluene at 77 K followed by melting, while **7** may be generated directly by photolysis of a cold solution (Scheme IV). The NMR data confirm the identity of these molecules and show that they vary

(29) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181.

(30) Whitwell, I. Ph.D. Thesis, University of Southampton, 1986.

(31) Haddleton, D. M. D.Phil Thesis, University of York, 1986.

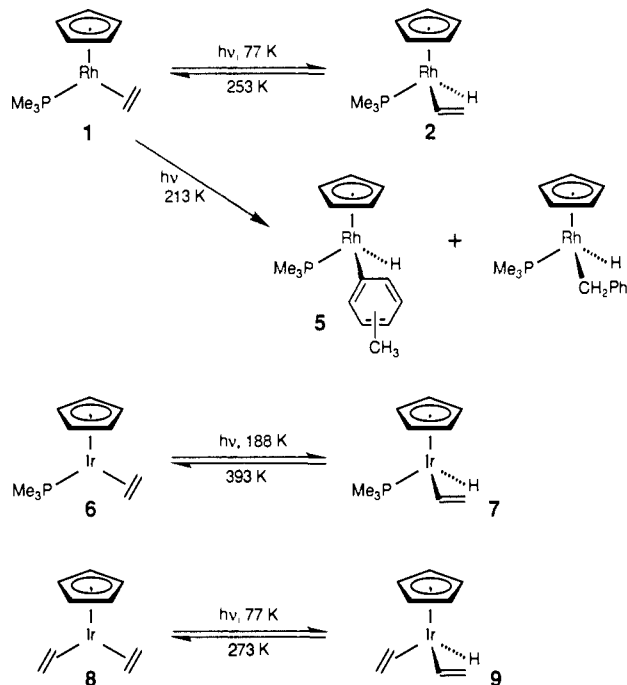
Scheme III. Matrix Photochemistry of $\text{CpM}(\text{PMe}_3)_2\text{C}_2\text{H}_4$ and $\text{CpIr}(\text{C}_2\text{H}_4)_2$ 

widely in their stability with respect to their ethene precursors. The rhodium complex **2** reverts to **1** at 253 K, **9** isomerizes slowly at 273 K, and **7** isomerizes slowly at 393 K. (The Cp^* analogue of **7** isomerizes to the ethene isomer at 453 K.)⁸ It is significant that attempts to isomerize **1** in liquid toluene result in insertion into toluene C–H bonds, unless the toluene is close to its freezing point (Scheme IV). Even then, intermolecular reaction accounts for about 50% of the products.

Matrix photolysis of **1** and **6** generates the vinyl hydrides exclusively, but there is an additional secondary photoproduct of **8** associated with expulsion of ethene. This species, **10**, is identified as the vinylidene complex, $\text{CpIr}(\text{CCH}_2)(\text{H})_2$, on the basis of comparisons with stable complexes and the effect of labeling the precursor with $\text{CH}_2=\text{CD}_2$.

Silvestre et al. have shown that the vinyl hydrides can be formed in two conformers with the C=C vectors pointing in different directions.¹⁵ The matrix IR spectra show multiple bands suggesting the presence of several trapping sites and/or conformers. The multiple trapping problem is ameliorated in the Ne matrix spectra of **9** but not eliminated. At present, we cannot distinguish site effects from conformer effects. A similar problem arises for **10**.

Scheme IV. Photolysis in Toluene Glasses and Solution



The reactions of **1** and **8** have been studied in N_2 and CO matrices, and that of **6** in CO matrices (Scheme III). Photo-substitution of ethene was apparent in all cases. However, isomerization to the vinyl hydride was also observed in all cases except for the photolysis of **1** in CO . When **8** is photolyzed in CO matrices, however, isomer **9** and $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$ are formed in addition to photosubstitution products. The analogue, $\text{Cp}^*\text{Ir}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$, has been identified on the basis of its $\nu(\text{CO})$ mode following photolysis of $\text{Cp}^*\text{Ir}(\text{CO})_2$ in ethene-doped argon matrices.³⁰ We have observed similar reactions in solution: e.g. photolysis of **8** in the presence of PPh_3 gives $\text{CpIr}(\text{PPh}_3)(\text{C}_2\text{H}_3)\text{H}$.^{6,32} Some additional products of **6** in CO matrices remain unidentified.^{33b}

The Mechanism of Ethene Insertion. There is now overwhelming evidence that η^2 -arene complexes are intermediates in arene C–H activation.^{11f,24} However, the reactions in Scheme I and those reported here demonstrate that a range of η^2 -ethene complexes are more stable than their vinyl hydride counterparts. They cannot, therefore, be intermediates in thermal C–H activation reactions of ethene.⁸ Here, the η^2 -ethene complexes act as the precursors in photochemical reactions, and the photon energy serves to overcome the thermodynamic barrier. Unfortunately, too little is known of the excited states of metal–ethene complexes to define the nature of the photoactive states, or to establish whether isomerization to the vinyl hydride takes place in the excited state. In previous studies in which ethene photodissociation was observed, irradiation was postulated to generate a ligand field excited state that is metal–ethene antibonding.^{11c}

Any mechanism must address the conditions under which the vinyl hydrides are formed: the matrix, whether toluene or argon, plays an essential role in the formation of **2** and **9** but is less important for **7**. The isomerization may be readily diverted by the presence of CO but less easily by nitrogen or toluene. Five mechanisms, I – V, for the formation of $\text{CpM}(\text{L})(\text{C}_2\text{H}_3)\text{H}$ are considered here (Scheme V). In mechanism V, photolysis dissociates ethene which diffuses freely, before it reacts with a CpML intermediate. This mechanism can be excluded at least for **6**, since

(32) Bell, T. W.; Perutz, R. N. Unpublished.

(33) (a) Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 167. It is also known that $\text{CpIr}(\text{CO})_2$ reacts in a CO matrix to form $(\eta^1\text{-C}_3\text{H}_5)\text{Ir}(\text{CO})_4$: Bloyce, P. E.; Rest, A. J.; Whitwell, I. *Ibid.* **1990**, 813. (b) There is one possible exception to the absence of ring slippage in these compounds: there are some unidentified carbonyl bands from the photolysis of $\text{CpIr}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)$ (**6**), which could be due to ring-slipped products. Their identity is the subject of further investigation.

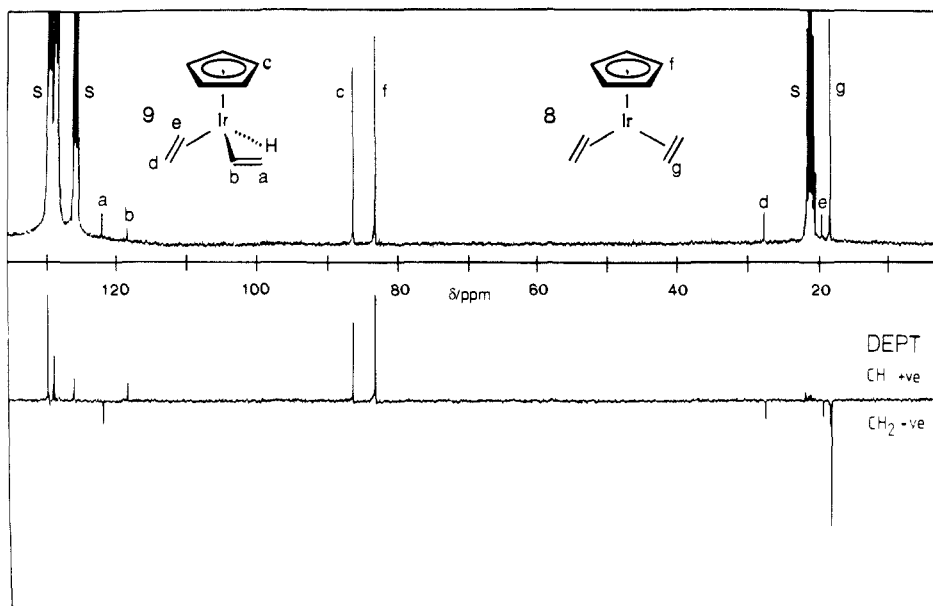


Figure 9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra recorded at 90.4 MHz (Bruker AM360) at 198 K showing formation of $\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ (**9**) following 7 h of photolysis ($\lambda > 290$ nm) of a frozen solution of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ (**8**) in d_8 -toluene at 77 K. Top: normal spectrum. Bottom: DEPT spectrum distinguishing CH and CH_2 protons. The labeling of the carbon atoms is shown in the figure (s = solvent).

solution photolysis in toluene would undoubtedly yield a tolyl deuteride as the major product rather than **7**. It can also be excluded for the isomerization of the osmium complexes (Scheme I, reactions G and H), since photolysis in solution under a C_2D_4 atmosphere yields the intramolecular product.¹⁰ The matrix experiments on **8** with excess C_2D_4 are less decisive, but they also point against this mechanism.

Mechanism IV, favored by Tanke and Crabtree, demands the photochemical release of ligand L and the isomerization of the remaining $\text{CpM}(\text{C}_2\text{H}_4)$ intermediate. Photolysis of **1** in argon matrices yields no bands attributable to free phosphine or $\text{CpRh}(\text{C}_2\text{H}_4)$, and the photolysis of **1** in reactive nitrogen and CO matrices shows no formation of $\text{CpRh}(\text{C}_2\text{H}_4)\text{N}_2$ or $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$. Since it is known that $\text{CpRh}(\text{C}_2\text{H}_4)$ reacts rapidly with nitrogen and CO,^{11c} mechanism IV is extremely unlikely. This model would predict that isomerization should be inhibited by excess ligand. This is not the case for the osmium complexes.¹⁰ In addition, we note that photolysis of **8** in solution in the presence of PPh_3 yields $\text{CpIr}(\text{PPh}_3)(\text{C}_2\text{H}_3)\text{H}$ at the same rate, with and without an ethene atmosphere.³²

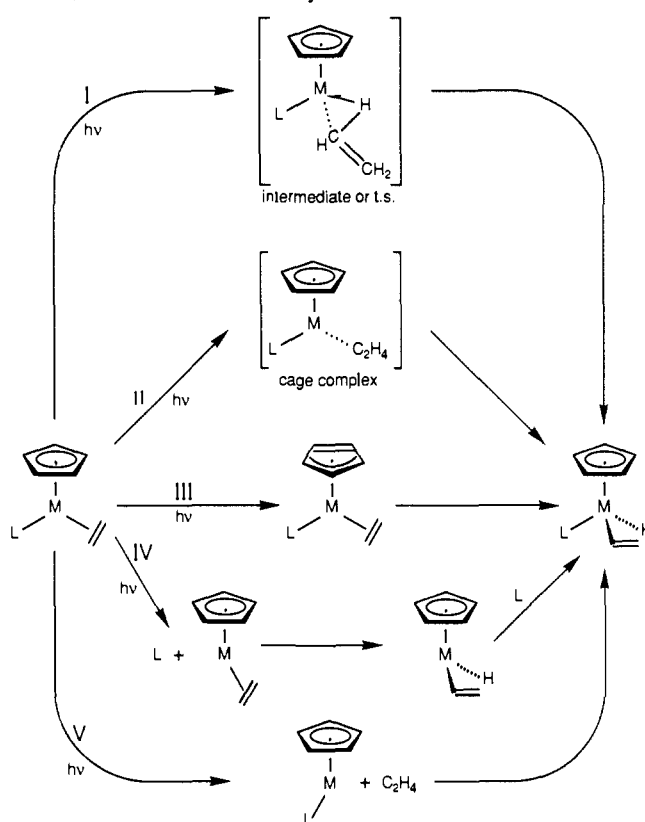
Mechanism III demands a ring slippage prior to isomerization. There is precedent for photochemical ring-slippage in CpML_2 compounds isolated in CO matrices (e.g. $\text{CpCo}(\text{CO})_2 \rightarrow (\eta^3\text{-Cp})\text{Co}(\text{CO})_3$).^{33a} Neither 16-electron $(\eta^3\text{-Cp})\text{ML}_2$ nor 18-electron ligand addition products derived from **1** or **8** have been observed (e.g. $(\eta^3\text{-Cp})\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)(\text{CO})$), although the 18-electron complexes should be stable in matrices. Thus, mechanism III is eliminated for **1** and **8**, but it remains a possibility for **6**.^{33b}

Two mechanisms remain at this stage: in mechanism I, the isomerization is completely intramolecular, whereas in mechanism II the ethene is ejected but reacts before it escapes from the solvent/matrix cage. The intermediates shown in Scheme V for these mechanisms could occupy electronic/vibrational excited states rather than ground states. However, it is unlikely that a second photon is required, since there should then be a sufficient buildup of the intermediate for observation in the matrix experiments.

The intramolecular mechanism accounts for most of the observations on **6**. Notably, the complex may be isomerized cleanly and efficiently in very cold, fluid toluene. However, photolysis in toluene solution at ambient temperature does generate additional products including ethene. In a CO matrix, isomerization and substitution are observed in a ratio of ca. 5:1, also implying that intramolecular isomerization is not the only pathway.

In contrast, the intramolecular mechanism fails to satisfy the evidence on **1**. Photolysis of **1** in a CO matrix results in the

Scheme V. Mechanisms for Vinylic C-H Insertion^a

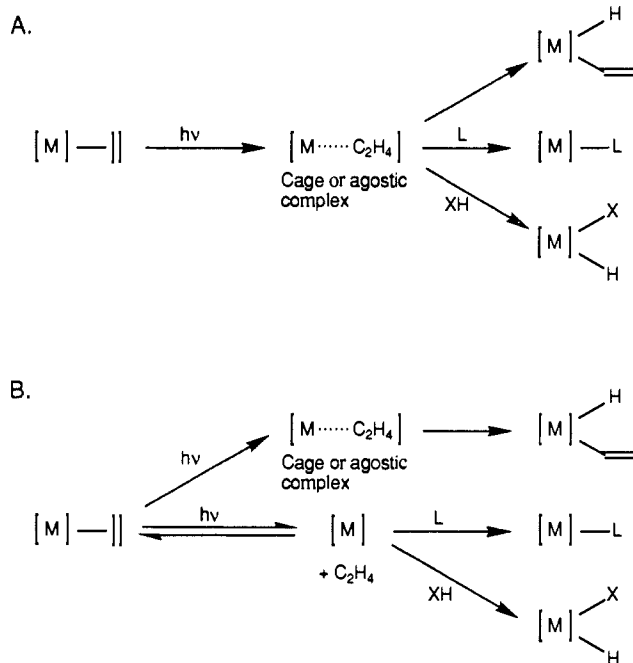


^a (i) The intermediates shown may occupy electronic/vibrational excited states. (ii) The geometry of the intermediate or transition state in mechanism I is symbolic rather than definitive.

formation of $\text{CpRh}(\text{PMe}_3)\text{CO}$ only. This observation indicates that ethene is photodissociated from **1** and that the resulting 16-electron $\text{CpRh}(\text{PMe}_3)$ intermediate reacts quickly with free CO. In nitrogen matrices, isomerization and ethene photosubstitution compete with one another. The changes in product ratios can be understood if isomerization takes place via mechanism II. Further support for this mechanism comes from the photochemistry of **1** in toluene. Whereas photolysis of **1** in a toluene glass at 77 K results in the formation of **2** as by far the major product, the production of **2** and **5** compete with one another in viscous

Scheme VI

Unified Reaction Mechanisms



toluene solution at 188 K. At higher temperatures, only insertion into toluene is observed. Thus both the IR and NMR experiments strongly support mechanism II, in which insertion occurs via dissociation and in-cage oxidative addition of ethene.

The photolysis of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ in nitrogen and CO matrices also generates both the ethene-activated vinyl hydride and ethene-substituted $\text{CpIr}(\text{L})(\text{C}_2\text{H}_4)$ ($\text{L} = \text{N}_2, \text{CO}$). While irradiation of toluene glasses containing **8** generates **9**, ethene-substituted complexes $\text{CpIr}(\text{L})(\text{C}_2\text{H}_4)$ and vinyl hydrides $\text{CpIr}(\text{L})(\text{C}_2\text{H}_3)\text{H}$ are formed on solution photolysis of **8** with ligands L ($\text{L} = \text{PPh}_3, \text{Me}_2\text{SO}$).^{6,32} The loss of ethene in solution is analogous to the photochemistry of **1**. Taken together, these results once more support mechanism II.

In conclusion, there is probably a gradation of mechanisms with **6** (and probably the Os complexes) isomerizing essentially intramolecularly, while **1** and **8** follow the in-cage mechanism. This notion can be incorporated into a unified mechanism (Scheme VIA) in which the outcome of the reaction is dependent upon the strength of the $\text{M}\cdots\text{H}-\text{CHCH}_2$ interaction within the cage complex. When the interaction is stronger the mechanism is close to the intramolecular limit as in **6**; with a weaker interaction, isomerization competes with attack by an external ligand, as in **1** and **8**. Even when **8** is photolyzed in solid neon at 4 K, these cage complexes are not observed in the matrix experiments, implying that the barrier to the formation of the vinyl hydride forms no obstacle to further reaction. As the interaction weakens further, the isomerization becomes a very minor process. At the extreme of weak interaction lies $\text{CpRh}(\text{C}_2\text{H}_4)_2$. Matrix experiments and most solution experiments on $\text{CpRh}(\text{C}_2\text{H}_4)_2$ suggest that C_2H_4 loss is the only photoprocess. However, scrambling of coordinated C_2H_4 with dissolved C_2D_4 indicates that there is some residual vinylic activation.¹⁴

It should be noted that the "degree of intramolecularity" of the isomerization follows the same order as the thermal stability of the corresponding vinyl hydride complexes, viz. $7 > 9 > 2$. The relationship between the isomerization reactions and the reactions with incoming ethene which also generate vinyl hydride complexes is likely to be a close one, but its precise nature remains to be explored. It is striking that the role we postulate for the cage complex is very similar to that postulated by Stoutland and Bergman in their studies of reactions of $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_6\text{H}_{11})\text{H}$ with ethene. They showed that the intermolecular stage of reaction leads to a σ -complex, equivalent to our cage complex, and is followed by intramolecular insertion.⁸ If the parallel is accepted,

the metal fragment in the cage complex must be in its ground electronic state. There is one σ -bonded complex that has been characterized, $\text{Fe}(\eta^1-\text{C}_2\text{H}_4)$: this is the best model for the cage/ σ -complex and exhibits vibrational frequencies perturbed remarkably little from ethene itself.⁴

The unified mechanism of Scheme VIA explains the product ratios by postulating that attack by external ligands takes place on the cage complex. There is a further alternative in which the vinyl hydride is formed via the cage complex, but the competing products are formed by attack on a coordinatively unsaturated intermediate in an independent pathway (Scheme VIB). In-cage recombination with ethene could prevent observation of the coordinatively unsaturated intermediate in matrices. This more conventional mechanism is hard to exclude rigorously and is certainly likely in some cases. However, the changes in the product ratios for reaction of **1** and **8** with matrix material are hard to explain since formation of the vinyl hydride appears irreversible at matrix temperatures. In this regard, Scheme VIA appears more satisfactory.

Conclusions

The matrix photochemistry of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ is startlingly different from its solution photochemistry and from the photochemistry of $\text{CpRh}(\text{C}_2\text{H}_4)_2$.¹¹ Irradiation of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ in rigid media (low-temperature matrix or toluene glass) results in the formation of the olefinic C-H insertion product $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$. Upon warming $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$, the photoreaction is reversed. The behavior of $\text{CpIr}(\text{C}_2\text{H}_4)_2$ proves similar to that of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$. On the other hand, $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ isomerizes to $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ upon irradiation either in matrices or in solution. The insertion of a CpML fragment into the C-H bond of ethene is recognizable by the IR vibrational signature of the vinyl group in the region 1200–1600 cm^{-1} , as well as by NMR in solution. The matrix results have been supported by extensive use of isotopic substitution. As expected, the third-row iridium vinyl hydrides prove thermally more stable than the rhodium vinyl hydride, but the contrast between the effects on the thermal stability of PMe_3 and C_2H_4 as coligands is particularly striking.

$\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$, the primary photoproduct of $\text{CpIr}(\text{C}_2\text{H}_4)_2$, is itself photosensitive. Upon irradiation, free ethene is released, and a secondary product with IR features consistent with a vinylidene complex, $\text{CpIr}(\text{CCH}_2)(\text{H})_2$, is generated.

Irradiation of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ in a CO matrix results in the formation of $\text{CpRh}(\text{PMe}_3)\text{CO}$ only. Upon irradiation of $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_4)$ in nitrogen matrices, both $\text{CpRh}(\text{PMe}_3)(\text{C}_2\text{H}_3)\text{H}$ and $\text{CpRh}(\text{PMe}_3)\text{N}_2$ are formed. The iridium analogue, $\text{CpIr}(\text{PMe}_3)(\text{C}_2\text{H}_4)$, reacts to form both isomerization and substitution products in a CO matrix. $\text{CpIr}(\text{C}_2\text{H}_4)_2$ also undergoes photosubstitution and insertion in reactive matrices. In CO-doped matrices, there are two ethene-insertion products: $\text{CpIr}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_3)\text{H}$ and $\text{CpIr}(\text{CO})(\text{C}_2\text{H}_3)\text{H}$.

All the observations may be incorporated into a single mechanism (Scheme VIA) in which the ratio of substitution to isomerization is determined by the strength of interaction between ethene and CpML in a cage complex. The pattern of energetics and reactivity of η^2 -ethene complexes relative to their vinyl hydride counterparts makes an intriguing contrast with the η^2 -arene and aryl hydride pair. It is gradually becoming clear that the energy difference between the members of either pair can be manipulated by choice of alkene/arene, metal, and other ligands. When the ethene complexes are much more stable than their vinyl hydride counterparts as in the 1/2 pair, photoisomerization may well be the only route to vinyl hydrides. As has often proved the case, matrix isolation has alerted us to a group of complexes that would otherwise have remained unobserved.

Experimental Section

General Methods and Materials. Syntheses and manipulations of chemicals were carried out under argon with standard Schlenk and high-vacuum techniques or in a nitrogen glovebox. Solvents were dried by refluxing over sodium/benzophenone and distilled under argon prior to use. Deuterated solvents were obtained from Aldrich. Gases used for

matrices were B.O.C. research grade (Ne, Ar, N₂, CO, 99.999%). C₂D₄ and CH₂CD₂ were obtained from MSD isotopes Ltd. (99.4 atom %) and other labeled gases from Amersham International (¹³CO, 99 atom %; ¹⁵N₂, 98 atom %). Rhodium trichloride hydrate, iridium trichloride hydrate, sodium hydride, TiCl₄, and [Ph₃C][PF₆] were purchased from Aldrich; trimethylphosphine was obtained from Strem Chemicals.

The photolysis source used in York for conventional solution and matrix reactions was a Philips HPK 125W medium-pressure Hg lamp with a quartz focussing lens and a water filter to remove excess heat. Occasionally, a Philips Cd arc 93162E (principal emission wavelengths 229 and 326 nm) was used as a UV source for photolysis of matrices. Photolysis of matrices in Hannover was achieved with a Heraeus TQ150 medium-pressure mercury arc with 1:1 quartz optics and water filter. Photochemical solution reactions were carried out in sealed 5-mm Pyrex NMR tubes. Low temperature (>183 K) irradiations were carried out by immersion of the sample in a dewar cooled by nitrogen gas and controlled by a JEOL temperature controller. Photolyses of frozen solutions at 77 K were carried out by immersion of the sample in a partially silvered dewar containing liquid nitrogen. For samples of **8**, a conventional NMR tube was used, but for **1** the NMR tube was sealed onto a Pyrex cuvette of 1 mm path length. After photolysis with the sample in the cuvette, the solution was thawed and the tube was inverted to record NMR spectra.

Spectroscopy. IR spectra (in York) were recorded on a Perkin-Elmer 580 grating spectrometer (4000–250 cm⁻¹) or a Mattson Sirius FTIR spectrometer with TGS detector and KBr beam splitter (4000–450 cm⁻¹). The Mattson spectrometer was continuously purged with water- and CO₂-free air. Typically, spectra of matrices were recorded with 1-cm⁻¹ resolution with 128 scans co-averaged (25K data points, 50K transform points) or 0.5-cm⁻¹ resolution with 256 scans co-averaged (42K data points) on the Mattson. UV-vis spectra were recorded on a Perkin-Elmer Lambda 7G spectrometer. Infrared spectra were recorded in Hannover on a Bruker IFS 113v FTIR spectrometer at a resolution of 1.0 or 0.5 cm⁻¹ operating in the reflection mode with a GeCu detector cooled by liquid helium.

NMR spectra were recorded with Bruker WP80, JEOL FX90, Bruker MSL300, and AM360 spectrometers. ¹H NMR chemical shifts are referenced to residual protonated solvent: *d*₅-benzene, δ = 7.13; *d*₇-toluene, δ = 2.1; *d*₁-dichloromethane, δ = 5.3 ppm. ¹³C NMR shifts are also referenced to solvent resonances: *d*₆-benzene, δ = 128.0; *d*₈-toluene, δ = 21.3; *d*₂-dichloromethane, δ = 53.8 ppm. ¹³C spectra were recorded with standard DEPT pulse sequences. ³¹P spectra were recorded with broad-band ¹H decoupling unless otherwise stated and are quoted relative to H₃PO₄ at 0 ppm.

Elemental analyses were carried out by Analytische Laboratorien (Gummersbach, FRG).

The matrix isolation apparatus in York for IR and UV-vis spectroscopy has been described in detail elsewhere.^{11c} Samples were deposited onto a CsI window cooled by an Air Products CS202 closed-cycle Displex refrigerator to 12–20 K. BaF₂ windows were used for combined IR and UV-vis spectroscopy. Experiments in Hannover were carried out with a continuous flow liquid helium Cryovac cryostat, which served to cool a nickel-plated copper block.³⁴ (The Hannover experiments were confined to the photochemistry of **8** in argon and neon matrices.) The organometallic was sublimed from a right-angled tube, with the temperature controlled by immersion of the tube in a dewar. Usually, the gas stream was allowed into the shroud via a separate inlet from the sample, but in some cases the stream was passed over the sample. Sublimations were carried out at the following temperatures: **1** 288–293 K, **6** at 290 K with the matrix gas passing over the sample, **8** at 281–293 K.

Syntheses. The following preparations were based on standard literature procedures: [Rh(C₂H₄)₂Cl]₂,³⁵ [(C₂D_{4-x}H_x)₂RhCl]₂,^{11c} CpRh-(PMe₃)(C₂H₄),³⁶ CpRh(PMe₃)(CO),³⁷ P(CD₃)₃,⁷ Na(C₅D₅),³⁸ [Ir(C₈H₁₄)₂Cl]₂,³⁹ [Ir(C₂H₄)₂Cl]₂.⁴⁰

1 and Its ²H-Labeled Analogues. CpRh(PMe₃)(C₂D_{4-x}H_x) was synthesized in an analogous way to **1**, replacing [(C₂H₄)₂RhCl]₂ by [(C₂D_{4-x}H_x)₂RhCl]₂. (C₅D₅)Rh(PMe₃)(C₂H₄) and CpRh[P(CD₃)₃](C₂H₄) were synthesized similarly, replacing NaC₅H₅ by NaC₅D₅, and P(CH₃)₃ by P(CD₃)₃, respectively. Mass spectral analysis indicated that the labeled ethene complex was 83% deuterated, the labeled cyclopentadienyl complex 91% deuterated, and the labeled phosphine complex >98% deuterated. Samples of **1** and its labeled analogues were purified by sublimation at 30 °C (10⁻⁴ mbar).

[(C₂D₄)₂IrCl]₂, [(C₈H₁₄)₂IrCl]₂ (0.23 g) was suspended in 10 cm³ of dry THF in a 250-cm³ round-bottomed flask and degassed. The flask was filled to a pressure of 570 Torr with C₂D₄ and stirred for 1 h, during which time all the dimer dissolved, the solution paled, and the pressure of C₂D₄ fell to 420 Torr. After being purged with Ar for 2 min, the color of the solution deepened to a dark red. The [(C₂D₄)₂IrCl]₂ was not isolated but converted to CpIr(C₂D₄)₂ immediately, following the procedure below. [(CH₂=CD₂)₂IrCl]₂ was synthesized similarly starting with CH₂=CD₂.

CpIr(C₂H₄)₂. The synthesis was based on the literature with some modifications.⁴¹ [(C₂H₄)₂IrCl]₂ (0.3 g, 5.3 × 10⁻⁴ mol) was dissolved in dry THF. CpTI (0.29 g, 1.1 × 10⁻³ mol) was added and the suspension stirred for 30 min. The solution was filtered and pumped to dryness to leave a light brown solid. The solid was extracted with 3 × 10 cm³ of dry hexane and eluted on a short alumina column (10 mm in diameter × 100 mm in length). The eluate was pumped to dryness to leave white CpIr(C₂H₄)₂, which was purified by sublimation at 35 °C and 10⁻³ mbar: yield 0.25 g (75%); ¹H NMR as in ref 41; ¹³C{¹H} NMR (100 MHz, *d*₈-toluene) δ 83.3 (s, Cp), 18.6 (s, C₂H₄).

CpIr(C₂D₄)₂ may be synthesized in a similar fashion by replacement of [(C₂H₄)₂IrCl]₂ with [(C₂D₄)₂IrCl]₂ (deuteration > 96%). The synthesis of CpIr(CH₂=CD₂)₂ follows an analogous route. The position of the isotopic label was verified by examination of the ¹³C{¹H} DEPT spectrum, which showed a negative signal corresponding to CH₂ at 18.4 ppm with small positive features, which were >4 times weaker.

[CpIr(PMe₃)(C₂H₄)H]PF₆. CpIr(PMe₃)(CH₃)₂ was synthesized via [CpIrCl]₂ by a procedure described elsewhere.⁴² CpIr(PMe₃)(CH₃)₂ (86 mg, 2.37 × 10⁻⁴ mol) was dissolved in 1.5 cm³ of dry C₂H₂Cl₂. The colorless solution was cooled to -80 °C, and 1 mol equiv (92 mg, 2.37 × 10⁻⁴ mol) of [Ph₃C][PF₆] in 2 cm³ of CH₂Cl₂ was added slowly, with vigorous stirring. Immediate reaction was observed. The solution was warmed to room temperature over 1 h, 2 cm³ of dry Et₂O were added, and the solution was cooled to 0 °C. A white precipitate slowly formed. The mildly air-sensitive precipitate was collected and washed with 5 × 10 cm³ of dry pentane: yield 72 mg (60%); NMR (CD₂Cl₂, 90 MHz) ¹H δ 5.74 (dd, 5 H, *J*(PH) = 1.0 Hz, *J*(HH) = 0.4 Hz, C₅H₅), 3.12 (m, 2 H, C₂H₄), 2.44 (m, 2 H, C₂H₄), 1.69 (d, 9 H, *J*(PH) = 11.4 Hz, CH₃), -16.3 (d, 1 H, *J*(PH) = 28.5 Hz, IrH); ³¹P NMR (CD₂Cl₂) δ -30.4 (s, IrP), -142.4 (septet, PF₆⁻). (A full assignment of the ethene resonances is not possible until variable-temperature data are obtained.)

CpIr(PMe₃)(C₂H₄). [CpIr(PMe₃)(C₂H₄)H]PF₆ (60 mg, 1.18 × 10⁻⁴ mol) was dissolved in 10 cm³ of dry THF. Excess solid NaH was added, in portions, with vigorous stirring. Evolution of gas was observed. Addition of NaH was continued until the evolution subsided. The solution was filtered and pumped to dryness. The resulting light brown solid was extracted with 3 × 10 cm³ of dry hexane and filtered. The filtrate was pumped to dryness, and pure CpIr(PMe₃)(C₂H₄) was sublimed as a very pale yellow solid (30 °C, 10⁻⁴ mbar): yield 40 mg (94%); NMR (*d*₈-toluene, 300 MHz) ¹H δ 4.91 (d, 5 H, *J*(PH) = 1.0 Hz, C₅H₅), 2.23 (m, 2 H, C₂H₄), 1.10 (m, 2 H, C₂H₄), 1.03 (9 H, *J*(PH) = 9.6 Hz, CH₃); ¹³C δ 80.4 (d, *J*(PC) = 4 Hz, C₅H₅), 20.6 (d, *J*(PC) = 36 Hz, CH₃), 4.1 (*J*(PC) = 2 Hz, C₂H₄); ³¹P δ -45.6 (s); mass spec (peaks are quoted for ¹⁹³Ir isotopomers) *m/z* 362 (55%, M⁺), 334 (35%, M⁺ - C₂H₄), 316 (27%), 302 (100%, M⁺ - MePCH₂). Anal. Calcd for (C₁₀H₁₈IrP): C, 33.23; H, 5.02. Found: C, 33.12; H, 4.94.

Acknowledgment. We are grateful to SERC, The Royal Society, British Gas, and the European Commission for financial support. We are grateful to Dr. S. B. Duckett and to the SERC high-field NMR service for recording some of the NMR spectra. We much appreciated discussions with Drs. S. T. Belt, P. Grebenik, R. J. Mawby, and S. Stahl.

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